

On the localization of random heteropolymers at the interface between two selective solvents

C. Monthus^a

CNRS-Laboratoire de Physique Théorique et Modèles Statistiques, DPT-IPN, Bât. 100, 91400 Orsay, France

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Abstract. To study the localization of random heteropolymers at an interface separating two selective solvents within the model of Garel, Huse, Leibler and Orland, [Europhys. Lett. **8**, 9 (1989)], we propose a disorder-dependent real space renormalization approach. This approach allows to recover that a chain with a symmetric distribution in hydrophobic/hydrophilic components is localized at any temperature in the thermodynamic limit, whereas a dissymmetric distribution in hydrophobic/hydrophilic components leads to a delocalization phase transition. It yields in addition explicit expressions for thermodynamic quantities as well as a very detailed description of the statistical properties of the heteropolymer conformations in the high temperature limit. In particular, scaling distributions are given for the lengths of the blobs in each solvent, for the polymer density, and for some correlation functions. In the case of a small dissymmetry in hydrophobic/hydrophilic components, the renormalization approach yields explicit expressions for the delocalization transition temperature and for the critical behaviors of various quantities: in particular, the free energy presents an essential singularity at the transition (the transition is thus of infinite order), the typical length of blobs in the preferred solvent diverges with an essential singularity, whereas the typical length of blobs in the other solvent diverges algebraically. Finite-size properties are also characterized in details in both cases. In particular, we give the probability distribution of the delocalization temperature for the ensemble of random chains of finite (large) length L , and the distribution of the numbers of blobs for the chains that are still localized at a given temperature. Finally, we discuss the non-equilibrium dynamics at temperature T starting from a zero-temperature initial condition.

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1 Introduction

Among the various subjects concerning the physics of polymers, the behavior of heteropolymers containing hydrophobic and hydrophilic components in solvents are of particular interest since they have obvious importance in biology [1]. It is well-known for instance that in a polar solvent, these heteropolymers prefer conformations where the hydrophilic components are in contact with the polar solvent, whereas hydrophobic components avoid contacts with the solvent. The behavior of heteropolymers in the presence of an interface separating two selective solvents, one favorable to the hydrophobic components and the other to the hydrophilic components, is less obvious, and has been much studied recently. In the pioneering work of Garel, Huse, Leibler and Orland [2], a model was proposed and studied *via* Imry-Ma arguments, an analysis of the replica Hamiltonian and numerics: it was found that a chain with a symmetric distribution in hydrophobic/hydrophilic components is always localized around the interface at any temperature (in the ther-

modynamic limit), whereas a chain with a dissymmetric distribution in hydrophobic/hydrophilic components presents a phase transition separating a localized phase at low temperatures from a delocalized phase into the most favorable solvent at high temperatures. Experimentally, the presence of copolymers was found to stabilize the interface between the two immiscible solvents [3], since the localization of the heteropolymers at the interface reduces the surface tension. By now, the predictions of reference [2] have been confirmed in the physics community by various approaches including molecular dynamics simulations [4], Monte-Carlo studies [5], variational methods for the replica Hamiltonian [6, 7], and exact bounds for the free-energy [8]. Mathematicians have also been interested in this model, but the exact results obtained up to now are still far from a complete explicit solution. The localization at all temperatures for the symmetric case was proven in references [9, 10] by various criteria of localization on the paths measure. In the dissymmetric case, the existence of a transition line in temperature *vs.* dissymmetry plane was proven in reference [11] where some bounds for the free-energy were obtained in the asymptotic regimes of low and

^a e-mail: monthus@ipno.in2p3.fr

high temperatures. Finally, the relations between various localization criteria concerning either free-energy or path properties have been studied in reference [12].

In this paper, we propose a new approach to study the model of Garel *et al.* [2], based on a disorder-dependent real space renormalization procedure. Since this type of approach is not usual in the context of the thermodynamics of classical disordered systems, it seems useful to recall how these methods have been successfully applied in other domains. Disordered-dependent real space renormalization approaches have first been introduced in the field of disordered quantum spin chains [13–17]. More recently they have been used to study random walkers in 1D disordered environments [18, 19], reaction-diffusion in 1D disordered environments [20] and non-equilibrium dynamics of disordered classical spin chains [18, 21]. A similar method has also been introduced independently to study the coarsening of the pure one-dimensional Φ^4 model at zero temperature [22]. In all these fields, these methods, which are not “exact from first principles”, have however been remarkably successful in reproducing the exact results that were already known (see Refs. [14, 19]), and in producing a lot of novel exact results for exponents and scaling functions for a large variety of physical quantities. These results apply in the large renormalization scale regime, corresponding respectively to low-temperature in the field of disordered quantum spin chains, and to large time behaviors in the other fields concerning dynamics. These new predictions have moreover been confirmed numerically whenever they have been tested [15, 23, 24].

For the random heteropolymer problem, the disorder-dependent real space renormalization procedure that we propose in this paper is defined to select the “important” configurations for the thermodynamics of a chain with a given realization of the disordered sequence in hydrophobic/hydrophilic components at a given temperature. We expect this renormalization approach to become accurate in the large renormalization scale regime, corresponding here to the region of high temperatures. Since the localized phase extends up to a critical temperature T_c that goes to infinity as the dissymmetry parameter of the distribution in hydrophobic/hydrophilic components goes to zero, our approach allows to study the localized phases of symmetric chains and slightly dissymmetric chains.

The paper is organized as follows. In the remainder of the introduction, we recall the model of Garel *et al.* [2] in Section 1.1, and give a summary of the main results of the present paper in Section 1.2. In Section 2, we recall the physics of the heteropolymer problem at $T = 0$ and at high temperatures, in order to motivate the introduction of a disorder-dependent real-space renormalization procedure in Section 3. The results of the renormalization approach are given for symmetric and dissymmetric chains in Sections 4 and 5 respectively. In Section 6, we characterize the finite-size properties of the problem by considering chains of finite (large) length. In Section 7, we discuss how the renormalization procedure also describes the non-equilibrium dynamics of a random chain at high temperature starting at $t = 0$ from a zero-temperature

initial condition. Finally Section 8 contains the conclusions. In the Appendix A, we compare some results of the renormalization approach with the corresponding results obtained by Garel and Orland *via* an extension of the usual Imry-Ma argument [25].

1.1 Model and notations

We consider the model introduced by Garel *et al.* [2] with some slightly different notations: a polymer chain consists of L monomers indexed by $i = 1, 2, \dots, L$, where each monomer i carries a quenched random charge q_i . The $\{q_i\}$ are independent identical random variables drawn with some probability distribution $C(q)$. An interface at $z = 0$ separates a solvent in the domain $z > 0$ favorable to positive charges $q > 0$, from a solvent in the domain $z < 0$ favorable to negative charges $q < 0$. More precisely, the energy of a configuration $\mathcal{C} = \{\mathbf{r}_i = (x_i, y_i, z_i)\}$ of the heteropolymer characterized by a realization $\{q_1, q_2, \dots, q_L\}$ reads

$$E(\mathcal{C}) = - \sum_{i=1}^L q_i \operatorname{sgn}(z_i), \quad (1.1)$$

and the partition function reads

$$Z_L(\beta; \{q_i\}) = \operatorname{Trace}_{\{\mathbf{r}_i\}} \prod_{i=1}^{L-1} \delta(|\mathbf{r}_{i+1} - \mathbf{r}_i| - a) \times \exp \left(\beta \sum_{i=1}^L q_i \operatorname{sgn}(z_i) \right). \quad (1.2)$$

In a continuum version of this model, the monomer index i becomes a continuous variable s , and the (x, y) coordinates play no role so that the partition function becomes a path integral over one-dimensional Brownian trajectories $\{z(s)\}$ [2]

$$Z_L(\beta; \{q(s)\}) = \int \mathcal{D}z(s) \times \exp \left(-\frac{1}{2D} \int_0^L ds \left(\frac{dz}{ds} \right)^2 + \beta \int_0^L ds q(s) \operatorname{sgn}(z(s)) \right). \quad (1.3)$$

In this paper, we propose a disorder-dependent real-space renormalization procedure, that should give valid results in the universal regime of large scales, where the details of the microscopic charge distribution $C(q)$ are not important, as long as the distribution $C(q)$ satisfy the hypothesis of the Central Limit Theorem. The important parameters of $C(q)$ will thus be the mean value and the variance

$$\bar{q} = \int_{-\infty}^{+\infty} dq q C(q) = q_0 \quad (1.4)$$

$$\overline{q^2} - q_0^2 = \int_{-\infty}^{+\infty} dq (q - q_0)^2 C(q) = 2\sigma. \quad (1.5)$$

To study the biased case $q_0 \neq 0$, we will always choose the convention $q_0 > 0$ and introduce the parameter δ defined as the non-vanishing root of the equation [19]

$$\overline{e^{-2\delta q}} \equiv \int_{-\infty}^{+\infty} dq e^{-2\delta q} C(q) = 1. \quad (1.6)$$

For instance, in the case of a Gaussian distribution considered in references [2, 6–8]

$$C(q) = \frac{1}{\sqrt{4\pi\sigma}} e^{-\frac{(q-q_0)^2}{4\sigma}}, \quad (1.7)$$

the parameter δ is simply the ratio between the mean value q_0 and the variance (2σ) [14]

$$\delta = \frac{q_0}{2\sigma}. \quad (1.8)$$

For the case of binary distribution considered in references [5, 8, 11, 12] where the charge q takes a positive value q_+ with probability c and a negative value $(-q_-)$ with probability $(1-c)$ then

$$q_0 = cq_+ - (1-c)q_-, \quad (1.9)$$

$$\sigma = \frac{c(1-c)}{2}(q_+ + q_-)^2, \quad (1.10)$$

and δ is the solution of

$$ce^{-2\delta q_+} + (1-c)e^{+2\delta q_-} = 1. \quad (1.11)$$

For instance in the case $q_- = q_+ = q_1$, we have

$$q_0 = (2c-1)q_1 \quad (1.12)$$

$$\sigma = 2c(1-c)q_1^2 \quad (1.13)$$

$$\delta = \frac{1}{2q_1} \ln \frac{c}{1-c}. \quad (1.14)$$

An important property of the parameter δ is that it becomes universal and coincides with the Gaussian expression in the limit of small dissymmetry $\delta \rightarrow 0$ [14]

$$\delta \simeq \frac{q_0}{2\sigma}. \quad (1.15)$$

Concerning the spatial behavior of the polymer, the only important parameter will be the diffusion coefficient D characterizing the large distance behavior of the free chain

$$\langle (z(s) - z(s'))^2 \rangle \simeq D|s - s'|. \quad (1.16)$$

We stress that in this paper, we do not take into account excluded volume effects because they do not have any crucial effect for the problem of the localization of the heteropolymer at the interface [2, 5, 8].

1.2 Quantities of interest and summary of main results

The quantities of interest to characterize the localized phase of heteropolymers around the interface are on one

hand the free-energy $f(T)$ per monomer that governs the thermodynamic, and on the other hand the statistical properties of the spatial conformations of the chain. In particular, the important characteristic lengths are the typical lengths $l_{\text{blob}}^{\pm}(T)$ of blobs in the (\pm) solvents as well as the typical distances $z_{\text{blob}}^{\pm}(T)$ between the chain and the interface. At a more refined level, one may also consider the probability distributions $P^{\pm}(l)$ of the lengths of (\pm) blobs, the density $\rho^{\pm}(z)$ of polymer at a distance z from the interface in the (\pm) solvents, and even correlation functions as for instance the solvent-solvent correlation $\langle \text{sgn}(z(s))\text{sgn}(z(s')) \rangle$. Finally, we will also be interested in the finite size effects of the problem.

Before introducing our approach and proceeding with the calculations of these quantities of interest, we now summarize the main results that will be derived from the real-space renormalization approach in the remainder of the paper.

1.2.1 Summary of main results for the symmetric case ($q_0 = 0$)

For the case of symmetric chains ($q_0 = 0$), the renormalization approach yields the following behaviors at high temperature

$$f(T) \sim -\frac{\sigma}{T \ln T}, \quad (1.17)$$

$$l_{\text{blob}}(T) \sim \frac{T^2}{\sigma} (\ln T)^2, \quad (1.18)$$

$$z(T) \sim \frac{T}{\sqrt{\sigma}} (\ln T), \quad (1.19)$$

in agreement with the Imry-Ma argument results [2] (see also Sect. 2.2 for the discussion of the presence of the logarithmic correction). In addition, we obtain that the rescaled length of blobs

$$\lambda = \frac{\sigma l}{9T^2 (\ln T)^2} \quad (1.20)$$

is distributed with the law

$$P(\lambda) = \sum_{n=-\infty}^{\infty} \left(n + \frac{1}{2} \right) \pi (-1)^n e^{-\pi^2 \lambda (n + \frac{1}{2})^2} \underset{\lambda \rightarrow \infty}{\simeq} \pi e^{-\frac{\pi^2}{4} \lambda} \quad (1.21)$$

$$\begin{aligned} &= \frac{1}{\sqrt{\pi} \lambda^{3/2}} \sum_{m=-\infty}^{\infty} (-1)^m \left(m + \frac{1}{2} \right) e^{-\frac{1}{\lambda} (m + \frac{1}{2})^2} \\ &\underset{\lambda \rightarrow 0}{\simeq} \frac{1}{\sqrt{\pi} \lambda^{3/2}} e^{-\frac{1}{4\lambda}}. \end{aligned} \quad (1.22)$$

The polymer density takes the scaling form $\rho(z)dz = R(Z)dZ$ where the rescaled distance to the interface

$$Z = \sqrt{\frac{2\sigma}{D}} \frac{z}{3T \ln T} \quad (1.23)$$

is distributed with the following law $R(Z)$ that decays exponentially at large distance

$$R(Z) = 4 \int_0^\infty d\lambda P(\lambda) \sqrt{\lambda} \int_{\frac{z}{\sqrt{\lambda}}}^\infty du e^{-u^2} \underset{Z \rightarrow \infty}{\simeq} \frac{8}{\pi} \sqrt{2Z} e^{-\pi Z}. \quad (1.24)$$

Finally, to characterize the finite size effects, we will compute the distribution of the delocalization temperature T_{deloc} over the ensemble of random cyclic finite chains of (large) length L . The result is that the rescaled variable

$$g = \frac{3}{\sqrt{\sigma L}} T_{\text{deloc}} \ln T_{\text{deloc}} \quad (1.25)$$

is distributed with the law

$$\begin{aligned} D(g) &= \frac{\pi^2}{g^3} \sum_{n=1}^{+\infty} (-1)^{n+1} n^2 e^{-\frac{n^2 \pi^2}{4g^2}} \underset{g \rightarrow 0}{\simeq} \frac{\pi^2}{g^3} e^{-\frac{\pi^2}{4g^2}} \quad (1.26) \\ &= \frac{2}{\sqrt{\pi}} \sum_{m=-\infty}^{+\infty} [2(2m+1)^2 g^2 - 1] e^{-(2m+1)^2 g^2} \\ &\underset{g \rightarrow \infty}{\simeq} \frac{4}{\sqrt{\pi}} g^2 e^{-g^2}. \end{aligned} \quad (1.27)$$

1.2.2 Summary of main results for the dissymmetric case ($q_0 > 0$)

For the case of dissymmetric chains ($q_0 > 0$), in the limit $\sigma \gg q_0$, the renormalization approach yields that the delocalization transition takes place at the critical temperature

$$T_c = \frac{4\sigma}{3q_0}, \quad (1.28)$$

in agreement with the scaling obtained previously by other methods [2, 6–8]. In addition, we obtain that the transition is of infinite order, with the following essential singularity for the free energy the free-energy $f(T)$

$$f(T) - f(T_c) \underset{T \rightarrow T_c^-}{\simeq} -2q_0 \left(\ln \frac{4\sigma}{q_0} \right) \exp \left[-\frac{\ln \frac{4\sigma}{q_0}}{\left(1 - \frac{T}{T_c}\right)} \right]. \quad (1.29)$$

For the statistical properties of the heteropolymer chain, we find that the typical length $l_{\text{blob}}^+(T)$ of blobs in the preferred solvent diverges with an essential singularity at the transition, whereas the typical length $l_{\text{blob}}^-(T)$ in the other solvent diverges algebraically

$$l_{\text{blob}}^+(T) \underset{T \rightarrow T_c^-}{\simeq} \frac{\sigma}{q_0^2} \exp \left[+\frac{\ln \frac{4\sigma}{q_0}}{\left(1 - \frac{T}{T_c}\right)} \right] \quad (1.30)$$

$$l_{\text{blob}}^-(T) \underset{T \rightarrow T_c^-}{\simeq} \frac{\sigma}{q_0^2} \frac{\ln \frac{4\sigma}{q_0}}{\left(1 - \frac{T}{T_c}\right)}. \quad (1.31)$$

The rescaled length of blobs in the preferred solvent, defined as

$$\lambda_+ = \frac{l_+}{\frac{\sigma}{q_0^2} \exp \left[\frac{\ln \frac{4\sigma}{q_0}}{\left(1 - \frac{T}{T_c}\right)} \right]} \quad (1.32)$$

is distributed with the exponential law $e^{-\lambda_+}$ near the transition. The polymer density $\rho^+(z)$ takes the scaling form $\rho^+(z) dz = R^+(Z) dZ$ where the rescaled distance to the interface

$$Z = \frac{z}{\sqrt{\frac{D}{2} \frac{\sigma}{q_0} \exp \left[+\frac{\ln \frac{4\sigma}{q_0}}{2\left(1 - \frac{T}{T_c}\right)} \right]}} \quad (1.33)$$

is distributed with the following scaling distribution that decays exponentially at large distance

$$R^+(Z) = 4 \int_0^\infty du e^{-u^2} \int_{\frac{z}{u}}^\infty dv v^2 e^{-v^2} \underset{Z \rightarrow \infty}{\simeq} \sqrt{\pi Z} e^{-2Z}. \quad (1.34)$$

Finally, to characterize the finite size effects, we will compute the distribution of the delocalization temperature T_{deloc} over the ensemble of random cyclic finite chains of (large) length L . The result is that the random variable

$$r = \frac{\sigma}{q_0^2 L} \left(\frac{4\sigma}{q_0} \right)^{\frac{T_{\text{deloc}}}{T_c - T_{\text{deloc}}}} \quad (1.35)$$

is distributed with the law

$$D^+(r) = \frac{1}{r^2} e^{-\frac{1}{r}}. \quad (1.36)$$

In particular, the typical value for the delocalization temperature presents a correction of order $(1/\ln L)$ with respect the critical temperature T_c

$$T_{\text{deloc}}^{\text{typ}} \sim T_c \left(1 - \frac{4\sigma}{q_0^2 \ln L} \right). \quad (1.37)$$

2 Physical picture at $T = 0$ and at high temperatures

In this section, we recall the physics of the heteropolymer problem at $T = 0$ and the Imry-Ma picture of reference [2] valid at high temperature. They will be useful to motivate the introduction of the real-space renormalization procedure in the next section.

2.1 Description of ground states

At $T = 0$, for a given realization $\{q_1, q_2, \dots, q_L\}$, each monomer i will be in its preferred solvent according to

$$\text{sgn}(z_i) = \text{sgn}(q_i). \quad (2.1)$$

The ground states have thus for energy

$$E_0 = - \sum_{i=1}^L |q_i|. \quad (2.2)$$

The corresponding configurations of the chain are all the random walks that cross the interface each time there is a change of signs in the realization $\{q_1, q_2, \dots, q_L\}$. More precisely, it is convenient to decompose the realization $\{q_1, q_2, \dots, q_L\}$ into groups (α) of consecutive charges of the same sign, each group (α) containing a number $l_\alpha = 1, 2, \dots$ of monomers, and carrying an absolute charge Q_α with

$$l_\alpha = \sum_{i \in \alpha} 1 \quad (2.3)$$

$$Q_\alpha = \left| \sum_{i \in \alpha} q_i \right|. \quad (2.4)$$

Then the ground states of the chain can be decomposed into blobs α containing $l_\alpha \sim O(1)$ monomers. The chain is thus localized around the interface with a typical distance of order $O(1)$.

2.2 Imry-Ma arguments at high temperature

In this section, we recall the Imry-Ma arguments [26] of Garel *et al.* [2], for the symmetric and dissymmetric cases respectively. They are expected to be valid at high temperature.

2.2.1 Imry-Ma argument for the symmetric case

The Imry-Ma argument exposed in [2] for the symmetric case ($q_0 = 0$) can be summarized as follows. Assuming that the chain is localized around the interface with typical blobs of length l in each solvent, the typical energy gain per blob scales as $\sqrt{\sigma l}$, whereas the reduction of entropy per blob scales as $\ln l$ (in [2], only powers of l were considered for the symmetric case, and thus $\ln l$ was replaced by $l^0 \sim 1$, but since this $\ln l$ dependence plays a crucial role in the dissymmetric case, we prefer to keep this $\ln l$ dependence everywhere in this paper). Neglecting prefactors of order 1, the optimization of the free-energy per monomer

$$f(l) \sim -\sqrt{\frac{\sigma}{l}} + T \frac{\ln l}{l} \quad (2.5)$$

with respect to l leads to

$$\frac{l}{(\ln l)^2} \sim \frac{T^2}{\sigma}. \quad (2.6)$$

At high temperature, the scaling of the typical blob length $l(T)$ and of the free-energy $f(T)$ are therefore given by:

$$l(T) \sim \frac{T^2 (\ln T)^2}{\sigma}, \quad (2.7)$$

$$f(T) \sim -\frac{\sigma}{T \ln T} \quad (2.8)$$

and thus the heteropolymer remains localized at any finite temperature.

2.2.2 Imry-Ma argument for the dissymmetric case

The Imry-Ma argument exposed in [2] for the dissymmetric case is actually much more subtle than in the symmetric case, because to describe correctly the blobs in the ($-$) solvent, it is necessary to consider the ‘‘rare events’’ where the sum of random variables q_i of positive mean $\bar{q}_i = q_0 > 0$ happens to be negative enough in order to make more favorable for the heteropolymer to make an excursion in the ($-$) solvent rather than to stay in the otherwise preferred ($+$) solvent. More precisely, the Imry-Ma argument of reference [2] is as follows in our notations: at high temperature, the heteropolymer is expected to be mostly in the preferred ($+$) solvent, except when a blob of length l^- in the ($-$) solvent becomes energetically favorable, with a blob energy $Q_- = -\sum_{i=j}^{j+l^-} q_i > 0$ that is ‘‘sufficient’’. The probability to have $\sum_{i=j}^{j+l^-} q_i = -Q^-$ is given by the Gaussian

$$\text{Prob}(Q^-) = \frac{1}{\sqrt{4\pi\sigma l^-}} e^{-\frac{(Q^- + q_0 l^-)^2}{4\sigma l^-}}. \quad (2.9)$$

Thus the typical spacing l^+ between two such events behaves as the inverse of this small probability

$$l^+ \sim e^{\frac{(Q^- + q_0 l^-)^2}{4\sigma l^-}}. \quad (2.10)$$

As a consequence, in a configuration with blobs of order (l^+, l^-) with $l^+ \gg l^-$, the energy gain Q^- due to one excursion in the ($-$) solvent behaves as

$$Q^- \sim \sqrt{4\sigma l^- \ln l^+} - q_0 l^-, \quad (2.11)$$

whereas the loss of entropy due to this excursion is of order $\ln l^+ + \ln l^- \simeq \ln l^+$. The free-energy difference per monomer between this localized state and the delocalized state in the preferred solvent can then be estimated as (neglecting prefactors of order 1):

$$\begin{aligned} f(T, l^+, l^-) - f_{\text{deloc}}(T) &\sim \frac{1}{l^+} (-Q^- + T \ln l^+) \\ &\sim \frac{1}{l^+} \left(q_0 l^- - \sqrt{4\sigma l^- \ln l^+} + T \ln l^+ \right). \end{aligned} \quad (2.12)$$

The optimization with respect to l^- leads to

$$l^- \sim \frac{\sigma}{q_0^2} \ln l^+ \quad (2.13)$$

and

$$Q^- \sim \frac{\sigma}{q_0} \ln l^+. \quad (2.14)$$

Thus both the energy gain Q^- and the entropy cost have the same $\ln l^+$ dependence! As a consequence, the free-energy difference factorizes into

$$f(T, l^+) - f_{\text{deloc}}(T) \sim (T - T_c) \frac{\ln l^+}{l^+}, \quad (2.15)$$

where the parameter

$$T_c \sim \frac{\sigma}{q_0} \quad (2.16)$$

thus represents the critical temperature between the localized phase $T < T_c$ and the delocalized phase $T > T_c$. Contrary to the symmetric case, the behavior of the free-energy with respect to the temperature remains unknown, since the typical blob length l^+ depends upon the temperature T in a way that is not determined by the present argument. Still, the relations (2.13, 2.15) between the typical blob lengths l^+ and l^- and the free-energy $f(T)$ represent non-trivial tests for any theory constructed to describe the heteropolymer problem.

3 Definition of an effective thermodynamics

To go beyond the Imry-Ma arguments of previous section, one needs to consider probability distributions of blob lengths and blob energies. In Appendix A, we reproduce an extension of the usual Imry-Ma argument which was introduced by Garel and Orland [25], and which shows how to get the asymptotic behavior of the probability distribution $P(l)$ of the blob length l in the limit of small l . Here, to study the probability distributions of blob lengths and blob energies, we will construct *via* a real-space renormalization procedure the “optimal” Imry-Ma domain structure associated with a given heteropolymer at a given temperature. We will then argue that the configurations corresponding to this optimal Imry-Ma domain structure dominate in the partition function asymptotically at high temperature.

3.1 Definition of a real-space renormalization procedure to construct the optimal Imry-Ma domain structure

At $T = 0$, we have seen in Section 2.1 that the chain is decomposed into blobs α containing l_α consecutive monomers of charges of the same sign, and carrying an absolute charge Q_α . As T grows from $T = 0$, we consider the configurations of the chain obtained from the ground states structure by iteratively flipping the blobs of smallest absolute charge $Q_{\min} \equiv \Gamma$. When we flip the blob $(Q_2 = \Gamma, l_2)$ surrounded by the two neighboring blobs (Q_1, l_1) and (Q_3, l_3) , we obtain a new blob of absolute charge Q and length l given by (see Fig. 1)

$$\begin{aligned} Q &= Q_1 + Q_3 - Q_2 \\ l &= l_1 + l_2 + l_3. \end{aligned} \quad (3.1)$$

The renormalization procedure corresponding to the rules (3.1) has already been extensively studied in the context of the Random Transverse Field Ising Chain [14], where the role of the absolute charges Q_i was played by the logarithm of the random couplings and random fields ($\ln J_i$ and $\ln h_i$), and in the context of Random walks in

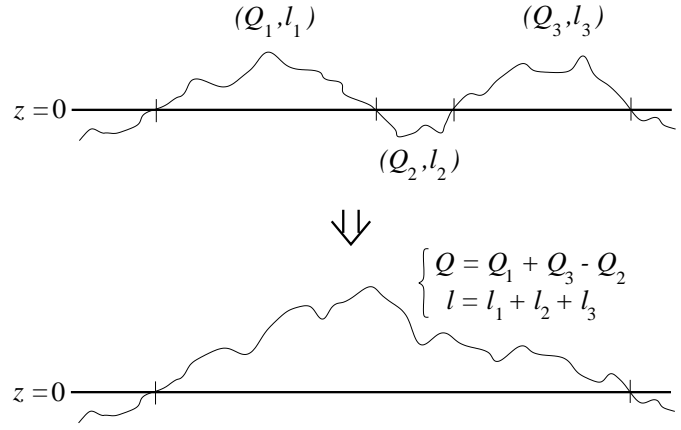


Fig. 1. Illustration of the real-space renormalization procedure: the flipping of the blob $(Q_2 = \Gamma, l_2)$ surrounded by the two neighboring blobs (Q_1, l_1) and (Q_3, l_3) gives a new blob (Q, l) with the rules (3.1).

disordered 1D environments [19] where the role of the absolute charges Q_i was played by the energy barriers F_i . As explained in details in reference [19], the renormalization procedure constructs iteratively the large scale extrema statistics of random walks, where only barriers bigger than a given scale Γ are kept. Here the corresponding random walk is simply given by the sum of the quenched charges $\sum_0^i q_j$ as a function of the monomer index i , and the renormalization procedure gives the “best” blob structure, given the constraint that only blobs of charges bigger than a given scale Γ are kept.

To establish a relation between the renormalization scale Γ and the temperature T , we now have to determine the conditions under which the flip of the blob (Q_2, l_2) is favorable. The cost in energy of the flip of the blob (Q_2, l_2) is simply

$$\Delta E^{\text{flip}} = 2Q_2, \quad (3.2)$$

whereas the corresponding gain in entropy reads

$$\Delta S^{\text{flip}} = \ln(\mathcal{M}(l_1 + l_2 + l_3)) - \ln[\mathcal{M}(l_1)\mathcal{M}(l_2)\mathcal{M}(l_3)], \quad (3.3)$$

where $\mathcal{M}(l)$ represents the number of 1D random walks of l steps going from $z = 0$ to $z = 0$ in the presence of an absorbing boundary at $z = 0^-$. As a consequence, the free-energy difference corresponding to this flip reads

$$\begin{aligned} \Delta F^{\text{flip}} &= \Delta E^{\text{flip}} - T \Delta S^{\text{flip}} \\ &= 2Q_2 - T \ln \left(\frac{\mathcal{M}(l_1 + l_2 + l_3)}{\mathcal{M}(l_1)\mathcal{M}(l_2)\mathcal{M}(l_3)} \right). \end{aligned} \quad (3.4)$$

The optimal Imry-Ma domain structure corresponding to a given realization of the disorder at a given temperature is thus constructed as follows: we iteratively flip the blobs of smallest absolute charge Q , starting from the ground-states blob structure, and continue as long as these flipping produce a decrease of the free-energy ($\Delta F^{\text{flip}} < 0$).

We stop the procedure when the next flipping would correspond to a raise of free-energy ($\Delta F^{\text{flip}} > 0$). We will define $\Gamma_{\text{eq}}(T)$ as the renormalization scale Γ where we have to stop the renormalization. We now present a dynamical interpretation of the renormalization procedure.

3.2 Dynamical interpretation of the renormalization procedure

The renormalization procedure defined above to construct the optimal blob structure at temperature T can be given a perhaps more direct physical meaning if one considers the dynamics at high temperature T for $t > 0$ starting from a zero-temperature initial condition at $t = 0$, *i.e.* after a quench to $T = 0$ for $t < 0$. Indeed, the time necessary to flip a blob of absolute charge Q follows an Arrhenius law $t \sim t_0 e^{\beta Q}$ (where t_0 is a microscopic time scale). The dynamics thus corresponds to the iterative flipping of the blobs of smallest absolute charge remaining in the chain described by the renormalization procedure, where the renormalization scale Γ now corresponds to time *via*

$$\Gamma = T \ln \frac{t}{t_0} \quad (3.5)$$

as in references [18,19]. The dynamics takes place up to time t_{eq} where equilibrium at temperature T is reached

$$T \ln \frac{t_{\text{eq}}}{t_0} = \Gamma_{\text{eq}}(T). \quad (3.6)$$

3.3 Discussion of the validity of the effective thermodynamics

Let us define the effective partition function $Z_L^{\text{eff}}(\beta; \{q_i\})$ as the sum over all the configurations that correspond to the disorder and temperature dependent optimal Imry-Ma domain structure constructed *via* the renormalization procedure defined above. The real partition function $Z_L(\beta; \{q_i\})$ can be decomposed into

$$Z_L(\beta; \{q_i\}) = Z_L^{\text{eff}}(\beta; \{q_i\}) + \text{sum corresponding to other Imry-Ma domains structures.} \quad (3.7)$$

The effective thermodynamics based on $Z_L^{\text{eff}}(\beta; \{q_i\})$ is of course very approximate at low temperatures. However, at high temperatures, the renormalization scale $\Gamma = Q_{\text{min}}$ will be large and the probability distributions of absolute charges of the blobs will become infinitely broad [14]. More precisely in the symmetric case, the difference between the typical value Q_{typ} of the absolute charges and the minimum value $Q_{\text{min}} = \Gamma$ will also be large and of order Γ : $Q_{\text{typ}} - Q_{\text{min}} \sim \Gamma$. As a consequence, we expect that all the configurations that do not correspond approximatively to the optimal Imry-Ma domain structure will be highly suppressed in the partition function, in comparison with the ‘‘optimal configurations’’. The validity of the effective

thermodynamics is thus based on the idea that, for a given heteropolymer at a given high temperature, the large scale Imry-Ma domain structure is essentially *unique*.

As explained in the introduction, in the other fields where disordered-dependent real space renormalization approaches have been used, they have been able to reproduce the non-trivial exact results obtained previously *via* other methods (see Refs. [14,19]). These agreements with the Mc Coy-Wu exact results in the field of disordered quantum spin chains [14], and with the Kesten-Golosov distribution in the field of 1D random walks in random media [19] have provided the best evidence for the asymptotic exactness of the renormalization approach in these fields, and give confidence in all its other novel predictions. Here for the heteropolymer problem, we do not have at our disposal so precise exact analytical results derived *via* other methods to ‘‘test’’ unambiguously the asymptotic exactness of the predictions of the renormalization approach. As a consequence, we hope that in the future, the explicit results of the renormalization approach presented in this paper will be tested precisely by numerical studies. It would be also very interesting to test more directly the idea of the dominance of the optimal Imry-Ma domain structure in the partition function, by comparing, sample by sample, the typical configurations of the heteropolymer at equilibrium at temperature T with the optimal blob structure obtained by the numerical implementation of the renormalization procedure up to scale $\Gamma_{\text{eq}}(T)$.

The remainder of the paper is devoted to the detailed study of the properties of the effective thermodynamics. To proceed now with the concrete calculations of the renormalization approach, it is again more convenient to discuss separately the symmetric case $q_0 = 0$ and the disymmetric case $q_0 > 0$.

4 Study of the symmetric case $Q_0 = 0$

4.1 Properties of the renormalization procedure

It was shown in reference [14] that with the above renormalization procedure (3.1), the probability distribution $P_\Gamma(Q, l)$ that a blob at renormalization scale Γ has absolute charge Q and length l flows towards a fixed point distribution $P^*(\eta, \lambda)$ in the rescaled variables

$$\eta = \frac{Q - \Gamma}{\Gamma} \quad \text{and} \quad \lambda = \frac{\sigma l}{\Gamma^2}, \quad (4.1)$$

with σ defined in (1.4), and that this fixed point distribution $P^*(\eta, \lambda)$ reads in Laplace transform with respect to λ

$$\begin{aligned} \mathcal{L}_{\lambda \rightarrow s}(P^*(\eta, \lambda)) &\equiv \int_0^\infty d\lambda e^{-s\lambda} P^*(\eta, \lambda) \\ &= \frac{\sqrt{s}}{\sinh \sqrt{s}} e^{-\eta \sqrt{s} \coth \sqrt{s}}. \end{aligned} \quad (4.2)$$

In particular, the distribution of the rescaled absolute charge η is a simple exponential

$$P^*(\eta) = \int_0^\infty d\lambda P^*(\eta, \lambda) = e^{-\eta}, \quad (4.3)$$

and the distribution of the rescaled length λ of a blob reads

$$\begin{aligned} P(\lambda) &= \int_0^\infty d\eta P^*(\eta, \lambda) = \mathcal{L}_{s \rightarrow \lambda}^{-1} \left(\frac{1}{\cosh(\sqrt{s})} \right) \\ &= \int_{-i\infty}^{+i\infty} \frac{ds}{2i\pi} \frac{e^{s\lambda}}{\cosh(\sqrt{s})} \\ &= \sum_{n=-\infty}^{\infty} \left(n + \frac{1}{2} \right) \pi(-1)^n e^{-\pi^2 \lambda (n + \frac{1}{2})^2} \\ &= \frac{1}{\sqrt{\pi} \lambda^{3/2}} \sum_{m=-\infty}^{\infty} (-1)^m \left(m + \frac{1}{2} \right) e^{-\frac{1}{\lambda} (m + \frac{1}{2})^2}. \end{aligned} \quad (4.4)$$

We also introduce the notation $P_{\text{flip}}(\lambda)$ for the distribution of the bonds which are about to be decimated (*i.e.* having $\eta = 0$)

$$\begin{aligned} P_{\text{flip}}(\lambda) &= \mathcal{L}_{s \rightarrow \lambda}^{-1} \left(\frac{\sqrt{s}}{\sinh(\sqrt{s})} \right) = \pi^2 \sum_{n=-\infty}^{\infty} (-1)^{n-1} n^2 e^{-\pi^2 n^2 \lambda} \\ &= \frac{1}{2\sqrt{\pi} \lambda^{3/2}} \sum_{m=-\infty}^{\infty} \left[\frac{2}{\lambda} \left(m + \frac{1}{2} \right)^2 - 1 \right] e^{-\frac{1}{\lambda} (m + \frac{1}{2})^2}. \end{aligned} \quad (4.5)$$

4.2 Relation between temperature and renormalization scale

We now examine the condition $\Delta F^{\text{flip}} < 0$, where the free-energy difference ΔF^{flip} due to a blob flip was given in equation (3.4). For large l , the number $\mathcal{M}(l)$ of 1D random walks of l steps going from $z = 0$ to $z = 0$ in the presence of an absorbing boundary at $z = 0^-$ behaves as

$$\mathcal{M}(l) \simeq \kappa \frac{\mu^l}{l^{3/2}}, \quad (4.6)$$

where κ is a constant, and where $\ln \mu$ characterizes the entropy of the free random walk (for instance $\mu = 2$ for the 1D lattice). In the effective thermodynamics at large renormalization scale Γ , the free-energy difference of a blob flip then reads

$$\Delta F^{\text{flip}} = 2Q_2 - T \ln \left(\frac{(l_1 l_2 l_3)^{3/2}}{\kappa^2 (l_1 + l_2 + l_3)^{3/2}} \right). \quad (4.7)$$

Using the rescaled variables $\lambda_i = \frac{\sigma l_i}{\Gamma^2}$, we obtain the average

$$\overline{\Delta F^{\text{flip}}} = 2\Gamma - 3T \ln \frac{\Gamma^2}{\sigma} + T \left(\frac{3}{2} K + \ln \kappa^2 \right), \quad (4.8)$$

where K is a pure numerical constant that can be obtained from the distributions (4.4, 4.5) as

$$\begin{aligned} K &= \int_0^\infty d\lambda_1 P^*(\lambda_1) \int_0^\infty d\lambda_2 P_{\text{flip}}^*(\lambda_2) \\ &\quad \times \int_0^\infty d\lambda_3 P^*(\lambda_3) \ln(\lambda_1 + \lambda_2 + \lambda_3) \\ &\quad - 2 \int_0^\infty d\lambda P^*(\lambda) \ln \lambda - \int_0^\infty d\lambda P_{\text{flip}}^*(\lambda) \ln \lambda. \end{aligned} \quad (4.9)$$

The scale $\Gamma_{\text{eq}}(T)$ where the renormalization procedure has to be stopped is the solution of $\Delta F^{\text{flip}}(\Gamma) = 0$ and $\partial_\Gamma \Delta F^{\text{flip}}(\Gamma) > 0$. For large Γ , and thus for large temperature, we find that $\Gamma_{\text{eq}}(T)$ is implicitly defined as the inverse of the function $T(\Gamma_{\text{eq}})$ given by

$$T(\Gamma_{\text{eq}}) \simeq \frac{\Gamma_{\text{eq}}}{3 \ln \Gamma_{\text{eq}}}. \quad (4.10)$$

As a consequence, for any arbitrary large temperature T , we find that the renormalization procedure has to be stopped at the *finite* large renormalization scale $\Gamma_{\text{eq}}(T)$. The polymer is thus always localized around the interface, with blobs of typical length $l^{\text{blob}}(T)$ behaving at high temperature as

$$l_{\text{blob}}(T) \sim \frac{\Gamma_{\text{eq}}^2}{\sigma} \sim \frac{T^2 (\ln T)^2}{\sigma}. \quad (4.11)$$

In this regime, the typical distance $z(T)$ to the interface behaves as

$$z(T) \sim \sqrt{D l_{\text{blob}}(T)} \sim \sqrt{\frac{D}{\sigma} \Gamma_{\text{eq}}} \sim \sqrt{\frac{D}{\sigma} T (\ln T)}. \quad (4.12)$$

These scaling behaviors are in agreement with the Imry-Ma argument of reference [2] (see Sect. 2.2, where the logarithmic correction is found to be present in the Imry-Ma argument) and with the exact free energy bounds of reference [8]. The Replica variational approaches of references [6, 7] give the same scaling behaviors without the logarithmic correction.

We now study more precisely various physical quantities for which the present renormalization approach yields explicit predictions.

4.3 Thermodynamic quantities

The energy of a blob is simply given by minus its absolute charge ($-Q$), and thus the energy per monomer $e(T)$ of the chain in the thermodynamic limit can be obtained through a decomposition into blobs indexed by α as

$$e(T) = - \frac{\sum_\alpha Q_\alpha}{\sum_\alpha l_\alpha} = - \frac{\int_{Q,l} Q P_{\Gamma_{\text{eq}}(T)}(Q, l)}{\int_{Q,l} l P_{\Gamma_{\text{eq}}(T)}(Q, l)} \quad (4.13)$$

with $\Gamma_{\text{eq}}(T)$ defined in (4.10). Using the fixed point solution of equations (4.1, 4.2), we obtain at large temperature

$$e(T) \simeq - \frac{4\sigma}{\Gamma_{\text{eq}}(T)} \sim - \frac{4\sigma}{3T \ln T}. \quad (4.14)$$

The entropy associated with the z direction for a blob of length l is given by $\ln(\mathcal{M}(l))$, where $\mathcal{M}(l)$ behaves as in equation (4.6) in the large l regime. As a consequence, the entropy per monomer $s(T)$ is given in the thermodynamic limit by

$$\begin{aligned} s(T) &= \frac{\sum_{\alpha} [l_{\alpha} \ln \mu + \ln \kappa - \frac{3}{2} \ln l_{\alpha}]}{\sum_{\alpha} l_{\alpha}} \\ &= \frac{\int_{Q,l} [l \ln \mu + \ln \kappa - \frac{3}{2} \ln l] P_{\Gamma_{\text{eq}}(T)}(Q, l)}{\int_{Q,l} l P_{\Gamma_{\text{eq}}(T)}(Q, l)}. \end{aligned} \quad (4.15)$$

Using again the fixed point solution (4.1, 4.2), we have at large temperature

$$\begin{aligned} s(T) &\simeq \ln \mu - \frac{6\sigma \ln(\Gamma_{\text{eq}}(T))}{\Gamma_{\text{eq}}^2(T)} + \frac{\sigma}{\Gamma_{\text{eq}}^2(T)} \\ &\quad \times \left(3 \ln \sigma + 2 \ln \kappa - 3 \int_0^{\infty} d\lambda P^*(\lambda) \ln \lambda \right) \\ &\simeq \ln \mu - \frac{2\sigma}{3T^2 \ln T} + O\left(\frac{1}{T^2 (\ln T)^2}\right). \end{aligned} \quad (4.16)$$

Finally, we obtain the free-energy per monomer $f(T)$ of the chain at large temperature

$$\begin{aligned} f(T) &\simeq -T \ln \mu - \frac{2\sigma}{\Gamma_{\text{eq}}(T)} + \frac{\sigma}{\Gamma_{\text{eq}}(T) \ln \Gamma_{\text{eq}}(T)} \\ &\quad \times \left(\int_0^{\infty} d\lambda P^*(\lambda) \ln \lambda - \ln \sigma - \frac{2}{3} \ln \kappa \right) \\ &\simeq -T \ln \mu - \frac{2\sigma}{3T \ln T} + O\left(\frac{1}{T (\ln T)^2}\right). \end{aligned} \quad (4.17)$$

The dominant behavior depending on the disorder parameter σ is in agreement with the Imry-Ma argument of reference [2] as explained in Section 2.2.

4.4 Distribution of the blob lengths

In the renormalization approach, the lengths of the different blobs are independent identical random variables, and the rescaled blob length defined as

$$\lambda = \frac{\sigma l_{\text{blob}}}{\Gamma_{\text{eq}}^2(T)} \quad (4.18)$$

is asymptotically distributed at high temperature with the distribution $P^*(\lambda)$ given in equation (4.4). In particular, its asymptotic behaviors for large and small λ are respectively given by

$$P(\lambda) \underset{\lambda \rightarrow \infty}{\simeq} \pi e^{-\frac{\pi^2}{4}\lambda} \quad (4.19)$$

$$P(\lambda) \underset{\lambda \rightarrow 0}{\simeq} \frac{1}{\sqrt{\pi} \lambda^{3/2}} e^{-\frac{1}{4\lambda}}. \quad (4.20)$$

As noted by Garel and Orland [25], the small λ behavior found in equation (4.20) for the distribution $P(\lambda)$ can be obtained *via* an extension of the usual Imry-Ma argument, as explained in the Appendix A.

4.5 Density $\rho(z)$ of polymer at a distance z from the interface

We now study the density $\rho(z)$ of polymer at a distance z from the interface as follows. We first need to introduce the probability $S_{\Gamma}(l, x)$ that a given point of the chain belongs at renormalization scale Γ to a blob of length l and is at distances $(x, l-x)$ from the ends of the blob. It reads

$$S_{\Gamma}(l, x) = \frac{P_{\Gamma}(l)}{\int_0^{\infty} dl l P_{\Gamma}(l)} \theta(x) \theta(l-x), \quad (4.21)$$

and is normalized to $\int_0^{\infty} dl \int_0^l dx S_{\Gamma}(l, x) = 1$. We then need the probability $B_{x,l}(z)$ to be at height z at “time” x for a Brownian motion of diffusion coefficient D starting at $z=0$ at $x=0$ and finishing at $z=0$ at $x=l$ in the presence of a reflexive boundary at $z=0$

$$B_{x,l}(z) = \frac{2}{\sqrt{\pi}} \left(\frac{l}{2Dx(l-x)} \right)^{1/2} e^{-z^2 \frac{l}{2Dx(l-x)}}. \quad (4.22)$$

It is normalized to $\int_0^{\infty} dz B_{x,l}(z) = 1$. The probability $\rho(z)$ that a given point of the polymer is at a distance z from the interface (normalized to $\int_0^{\infty} dz \rho(z) = 1$) can be now expressed within the renormalization picture as

$$\begin{aligned} \rho(z) &= \int_0^{\infty} dl \int_0^l dx S_{\Gamma_{\text{eq}}(T)}(l, x) B_{x,l}(z) \\ &= \frac{1}{\int_0^{\infty} dl l P_{\Gamma}(l)} \int_0^{\infty} dl P_{\Gamma}(l) 4 \sqrt{\frac{l}{2D}} \int_{\frac{2z}{\sqrt{2Dl}}}^{\infty} du e^{-u^2}. \end{aligned} \quad (4.23)$$

Introducing again the rescaled variable $\lambda = \frac{\sigma l}{\Gamma^2}$, we thus obtain the scaling form

$$\rho(z) dz = R(Z) dZ, \quad (4.24)$$

where the rescaled distance Z to the interface, defined as

$$Z = \sqrt{\frac{2\sigma}{D}} \frac{z}{\Gamma_{\text{eq}}(T)}, \quad (4.25)$$

is distributed with the following scaling function

$$R(Z) = 4 \int_0^{\infty} d\lambda P^*(\lambda) \sqrt{\lambda} \int_{\frac{Z}{\sqrt{\lambda}}}^{\infty} du e^{-u^2} \quad (4.26)$$

where $P^*(\lambda)$ is the fixed point distribution of equation (4.4). Deriving with respect to Z yields

$$\begin{aligned} R'(Z) &= -4 \int_0^{\infty} d\lambda P^*(\lambda) e^{-\frac{Z^2}{\lambda}} \\ &= -16Z \sum_{n=0}^{\infty} (-1)^n K_1[(2n+1)\pi Z] \end{aligned} \quad (4.27)$$

in terms of the Bessel function $K_1(y)$.

In particular, the asymptotic behaviors at $Z \rightarrow 0$ and $Z \rightarrow \infty$ are given respectively by

$$R(Z) = R(0) - 4Z + O(Z^2), \quad (4.28)$$

$$R(0) = 2\sqrt{\pi} \int_0^\infty d\lambda P^*(\lambda) \sqrt{\lambda} = \frac{8}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^2}, \quad (4.29)$$

and

$$R(Z) \underset{Z \rightarrow \infty}{\simeq} \frac{8}{\pi} \sqrt{2Z} e^{-\pi Z}. \quad (4.30)$$

We may also compute the moments

$$\begin{aligned} \int_0^\infty dZ Z^k R(Z) &= 2 \frac{\Gamma(1 + \frac{k}{2})}{k+1} \int_0^\infty d\lambda P^*(\lambda) \lambda^{1 + \frac{k}{2}} \\ &= 4 \frac{\Gamma(1 + \frac{k}{2}) \Gamma(2 + \frac{k}{2})}{(k+1) \pi^{3+k}} \sum_{n=0}^{\infty} \frac{(-1)^n}{(n + \frac{1}{2})^{3+k}}. \end{aligned} \quad (4.31)$$

In particular, the mean value of the square distance to the interface is given at high temperature by

$$\begin{aligned} \overline{\langle z^2 \rangle} &\simeq \Gamma_{\text{eq}}^2(T) \frac{D}{2\sigma} \int_0^\infty dZ Z^2 R(Z) = \frac{5D}{36\sigma} \Gamma_{\text{eq}}^2(T) \\ &\simeq \frac{5D}{4\sigma} T^2 (\ln T)^2. \end{aligned} \quad (4.32)$$

4.6 Density $\rho_{a,b}(z, z')$ for two thermal copies of the same chain

To compare our approach with the Replica Gaussian Variational description of reference [7], we now compute the probability $\rho_{a,b}(z, z')$ that a given monomer of a given polymer chain is at distance z from the interface in a configuration (a) and at a distance z' from the interface in a configuration (b) (note that in the effective thermodynamics, we have $\text{sgn}(z) = \text{sgn}(z')$). Using the same notations as in the previous section, the joint distribution of z and z' can be obtained as

$$\begin{aligned} \rho_{a,b}(z, z') &= \int_0^\infty dl \int_0^l dx S_{\Gamma_{\text{eq}}(T)}(l, x) B_{x,l}(z) B_{x,l}(z') \\ &= \frac{1}{\int_0^\infty dl l P_\Gamma(l)} \int_0^\infty dl P_\Gamma(l) \frac{4}{\pi D} e^{-\frac{z^2+z'^2}{Dl^2}} K_0 \left(\frac{z^2 + z'^2}{Dl^2} \right). \end{aligned} \quad (4.33)$$

Using again the rescaled variable $\lambda = \frac{\sigma l}{T^2}$, we obtain the scaling form

$$\begin{aligned} \rho_{a,b}(z, z') dz dz' &= R_{a,b}(Z, Z') dZ dZ' \\ \text{with } Z &= \sqrt{\frac{2\sigma}{D}} \frac{z}{\Gamma_{\text{eq}}(T)}. \end{aligned} \quad (4.34)$$

The scaling function $R_{a,b}(Z, Z')$ reads in terms of the fixed point distribution $P^*(\lambda)$ of equation (4.4)

$$R_{a,b}(Z, Z') = \frac{4}{\pi} \int_0^\infty d\lambda P^*(\lambda) e^{-\frac{z^2+z'^2}{2\lambda}} K_0 \left(\frac{Z^2 + Z'^2}{2\lambda} \right). \quad (4.35)$$

It is interesting to note that it is actually a function of the single variable $(Z^2 + Z'^2)$.

The probability that a given monomer is at the same z -coordinate in the two configurations (a) and (b) thus behaves at high temperature as

$$\begin{aligned} \int_0^\infty dz \rho_{a,b}(z, z) &= \sqrt{\frac{2\sigma}{D}} \frac{1}{\Gamma_{\text{eq}}(T)} \int_0^\infty dZ R_{a,b}(Z, Z) \\ &\underset{T \rightarrow \infty}{\sim} \frac{1}{T \ln T}, \end{aligned} \quad (4.36)$$

as compared to the decay as $(1/T)$ found in reference [7] for the Replica symmetric solution.

4.7 Solvent-solvent correlation function

$$\overline{\langle \text{sgn}(z(s)) \text{sgn}(z(s')) \rangle}$$

Within the renormalization picture, the correlation function $\overline{\langle \text{sgn}(z(s)) \text{sgn}(z(s')) \rangle}$ of the solvents seen by two monomers at distance $(s - s')$ along the polymer chain turns out to correspond exactly to the spin correlation function $\overline{\langle S_0(t) S_x(t) \rangle}$ of the random field Ising model in the Glauber dynamics starting from a random initial condition computed in references [18,21]. We thus only quote the result

$$\begin{aligned} \overline{\langle \text{sgn}(z(s)) \text{sgn}(z(s')) \rangle} &= \\ \mathcal{L}_{p \rightarrow X = \sigma \frac{|s-s'|}{T^2}}^{-1} &\left[\frac{1}{p} - \frac{4}{p^2} \tanh^2 \left(\frac{\sqrt{p}}{2} \right) \right] = \\ \sum_{n=-\infty}^{\infty} &\frac{48(2n+1)^2 \pi^2 + 32\sigma \frac{|s-s'|}{T^2}}{(2n+1)^4 \pi^4} e^{-(2n+1)^2 \pi^2 \sigma \frac{|s-s'|}{T^2}}, \end{aligned} \quad (4.37)$$

where $\Gamma = \Gamma_{\text{eq}}(T)$. In particular, the correlation length $\xi(T)$ associated with this correlation function is given by the decay of the dominant exponential at large separation $|s - s'|$

$$\xi(T) = \frac{\Gamma_{\text{eq}}^2(T)}{\pi^2 \sigma} \simeq \frac{9T^2 (\ln T)^2}{\pi^2 \sigma}. \quad (4.38)$$

5 Study the biased case $Q_0 > 0$

5.1 Properties of the renormalization procedure

In the biased case, it is necessary to introduce two probability distributions $P_\Gamma^+(Q, l)$ and $P_\Gamma^-(Q, l)$ representing the probabilities for a blob at scale Γ in the (\pm) solvent to

have absolute charge Q and length l . It was shown in reference [14] that with the renormalization procedure (3.1), these probability distributions flow at large Γ towards

$$\begin{aligned} P_F^\pm(Q, l) &= \mathcal{L}_{p \rightarrow l}^{-1} \left(U_F^\pm(p) e^{-(Q-\Gamma)u_F^\pm(p)} \right) \\ u_F^\pm(p) &= \Delta(p) \coth[\Gamma \Delta(p)] \mp \delta \\ U_F^\pm(p) &= \frac{\Delta(p)}{\sinh[\Gamma \Delta(p)]} e^{\mp \delta \Gamma} \\ \Delta(p) &= \sqrt{\delta^2 + \frac{p}{\sigma}}, \end{aligned} \quad (5.1)$$

where σ and δ have been defined in equations (1.4, 1.6) in terms of the initial charge distribution $C(q)$. The solutions (5.1) are valid in the scaling regime of large Γ , small δ and small p with $\delta\Gamma$ fixed and $p\Gamma^2$ fixed [14].

In particular, the distributions of the absolute charge $Q \geq \Gamma$ are simple exponentials:

$$P_F^+(Q) = u_F^+ e^{-(Q-\Gamma)u_F^+} \quad \text{with} \quad u_F^+ = \frac{2\delta}{e^{2\Gamma\delta} - 1}, \quad (5.2)$$

$$P_F^-(Q) = u_F^- e^{-(Q-\Gamma)u_F^-} \quad \text{with} \quad u_F^- = \frac{2\delta}{1 - e^{-2\Gamma\delta}}, \quad (5.3)$$

whereas the distributions of the length of blobs have the form of an infinite series of exponentials [19]

$$\begin{aligned} P_F^\pm(l) &= \mathcal{L}_{p \rightarrow l}^{-1} \left(\frac{\Delta(p) e^{\mp \delta \Gamma}}{\Delta(p) \cosh[\Gamma \Delta(p)] \mp \delta \sinh[\Gamma \Delta(p)]} \right) \\ &= \frac{\sigma}{\Gamma^2} \sum_{n=0}^{\infty} J_n^\pm(\gamma = \delta\Gamma) e^{-\frac{\sigma l}{\Gamma^2} s_n^\pm(\gamma = \delta\Gamma)}, \end{aligned} \quad (5.4)$$

where the functions $s_n^\pm(\gamma)$ and $J_n^\pm(\gamma)$ are defined in terms of the roots $\alpha_n^\pm(\gamma)$ ($n = 0, 1, \dots$) of the equation

$$\alpha_n^\pm(\gamma) \cotan(\alpha_n^\pm(\gamma)) = \pm \gamma \quad \text{with} \quad n\pi < \alpha_n^\pm(\gamma) < (n+1)\pi. \quad (5.5)$$

For $\gamma > 1$, the root $\alpha_0^+(\gamma)$ does not exist, but is replaced by the positive root $\tilde{\alpha}_0^+(\gamma)$ of the equation $\tilde{\alpha}_0^+(\gamma) \coth(\tilde{\alpha}_0^+(\gamma)) = \gamma$. In terms of these roots, we have

$$s_n^\pm(\gamma) = \gamma^2 + (\alpha_n^\pm(\gamma))^2, \quad (5.6)$$

$$J_n^\pm(\gamma) = \frac{2(-1)^n (\alpha_n^\pm(\gamma))^2 \sqrt{\gamma^2 + (\alpha_n^\pm(\gamma))^2} e^{\mp \gamma}}{\gamma^2 + (\alpha_n^\pm(\gamma))^2 \mp \gamma}, \quad (5.7)$$

except for the (+) $n = 0$ term in the domain $\gamma > 1$ for which

$$s_0^+(\gamma > 1) = \gamma^2 - (\tilde{\alpha}_0^+(\gamma))^2 \quad (5.8)$$

$$J_0^+(\gamma > 1) = \frac{2(\tilde{\alpha}_0^+(\gamma))^2 \sqrt{\gamma^2 - (\tilde{\alpha}_0^+(\gamma))^2} e^{-\gamma}}{\gamma + (\tilde{\alpha}_0^+(\gamma))^2 - \gamma^2}. \quad (5.9)$$

The mean lengths of the blobs in the domains (\pm) have simple expressions

$$\overline{l}_F^+ = \frac{1}{4\delta^2\sigma} (e^{2\delta\Gamma} - 2\delta\Gamma - 1), \quad (5.10)$$

$$\overline{l}_F^- = \frac{1}{4\delta^2\sigma} (2\delta\Gamma - 1 + e^{-2\delta\Gamma}), \quad (5.11)$$

but the mean values of $\ln l^\pm$ are unfortunately much more complicated:

$$\begin{aligned} \overline{\ln l^\pm} &= \int_0^\infty dl (\ln l) P_F^\pm(l) \\ &= \sum_{n=0}^{\infty} \frac{J_n^\pm(\gamma)}{s_n^\pm(\gamma)} \ln \left(\frac{1}{s_n^\pm(\gamma)} \right) + \ln \left(\frac{\Gamma^2}{\sigma} \right) - C_{\text{Euler}}, \end{aligned} \quad (5.12)$$

where C_{Euler} is the Euler constant.

5.2 Relation between temperature and renormalization scale

Using again equation (4.6), the averaged free-energy difference corresponding to the flip of a blob out of the domain (\pm) reads

$$\overline{\Delta F^{\text{flip}(\pm)}} = 2\Gamma - T \ln \left(\frac{(l_1^\mp l_2^\mp l_3^\mp)^{3/2}}{(l_1^\mp + l_2^\mp + l_3^\mp)^{3/2} \kappa^2} \right), \quad (5.13)$$

which yields to a quite complicated expression for arbitrary $\gamma = \delta\Gamma$.

In the following, we consider the case of large $\gamma \gg 1$, where the distribution P_F^+ is dominated by the $n = 0$ term [19]

$$P_F^+(l) \simeq a^+(\gamma) e^{-a^+(\gamma)l} \quad \text{with} \quad a^+(\gamma) \simeq 4\delta^2\sigma e^{-2\gamma}, \quad (5.14)$$

leading to

$$\overline{\ln l^+} \simeq \ln \frac{1}{a^+(\gamma)} - C_{\text{Euler}} = 2\gamma + \ln \frac{1}{4\delta^2\sigma} - C_{\text{Euler}}. \quad (5.15)$$

In this regime, the probabilities to have blobs with absolute charge $Q = \Gamma$ in the (\pm) domain read respectively (5.2)

$$P^+(Q = \Gamma) = u_F^+ \simeq 2\delta e^{-2\Gamma\delta}, \quad (5.16)$$

$$P^-(Q = \Gamma) = u_F^- \simeq 2\delta, \quad (5.17)$$

and thus the renormalization consists asymptotically in flipping only blobs out of the ($-$) domain. We thus now concentrate on the free-energy difference corresponding to the flip of a ($-$) blob, which can be estimated as follows

$$\begin{aligned} \overline{\Delta F^{\text{flip}(-)}} &= 2Q_2 - T \ln \left(\frac{(l_1^+ l_2^- l_3^+)^{3/2}}{(l_1^+ + l_2^- + l_3^+)^{3/2} \kappa^2} \right) \\ &\simeq 2\Gamma - \frac{3}{2}T \left[2\overline{\ln(l_1^+)} - \overline{\ln(l_1^+ + l_3^+)} \right] \\ &\simeq 2\Gamma - \frac{3}{2}T \left[2\delta\Gamma + \ln \frac{1}{4\delta^2\sigma} - C_{\text{Euler}} - 1 \right], \end{aligned} \quad (5.18)$$

so that finally, in the regime $\delta \rightarrow 0$, $\Gamma \rightarrow \infty$, with $\delta\Gamma \gg 1$ fixed, and large temperatures, we have

$$\overline{\Delta F^{\text{flip}(-)}} \simeq \Gamma(2 - 3\delta T) - \frac{3}{2}T \ln \frac{1}{\delta^2\sigma}. \quad (5.19)$$

Since the renormalization procedure has to be performed as long as $\overline{\Delta F^{\text{flip}(-)}} < 0$, we obtain a transition at the temperature

$$T_c = \frac{2}{3\delta}, \quad (5.20)$$

where δ is the parameter characterizing the distribution of quenched charges (1.6). For $T < T_c$, the renormalization procedure has to be stopped at scale $\Gamma_{\text{eq}}(T)$ given by

$$\Gamma_{\text{eq}}(T) = \frac{3T \ln \frac{1}{\delta^2\sigma}}{2(2 - 3\delta T)} = \frac{3T \ln \frac{1}{\delta^2\sigma}}{4(1 - \frac{T}{T_c})}. \quad (5.21)$$

At the temperature $T = T_c$, the renormalization scale $\Gamma_{\text{eq}}(T)$ diverges: this corresponds to the delocalization transition found previously in references [2,5–8,11].

5.3 Comparison with previous results for the critical temperature

5.3.1 Case of Gaussian distribution for the quenched charges

For the case where the initial distribution of charges is Gaussian (1.7), we get

$$T_c = \frac{2}{3\delta} = \frac{4\sigma}{3q_0}, \quad (5.22)$$

in agreement with the scaling obtained previously [2,6,7] and with the bounds established in reference [8], which read in terms of our notations

$$\frac{2\sigma}{\sqrt{\pi} \ln 2} < T_c < \frac{2\sigma}{q_0}. \quad (5.23)$$

We note moreover that the value of the transition temperature obtained here coincides with the critical temperature obtained by Stepanow *et al.* [6] and is lower than the critical temperature obtained by Trovato *et al.* [7], since their results read respectively in our notations:

$$T_c^{\text{Stepanow et al.}} = \frac{4\sigma}{3q_0}, \quad (5.24)$$

$$T_c^{\text{Trovato et al.}} = \frac{2\sigma}{q_0}. \quad (5.25)$$

5.3.2 Case of binary distribution for the quenched charges

For the case where the initial distribution of charges is a binary distribution, we obtain that T_c is the solution of the equation (1.11)

$$ce^{-\frac{4}{3T_c}q_+} + (1-c)e^{+\frac{4}{3T_c}q_-} = 1. \quad (5.26)$$

In particular for the case $q_- = q_+ = q_1$ (1.12), we obtain

$$T_c = \frac{4q_1}{3 \ln \left(\frac{c}{1-c} \right)}, \quad (5.27)$$

which is consistent with the bounds given in reference [8] reading in our notations:

$$T_c < \frac{4q_1}{\ln \left(\frac{c}{1-c} \right)}. \quad (5.28)$$

We may also compare with the bounds obtained in reference [11] concerning the binary case with $c = \frac{1}{2}$, $q_+ = 1+h$ and $q_- = 1-h$ where $0 < h < 1$ for which we have:

$$q_0 = h, 2\sigma = 1, e^{-2\delta h} \cosh \delta = 1. \quad (5.29)$$

Our renormalization approach yields thus for this case the following behavior for the critical line $h_c(T)$ at high temperature

$$\begin{aligned} h_c(T) &= \left(\frac{1}{2\delta} \ln \cosh \delta \right) \Big|_{\delta=\frac{2}{3T}} = \frac{3T_c}{4} \ln \cosh \left(\frac{2}{3T_c} \right) \\ &= \frac{1}{6T} - \frac{1}{81T^3} + O\left(\frac{1}{T^5}\right), \end{aligned} \quad (5.30)$$

which satisfies the bounds established in reference [11]

$$0 < \lim_{T \rightarrow \infty} (Th_c(T)) \leq 1. \quad (5.31)$$

5.4 Thermodynamic quantities

Following the computations done for the symmetric case in Section 4.3, we obtain that the energy per monomer $e(T)$ of the chain in the thermodynamic limit can be obtained as

$$e(T) = - \frac{\int_{Q,l} Q [P_{\Gamma_{\text{eq}}^+(T)}^+(Q,l) + P_{\Gamma_{\text{eq}}^-(T)}^-(Q,l)]}{\int_{Q,l} l [P_{\Gamma_{\text{eq}}^+(T)}^+(Q,l) + P_{\Gamma_{\text{eq}}^-(T)}^-(Q,l)]}, \quad (5.32)$$

with $\Gamma_{\text{eq}}(T)$ defined in equation (5.21).

Using the fixed point solution of equations (5.1), we have at large temperature

$$\begin{aligned} e(T) &\simeq -2\delta\sigma \coth[\delta\Gamma_{\text{eq}}(T)] - \frac{2\delta^2\sigma\Gamma_{\text{eq}}(T)}{\sinh^2[\delta\Gamma_{\text{eq}}(T)]} \\ &\simeq -2\delta\sigma - 8\sigma\delta^2\Gamma_{\text{eq}}(T)e^{-2\delta\Gamma_{\text{eq}}(T)} + \dots \end{aligned} \quad (5.33)$$

Since in the limit of small dissymmetry $\delta \rightarrow 0$, we have the relation (1.15), the energy per monomer at the transition T_c is simply

$$e(T_c) = -q_0, \quad (5.34)$$

and coincides of course with the energy per monomer when the heteropolymer is delocalized in the solvent (+) for $T > T_c$. Surprisingly however, we find that the critical

behavior near T_c is governed by the following essential singularity:

$$e(T) - e(T_c) \simeq -8\sigma\delta^2\Gamma_{\text{eq}}(T)e^{-2\delta\Gamma_{\text{eq}}(T)} \\ \underset{T \rightarrow T_c^-}{\simeq} -2q_0 \frac{\ln \frac{4\sigma}{q_0}}{\left(1 - \frac{T}{T_c}\right)} \exp \left[-\frac{\ln \frac{4\sigma}{q_0}}{\left(1 - \frac{T}{T_c}\right)} \right]. \quad (5.35)$$

The entropy per monomer $s(T)$ is given in the thermodynamic limit by the generalization of equation (4.15)

$$s(T) = \frac{\int_{Q,l} [l \ln \mu + \ln \kappa - \frac{3}{2} \ln l] [P_{\Gamma_{\text{eq}}(T)}^+(Q,l) + P_{\Gamma_{\text{eq}}(T)}^-(Q,l)]}{\int_{Q,l} l [P_{\Gamma_{\text{eq}}(T)}^+(Q,l) + P_{\Gamma_{\text{eq}}(T)}^-(Q,l)]} \\ = \ln \mu - \frac{3}{2} \frac{\overline{\ln l^+} + \overline{\ln l^-}}{\overline{l^+} + \overline{l^-}} - 2 \frac{\ln \kappa}{\overline{l^+} + \overline{l^-}}, \quad (5.36)$$

where the averages have to be computed with the probability distributions $P_{\Gamma}^{\pm}(Q,l)$ given in equations (5.1). Considering as before the regime $\delta \rightarrow 0$, $\Gamma \rightarrow \infty$, with $\gamma = \delta\Gamma \gg 1$ fixed where we can use equation (5.14), we get

$$s(T) \simeq \ln \mu - 12\sigma\delta^3\Gamma_{\text{eq}}(T)e^{-2\delta\Gamma_{\text{eq}}(T)} + \dots \\ \underset{T \rightarrow T_c^-}{\simeq} \ln \mu - \frac{3q_0^2}{2\sigma} \frac{\ln \frac{4\sigma}{q_0}}{\left(1 - \frac{T}{T_c}\right)} \exp \left[-\frac{\ln \frac{4\sigma}{q_0}}{\left(1 - \frac{T}{T_c}\right)} \right]. \quad (5.37)$$

We finally give the expression of the free-energy per monomer

$$f(T) \simeq f(T_c) - 8\sigma\delta^2\Gamma_{\text{eq}}(T)e^{-2\delta\Gamma_{\text{eq}}(T)} \\ + 12\sigma\delta^3T\Gamma_{\text{eq}}(T)e^{-2\delta\Gamma_{\text{eq}}(T)} \dots \\ \underset{T \rightarrow T_c^-}{\simeq} f(T_c) - 2q_0 \left(\ln \frac{4\sigma}{q_0} \right) \exp \left[-\frac{\ln \frac{4\sigma}{q_0}}{\left(1 - \frac{T}{T_c}\right)} \right] \quad (5.38)$$

which again presents an essential singularity near T_c : the delocalization transition is thus found to be of infinite order.

The well-known *pure* models presenting infinite order transitions are the two-dimensional XY model [27] and the 1D Ising or Potts model with inverse square long range interactions [28, 29]. The important property of these systems is that the interaction between two defects (two vortices in the XY model or two kinks in the spin chain) is logarithmic at large distances. The usual estimation of the free-energy for a pair of defects, where both the energy and the entropy behave as the logarithm of the size L of the system, leads to a factorization of $\ln L$ as in the Imry-Ma argument leading to equation (2.15) for the heteropolymer problem. It would be interesting to discuss in more details the similarities/differences between these systems, but this goes beyond the scope of the present paper.

5.5 Statistical properties of blobs

In the localized phase $T < T_c$, we find that the blobs in the domain $z > 0$ and $z < 0$ have respectively the typical lengths (5.10)

$$l_{\text{blob}}^+(T) \simeq \overline{l^+}_{\Gamma_{\text{eq}}(T)} \simeq \frac{1}{4\delta^2\sigma} (e^{2\delta\Gamma_{\text{eq}}(T)} - 2\delta\Gamma_{\text{eq}}(T) - 1) \quad (5.39)$$

$$l_{\text{blob}}^-(T) \simeq \overline{l^-}_{\Gamma_{\text{eq}}(T)} \simeq \frac{1}{4\delta^2\sigma} (2\delta\Gamma_{\text{eq}}(T) - 1 + e^{-2\delta\Gamma_{\text{eq}}(T)}). \quad (5.40)$$

As T approaches T_c^- , $l_{\text{blob}}^+(T)$ thus diverges with an essential singularity as

$$l_{\text{blob}}^+(T) \underset{T \rightarrow T_c^-}{\simeq} \frac{1}{4\delta^2\sigma} \left(\frac{1}{\delta^2\sigma} \right)^{\frac{1}{\left(1 - \frac{T}{T_c}\right)}} \\ = \frac{\sigma}{q_0^2} \exp \left[+\frac{\ln \frac{4\sigma}{q_0}}{\left(1 - \frac{T}{T_c}\right)} \right], \quad (5.41)$$

whereas $l_{\text{blob}}^-(T)$ also diverges but only algebraically as

$$l_{\text{blob}}^-(T) \underset{T \rightarrow T_c^-}{\simeq} \frac{\ln \frac{1}{\delta^2\sigma}}{4\delta^2\sigma} \frac{1}{\left(1 - \frac{T}{T_c}\right)} \\ = \frac{\sigma}{q_0^2} \frac{\ln \frac{4\sigma}{q_0}}{\left(1 - \frac{T}{T_c}\right)}. \quad (5.42)$$

We note that these behaviors are compatible with the relation (2.13) between the typical lengths l_{blob}^- and l_{blob}^+ obtained in reference [2] *via* an Imry-Ma argument, since we have obtained

$$l_{\text{blob}}^- \simeq \frac{\sigma}{q_0^2} \ln l_{\text{blob}}^+. \quad (5.43)$$

Our results (5.38, 5.41) also satisfy the relation (2.15) between the free-energy and the typical blob length l_{blob}^+ in the preferred solvent obtained again in reference [2] *via* an Imry-Ma argument, since we have

$$f(T) - f(T_c) \simeq -\frac{3}{2}(T_c - T) \frac{\ln l_{\text{blob}}^+}{l_{\text{blob}}^+}. \quad (5.44)$$

As a direct consequence of equations (5.41, 5.42), we obtain that the typical distances $z^{\pm}(T)$ to the interface in the domain $z > 0$ and $z < 0$ diverge respectively as $T \rightarrow T_c^-$ as

$$z^+(T) \sim \sqrt{Dl^{+\text{blob}}(T)} \underset{T \rightarrow T_c^-}{\simeq} = \frac{\sqrt{D\sigma}}{q_0} \exp \left[\frac{\ln \frac{4\sigma}{q_0}}{2 \left(1 - \frac{T}{T_c}\right)} \right] \quad (5.45)$$

$$z^-(T) \sim \sqrt{Dl^{-\text{blob}}(T)} \underset{T \rightarrow T_c^-}{\simeq} = \frac{\sqrt{D\sigma}}{q_0} \left[\frac{\ln \frac{4\sigma}{q_0}}{\left(1 - \frac{T}{T_c}\right)} \right]^{1/2}. \quad (5.46)$$

As in the symmetric case, the lengths l^\pm of the blobs are independent random variables distributed respectively with the probability distributions $P_{\Gamma_{\text{eq}}}^\pm(l)$. In particular, near T_c , the rescaled variable

$$\lambda_+ = 4\delta^2\sigma \frac{l}{e^{2\delta\Gamma_{\text{eq}}(T)}} \underset{T \rightarrow T_c^-}{\simeq} \frac{l_+}{\frac{\sigma}{q_0} \exp\left[\frac{\ln \frac{4\sigma}{q_0}}{\left(1 - \frac{T}{T_c}\right)}\right]} \quad (5.47)$$

is distributed with a simple exponential law $e^{-\lambda_+}$ (see Eq. (5.14)).

5.6 Density profiles $\rho^\pm(z)$

Following the calculations done previously in the symmetric case, we obtain that the probabilities $\rho^\pm(z)$ that a given point of the polymer is at a distance z from the interface in the (\pm) domain (with the normalization $\int_0^\infty dz(\rho^+(z) + \rho^-(z)) = 1$) reads

$$\rho^\pm(z) = \frac{1}{\int_0^\infty dl l (P_\Gamma^+(l) + P_\Gamma^-(l))} \times \int_0^\infty dl P_\Gamma^\pm(l) 4\sqrt{\frac{l}{2D}} \int_{\frac{z}{\sqrt{2Dt}}}^\infty du e^{-u^2}. \quad (5.48)$$

In the regime $\delta\Gamma \gg 1$ studied above where $P_\Gamma^+(l)$ has the asymptotic simple form of equation (5.14), we get the following scaling form

$$\rho^+(z)dz = R^+(Z)dZ, \quad (5.49)$$

where the rescaled distance Z to the interface and the scaling function $R(Z)$ read

$$Z = \frac{4\delta z}{\sqrt{2D}e^{\delta\Gamma_{\text{eq}}(T)}} \underset{T \rightarrow T_c^-}{\simeq} \frac{z}{\sqrt{\frac{D}{2} \frac{\sigma}{q_0} \exp\left[\frac{\ln \frac{4\sigma}{q_0}}{2\left(1 - \frac{T}{T_c}\right)}\right]}}, \quad (5.50)$$

and

$$R^+(Z) = 4 \int_0^\infty du e^{-u^2} \int_{\frac{Z}{u}}^\infty dv v^2 e^{-v^2}. \quad (5.51)$$

Deriving with respect to Z yields

$$\frac{dR^+(Z)}{dZ} = -4Z^2 \int_0^\infty du e^{-u^2 - \frac{Z^2}{u^2}} \frac{1}{u^3} = -4ZK_1(2Z). \quad (5.52)$$

In particular, the asymptotic behaviors at $Z \rightarrow 0$ and $Z \rightarrow \infty$ are given respectively by

$$R^+(Z) = \frac{\pi}{2} - 2Z + O(Z^2) \quad (5.53)$$

and

$$R^+(Z) \underset{Z \rightarrow \infty}{\simeq} \sqrt{\pi Z} e^{-2Z}. \quad (5.54)$$

5.7 Correlation function $\overline{\langle \text{sgn}(z(s))\text{sgn}(z(s')) \rangle}$

Within the renormalization picture, the correlation function $\overline{\langle \text{sgn}(z(s))\text{sgn}(z(s')) \rangle}$ of the solvents seen by two monomers at distance $(s - s')$ along the polymer chain containing a dissymmetric distribution in hydrophilic/hydrophobic components corresponds exactly to the spin correlation function $\overline{\langle S_0(t)S_x(t) \rangle}$ of the random field Ising model in the Glauber dynamics starting from a random initial condition in the presence of an external field, which is computed in reference [21]. Here we do not give the full result, but only the correlation length $\xi(T)$ which, not surprisingly, is simply given in the regime $\delta\Gamma \gg 1$ that we consider by the typical behavior of $l_{\text{blob}}^+(T)$ obtained in equation (5.39)

$$\xi(T) \simeq l_{\text{blob}}^+(T) \underset{T \rightarrow T_c^-}{\simeq} \frac{\sigma}{q_0} \exp\left[+\frac{\ln \frac{4\sigma}{q_0}}{\left(1 - \frac{T}{T_c}\right)}\right]. \quad (5.55)$$

6 Finite size properties

Up to now we have always considered the thermodynamic limit of heteropolymers of infinite length $L \rightarrow \infty$. In this section, we study the finite-size properties of the localization at the interface for the case of periodic boundary conditions, *i.e.* we consider cyclic chains $(q_1, q_2, \dots, q_L, q_{L+1} = q_1)$ of finite (but large) size L , with positions $(z_1, \dots, z_{L+1} = z_1)$. We can apply the renormalization procedure as before, but the procedure will now stop at some finite renormalization scale Γ_{deloc} , where the chain delocalizes from the interface. This renormalization scale depends upon the realization of the quenched charges and corresponds to some temperature T_{deloc} *via* the relation

$$\Gamma_{\text{deloc}} = \Gamma_{\text{eq}}(T_{\text{deloc}}) \quad (6.1)$$

given in equations ((4.10), (5.21)) respectively for the symmetric case and the biased case. In the following, we characterize the distribution of T_{deloc} for the ensemble of finite chains of size L , and the probability distribution of the number of blobs for the chains of length L that are still localized at a given temperature.

6.1 Probability measure for the blobs of a cyclic chain of length L

As shown in references [15,19], it is possible to follow the renormalization procedure for finite size systems. Here we deal with periodic boundary conditions, and to avoid problems with the translation invariance along the chain, it is convenient to mark a point of the chain, called “the origin” in the following, and to give an orientation to the chain. For $k = 1, 2, \dots$, we define $N_{\Gamma, L}^{2k, \pm}(Q_1, l_1; Q_2, l_2; \dots, Q_{2k}, l_{2k})$ as the probability that in the chain of length L at renormalization scale Γ , the origin belongs to a blob (Q_1, l_1) in the domain (\pm), and

$$\begin{aligned}
\partial_\Gamma N_{\Gamma,L}^{2k,\pm}(Q_1, l_1; Q_2, l_2; \dots Q_{2k}, l_{2k}) = & \\
& \sum_{i=2}^{2k} \int_{Q+Q''-\Gamma=Q_i, l+l'+l''=l_i} N_{\Gamma,L}^{2k+2,\pm}(Q_1, l_1; \dots; Q_{i-1}, l_{i-1}; Q, l; \Gamma, l'; Q'', l''; Q_{i+1}, l_{i+1} \dots; Q_{2k}, l_{2k}) \\
& \times \int_{Q+Q''-\Gamma=Q_1, l+l'+l''=l_1} N_{\Gamma,L}^{2k+2,\pm}(Q, l; \Gamma, l'; Q'', l''; Q_2, l_2 \dots; Q_{2k}, l_{2k}) \\
& + \int_{Q+Q''-\Gamma=Q_1, l+l'+l''=l_1} N_{\Gamma,L}^{2k+2,\pm}(Q'', l''; Q_2, l_2; \dots; Q_{2k}^-, l_{2k}^-; Q, l; \Gamma, l') \\
& + \int_{Q+Q''-\Gamma=Q_1, l+l'+l''=l_1} N_{\Gamma,L}^{2k+2,\mp}(\Gamma, l'; Q'', l''; Q_2, l_2; \dots; Q_{2k}^-, l_{2k}^-; Q, l), \quad (6.3)
\end{aligned}$$

that there are exactly $(2k - 1)$ other blobs in the chain of absolute charges and lengths given by the sequence $(Q_2, l_2; \dots Q_{2k}, l_{2k})$. We also need to introduce the probability $N_{\Gamma,L}^{1,\pm}(Q)$ that the chain at scale Γ is already delocalized in the (\pm) solvent with absolute charge Q . The normalization of these probabilities read

$$\begin{aligned}
& \sum_{k=1}^{\infty} \int_{Q_i \geq \Gamma, l_i} N_{\Gamma,L}^{2k,+}(Q_1, l_1; Q_2, l_2; \dots Q_{2k}, l_{2k}) \\
& + \sum_{k=1}^{\infty} \int_{Q_i \geq \Gamma, l_i} N_{\Gamma,L}^{2k,-}(Q_1, l_1; Q_2, l_2; \dots Q_{2k}, l_{2k}) \\
& + \int_0^\infty dQ N_{\Gamma,L}^{1,+}(Q) + \int_0^\infty dQ N_{\Gamma,L}^{1,-}(Q) = 1. \quad (6.2)
\end{aligned}$$

Note that in the last two terms, the absolute charge Q is a random variable of the domain $[0, +\infty[$, contrary to the other terms where by definition of the renormalization rule we have $Q_i \geq \Gamma$.

The renormalization equations for these probabilities read for $k = 1, 2, \dots$

see equation (6.3) above

and

$$\begin{aligned}
\partial_\Gamma N_{\Gamma,L}^{1,\pm}(Q) = & \int_{l_1, l_2} N_{\Gamma,L}^{2,\pm}(Q + \Gamma, l_1; \Gamma, l_2) \\
& + \int_{l_1, l_2} N_{\Gamma,L}^{2,\mp}(\Gamma, l_1; Q + \Gamma, l_2). \quad (6.4)
\end{aligned}$$

As already obtained in references [15,19] for the case of fixed boundary conditions, the above renormalization equations concerning periodic boundary conditions are solved by a quasi-factorized form for $k = 1, 2, \dots$

$$\begin{aligned}
N_{\Gamma,L}^{2k,\pm}(Q_1, l_1; Q_2, l_2; \dots Q_{2k}, l_{2k}) = & l_1 P_\Gamma^\pm(Q_1, l_1) \\
& \times P_\Gamma^\mp(Q_2, l_2) \dots P_\Gamma^\pm(Q_{2k-1}, l_{2k-1}) P_\Gamma^\mp(Q_{2k}, l_{2k}) \delta\left(L - \sum_{i=1}^{2k} l_i\right), \quad (6.5)
\end{aligned}$$

where $P_\Gamma^\pm(Q, l)$ are the bulk distributions given in equation (5.1), satisfying

$$\begin{aligned}
\partial_\Gamma P_\Gamma^\pm(Q, l) = & \\
& \int_{Q_1+Q_3-\Gamma=Q, l_1+l_2+l_3=l} P_\Gamma^\mp(\Gamma, l_2) P_\Gamma^\pm(Q_1, l_1) P_\Gamma^\pm(Q_3, l_3) \\
& + P_\Gamma^\pm(Q, l) \int_0^\infty dl' (P_\Gamma^\pm(\Gamma, l') - P_\Gamma^\mp(\Gamma, l')). \quad (6.6)
\end{aligned}$$

Note that in the measure (6.5), the first bond plays a special role as it is defined as the bond containing the origin.

The equation (6.4) now reads

$$\begin{aligned}
\partial_\Gamma N_{\Gamma,L}^{1,\pm}(Q) = & \int_{l_1, l_2} l_1 P_\Gamma^\pm(Q + \Gamma, l_1) P_\Gamma^\mp(\Gamma, l_2) \delta(L - (l_1 + l_2)) \\
& + \int_{l_1, l_2} l_1 P_\Gamma^\mp(\Gamma, l_1) P_\Gamma^\pm(Q + \Gamma, l_2) \delta(L - (l_1 + l_2)) \\
& = L P_\Gamma^\pm(Q + \Gamma, \cdot) * L P_\Gamma^\mp(\Gamma, \cdot). \quad (6.7)
\end{aligned}$$

Using now the explicit expressions (5.1), we get in Laplace transform with respect to L

$$\begin{aligned}
& \int_0^\infty dL e^{-pL} \left(\partial_\Gamma N_{\Gamma,L}^{1,\pm}(Q) \right) = \\
& - \partial_p \left(\frac{\Delta^2(p)}{\sinh^2[\Gamma \Delta(p)]} e^{-Q(\Delta(p) \coth[\Gamma \Delta(p)] \mp \delta)} \right) \quad (6.8)
\end{aligned}$$

where $\Delta(p) = \sqrt{\delta^2 + \frac{p}{\sigma}}$.

6.2 Probability for a chain to be delocalized at renormalization scale Γ

The equations (6.7) for the probabilities $N_{\Gamma,L}^{1,\pm}(Q)$ that a chain of length L is already delocalized at scale Γ with an absolute charge Q in the domain (\pm) can be integrated with respect to Γ to yield

$$\begin{aligned}
& \int_0^\infty dL e^{-pL} N_{\Gamma,L}^{1,\pm}(Q) = \\
& \frac{1}{2\sigma} \left(\frac{\coth[\Gamma \Delta(p)]}{\Delta(p)} - \frac{\Gamma}{\sinh^2[\Gamma \Delta(p)]} \right) e^{-Q(\Delta(p) \coth[\Gamma \Delta(p)] \mp \delta)}. \quad (6.9)
\end{aligned}$$

$$N_{\Gamma,L}^{1,\pm} = \int_0^\infty dQ N_{\Gamma,L}^{1,\pm}(Q) = \mathcal{L}_{p \rightarrow L}^{-1} \left[\frac{1}{2\sigma(\Delta(p) \cosh[\Gamma\Delta(p)] \mp \delta \sinh[\Gamma\Delta(p)])} \left(\frac{\cosh[\Gamma\Delta(p)]}{\Delta(p)} - \frac{\Gamma}{\sinh[\Gamma\Delta(p)]} \right) \right]. \quad (6.11)$$

We may check that $N_{\Gamma,L}^{1,\pm}(Q)$ vanishes as it should for $\Gamma \rightarrow 0$. In the limit $\Gamma \rightarrow \infty$, the chain is expected to be always delocalized, with a charge corresponding to the sum $\sum_{i=1}^L q_i$ of L independent identical random variables. Indeed, using (1.15), we find

$$\begin{aligned} N_{\Gamma \rightarrow \infty, L}^{1,\pm}(Q) &= \mathcal{L}_{p \rightarrow L}^{-1} \left[\frac{e^{-Q(\sqrt{\delta^2 + \frac{p}{\sigma}} \mp \delta)}}{2s\sqrt{\delta^2 + \frac{p}{\sigma}}} \right] \\ &= \frac{1}{2\sqrt{2\sigma L}} e^{-\frac{(Q \mp Lq_0)^2}{4\sigma L}}, \end{aligned} \quad (6.10)$$

as expected from the Central Limit Theorem.

For arbitrary Γ , we can obtain the total probabilities $N_{\Gamma,L}^{1,\pm}$ that the chain is already delocalized at scale Γ in the domain (\pm) as

see equation (6.11) above.

In particular for the symmetric case $\delta = 0$, we have

$$N_{\Gamma,L}^{1,\pm} = \frac{1}{2} \mathcal{N} \left(\lambda \equiv \frac{\sigma L}{\Gamma^2} \right). \quad (6.12)$$

The scaling function $\mathcal{N}(\lambda)$ represents the total probability for a symmetric chain of length L to be delocalized at temperature T corresponding to the renormalization scale $\Gamma = \Gamma_{\text{eq}}(T)$ defined in equation (4.10). It reads

$$\begin{aligned} \mathcal{N}(\lambda) &= \mathcal{L}_{s \rightarrow \lambda}^{-1} \left(\frac{1}{s} - \frac{2}{\sqrt{s} \sinh(2\sqrt{s})} \right) \\ &= 1 - \sum_{n=-\infty}^{+\infty} (-1)^n e^{-\lambda n^2 \frac{\pi^2}{4}} \\ &= 1 - \frac{2}{\sqrt{\pi\lambda}} \sum_{m=-\infty}^{+\infty} e^{-\frac{(2m+1)^2}{\lambda}}. \end{aligned} \quad (6.13)$$

6.2.1 Distribution of the delocalization temperature for symmetric finite chains

The probability that the polymer chain delocalizes from the interface between Γ and $\Gamma+d\Gamma$ is given by $(\partial_\Gamma[\mathcal{N}(\lambda)])$. To characterize the distribution of the delocalization temperature T_{deloc} for the ensemble of the symmetric finite chains of length L , it is thus convenient to define the rescaled variable

$$g = \frac{\Gamma_{\text{eq}}(T_{\text{deloc}})}{\sqrt{\sigma L}}, \quad (6.14)$$

where the function $\Gamma_{\text{eq}}(T)$ has been defined in equation (4.10). The final result is that g is distributed with the law:

$$D(g) = -\frac{2}{g^3} \mathcal{N}' \left(\frac{1}{g^2} \right) = \frac{\pi^2}{g^3} \sum_{n=1}^{+\infty} (-1)^{n+1} n^2 e^{-\frac{n^2 \pi^2}{4g^2}} \quad (6.15)$$

$$= \frac{2}{\sqrt{\pi}} \sum_{m=-\infty}^{+\infty} [2(2m+1)^2 g^2 - 1] e^{-(2m+1)^2 g^2}. \quad (6.16)$$

6.2.2 Distribution of the delocalization temperature for dissymmetric finite chains

In the biased case, the probability that a chain of length L delocalizes from the interface between Γ and $\Gamma+d\Gamma$ in the domain (\pm) is given by

$$\begin{aligned} \partial_\Gamma N_{\Gamma,L}^{1,\pm} &= \mathcal{L}_{p \rightarrow L}^{-1} \\ &\times \left[-\partial_p \left(\frac{\Delta^2(p)}{\sinh[\Gamma\Delta(p)](\Delta(p) \cosh[\Gamma\Delta(p)] \mp \delta \sinh[\Gamma\Delta(p)])} \right) \right]. \end{aligned} \quad (6.17)$$

In the regime $\gamma = \delta\Gamma \gg 1$ considered before (see Eq. (5.14)), the inverse Laplace transform is dominated by a single pole contribution

$$\partial_\Gamma N_{\Gamma,L}^{1,+} \simeq 2\delta a^+(\gamma) L e^{-La^+(\gamma)}, \quad (6.18)$$

where $a^+(\gamma) = 4\sigma\delta^2 \exp(-2\gamma)$ has been introduced in (5.14). We now use the correspondence between temperature and renormalization scale given by $\Gamma = \Gamma_{\text{eq}}(T)$ (5.21). To characterize the distribution of the delocalization temperature T_{deloc} for the ensemble of dissymmetric finite chains of large length L , it is thus convenient to define the random variable

$$r = \frac{1}{4\delta^2\sigma L} \left(\frac{1}{\delta^2\sigma} \right)^{\frac{T_{\text{deloc}}}{T_c - T_{\text{deloc}}}}. \quad (6.19)$$

The final result is that r is distributed with the law

$$D^+(r) = \frac{1}{r^2} e^{-\frac{1}{r}}. \quad (6.20)$$

In particular, the typical value for the delocalization temperature corresponds to $r \sim 1$ and thus presents a correction in $1/(\ln L)$ with respect to the critical temperature T_c

$$T_{\text{deloc}}^{\text{typ}} \sim T_c \left(1 - \frac{1}{\delta^2\sigma \ln L} \right). \quad (6.21)$$

$$\begin{aligned}
\langle (2k)^2 \rangle_{L,\Gamma} &\equiv \sum_{k=0}^{\infty} 4k^2 B_L^{2k}(\Gamma) = \mathcal{L}_{p \rightarrow L}^{-1} \left(4 \left[-\partial_p (P_{\Gamma}^+(p)P_{\Gamma}^-(p)) \right] \frac{1 + P_{\Gamma}^+(p)P_{\Gamma}^-(p)}{(1 - P_{\Gamma}^+(p)P_{\Gamma}^-(p))^3} \right) \\
&= \mathcal{L}_{p \rightarrow L}^{-1} \left(4 \frac{(2\delta^2\sigma + p(\cosh^2[\Gamma\Delta(p)] + 1))(\delta^2\sigma + p\Gamma\Delta(p) \coth[\Gamma\Delta(p)])}{p^3 \sinh^4[\Gamma\Delta(p)]} \right) \\
&= \frac{4\sigma^2 L^2 \delta^4}{\sinh^4(\delta\Gamma)} + \frac{2\sigma L \delta^2}{\sinh^4(\delta\Gamma)} (\cosh(2\delta\Gamma) - 4\delta\Gamma \coth(\delta\Gamma) + 3) + \sum_{n=1}^{\infty} e^{-\sigma L(\delta^2 + \frac{n^2\pi^2}{\Gamma^2})} (\dots). \quad (6.25)
\end{aligned}$$

6.3 Distribution of the number of blobs at scale Γ

The probability that a chain is still localized around the interface at scale Γ and is in a state with $(2k)$ blobs read for $k = 1, 2, \dots$

$$\begin{aligned}
B_L^{2k}(\Gamma) &= \int_{Q_i, l_i} N_{\Gamma, L}^{2k,+}(Q_1, l_1; Q_2, l_2; \dots Q_{2k}, l_{2k}) \\
&\quad + \int_{Q_i, l_i} N_{\Gamma, L}^{2k,-}(Q_1, l_1; Q_2, l_2; \dots Q_{2k}, l_{2k}). \quad (6.22)
\end{aligned}$$

The Laplace transform of the generating function of the probabilities $B_L^{2k}(\Gamma)$ reads

$$\begin{aligned}
\int_0^{\infty} dL e^{-pL} \left(\sum_{k=1}^{\infty} z^k B_L^{2k}(\Gamma) \right) &= \\
&= \frac{[-\partial_p (P_{\Gamma}^+(p)P_{\Gamma}^-(p))] \frac{z}{1 - zP_{\Gamma}^+(p)P_{\Gamma}^-(p)}}{\frac{z \sinh[\Gamma\Delta(p)](\delta^2\sigma \sinh[\Gamma\Delta(p)] + p\Gamma\Delta(p) \cosh[\Gamma\Delta(p)])}{(\delta^2\sigma(1-z) + p(\cosh^2[\Gamma\Delta(p)] - z))(\delta^2\sigma + p \cosh^2[\Gamma\Delta(p)])}}. \quad (6.23)
\end{aligned}$$

In particular, the average number of blobs reads

$$\begin{aligned}
\langle 2k \rangle_{L,\Gamma} &\equiv \sum_{k=1}^{\infty} 2k B_L^{2k}(\Gamma) \\
&= \mathcal{L}_{p \rightarrow L}^{-1} \left(2 \left[-\partial_p (P_{\Gamma}^+(p)P_{\Gamma}^-(p)) \right] \frac{1}{(1 - P_{\Gamma}^+(p)P_{\Gamma}^-(p))^2} \right) \\
&= \mathcal{L}_{p \rightarrow L}^{-1} \left(2 \frac{\delta^2\sigma + p\Gamma\Delta(p) \coth[\Gamma\Delta(p)]}{p^2 \sinh^2[\Gamma\Delta(p)]} \right) \\
&= \frac{2\sigma L \delta^2}{\sinh^2(\delta\Gamma)} + \sum_{n=1}^{\infty} e^{-\sigma L(\delta^2 + \frac{n^2\pi^2}{\Gamma^2})} 4 \frac{\sigma L n^2 \pi^2}{\Gamma^2(n^2\pi^2 + \delta^2\Gamma^2)} \\
&\quad \times \left(1 + \frac{2\delta^2\Gamma^2}{n^2\pi^2 + \delta^2\Gamma^2} - 2 \frac{\sigma L n^2 \pi^2}{\Gamma^2} \right). \quad (6.24)
\end{aligned}$$

The first term is proportional to L and corresponds of course to the ratio $\frac{2L}{l_{\Gamma}^+ + l_{\Gamma}^-}$ that could have been anticipated from the study of Section 5 concerning the thermodynamic limit $L \rightarrow \infty$. The other terms, which represent the finite-size corrections to this dominant contribution, decay exponentially with L .

We may also compute the second moment

see equation (6.25) above.

The dominant behavior of the variance of the number of blobs is thus given by

$$\begin{aligned}
\langle (2k)^2 \rangle_{L,\Gamma} - (\langle 2k \rangle_{L,\Gamma})^2 &= \\
&= \frac{2\sigma L \delta^2}{\sinh^4(\delta\Gamma)} (\cosh(2\delta\Gamma) - 4\delta\Gamma \coth(\delta\Gamma) + 3) + \dots \quad (6.26)
\end{aligned}$$

In the symmetric case $\delta = 0$, the generating function may be more explicitly computed as

$$\begin{aligned}
\sum_{k=1}^{\infty} z^k B_L^{2k}(\Gamma) &= \mathcal{L}_{p \rightarrow L}^{-1} \left(\frac{\Gamma z \tanh[\Gamma\Delta(p)]}{\sqrt{p\sigma}(\cosh^2[\Gamma\Delta(p)] - z)} \right) \\
&= \sum_{n=-\infty}^{+\infty} \left(e^{-\frac{\sigma L}{\Gamma^2}(\alpha+n\pi)^2} - e^{-\frac{\sigma L}{\Gamma^2}(\frac{\pi}{2}+n\pi)^2} \right), \quad (6.27)
\end{aligned}$$

where $\alpha = \text{ArcCos}\sqrt{z} \in (0, \frac{\pi}{2})$ for $z \in (0, 1)$. In particular, the average and the variance of the number of blobs read:

$$\langle 2k \rangle_{L,\Gamma} = 2 \frac{\sigma L}{\Gamma^2} + \sum_{n=1}^{+\infty} 4 \frac{\sigma L}{\Gamma^2} \left(1 - 2 \frac{\sigma L}{\Gamma^2} n^2 \pi^2 \right) e^{-\frac{\sigma L}{\Gamma^2} n^2 \pi^2} \quad (6.28)$$

$$\langle (2k)^2 \rangle_{L,\Gamma} - (\langle 2k \rangle_{L,\Gamma})^2 = \frac{4\sigma L}{3\Gamma^2} + \dots, \quad (6.29)$$

where $\Gamma = \Gamma_{\text{eq}}(T)$, and where the dots represent terms that are exponentially small in (L/Γ^2) .

7 Non-equilibrium dynamics starting from a zero-temperature initial condition

As explained in Section 3.2, the dynamics at temperature T for $t > 0$ starting from a zero-temperature initial condition at $t = 0$, *i.e.* after a quench to $T = 0$ for $t < 0$, can be described by the renormalization procedure, where the renormalization scale Γ now corresponds to time *via*

$$\Gamma(t) = T \ln \frac{t}{t_0} \quad (7.1)$$

as in references [18,19]. The dynamics takes place up to time t_{eq} where equilibrium at temperature T is reached:

$$T \ln \frac{t_{\text{eq}}}{t_0} = \Gamma_{\text{eq}}(T). \quad (7.2)$$

In the symmetric case, we thus have the scaling

$$t_{\text{eq}} \sim \Gamma_{\text{eq}}^3(T) \sim T^3(\ln T)^3, \quad (7.3)$$

whereas in the biased case

$$t_{\text{eq}} \sim \exp\left(\frac{3 \ln \frac{1}{\delta^2 \sigma}}{4 \left(1 - \frac{T}{T_c}\right)}\right). \quad (7.4)$$

All the quantities computed before for the equilibrium at temperature T as functions of $\Gamma_{\text{eq}}(T)$ have the same expressions for the dynamics as functions of $\Gamma(t) = T \ln t$ for large time $t < t_{\text{eq}}$. For instance, in the symmetric case, the typical length of blobs behaves as

$$l(t) \sim \frac{\Gamma^2(t)}{\sigma} \sim \frac{(T \ln t)^2}{\sigma}, \quad (7.5)$$

whereas in the biased case, the typical lengths of blobs in the domains $z > 0$ and $z < 0$ behave respectively as

$$l^+(t) \sim \frac{1}{4\delta^2\sigma} e^{2\delta\Gamma(t)} \sim \frac{1}{4\delta^2\sigma} t^{2\delta T} = \frac{\sigma}{q_0^2} t^{\frac{q_0 T}{\sigma}}, \quad (7.6)$$

$$l^-(t) \sim \frac{\Gamma(t)}{2\delta\sigma} \sim \frac{T \ln t}{2\delta\sigma} = \frac{T \ln t}{q_0}. \quad (7.7)$$

8 Conclusion

In this paper, we have proposed a new approach based on a disorder-dependent renormalization procedure to study the localization of random heteropolymers at the interface between two selective solvents within the model of Garel *et al.* [2]. The renormalization procedure has been defined to construct an effective thermodynamics, where one only considers the heteropolymer configurations that correspond to the optimal Imry-Ma domain structure. At high temperatures, where the distribution of absolute charges of blobs generated by the renormalization procedure becomes infinitely broad, the effective thermodynamics is expected to become accurate and to give asymptotic exact results. With the renormalization approach, we have recovered that a chain with a symmetric distribution in hydrophilic/hydrophobic components is localized at the interface at any finite temperature in the thermodynamic limit, whereas a dissymmetry in hydrophilic/hydrophobic components leads to a delocalization phase transition, in agreement with previous studies. In addition, for both cases, we have given explicit expressions for the high temperature behaviors of various physical quantities characterizing the localized phase, including in particular the free-energy per monomer, the distribution of the blob lengths in each solvent and the polymer density in the direction perpendicular to the interface. For the case of a small dissymmetry in hydrophobic/hydrophilic components, where the delocalization transition takes place at high temperature, the renormalization approach allows to study the critical behaviors near the transition: we have found that the free energy presents an essential singularity

at the transition, making all of its derivatives continuous at T_c (infinite order transition), that the typical length of blobs in the preferred solvent diverges with an essential singularity, whereas the typical length of blobs in the other solvent diverges algebraically. We have then studied the finite-size properties of the problem by considering cyclic finite (large) chains. In particular, we have given the probability distribution of the delocalization temperature for the ensemble of chains of fixed finite length L , and the distribution of the numbers of blobs in the chain still localized at some temperature. Finally, we have briefly discussed the non-equilibrium dynamics at temperature T starting from a zero-temperature initial condition.

In conclusion, the disorder-dependent renormalization approach yields explicit predictions for the high temperature behaviors of various physical quantities, that would certainly be interesting to test precisely by numerical studies. In particular, the predictions concerning the critical behaviors near the delocalization transition are certainly surprising, and disagree with the Monte-Carlo studies of reference [5] where power laws were found, and with the Replica Gaussian variational approach of reference [7] where the transition was found to be of second order. It would thus be particularly worthy to test numerically more precisely the order of the transition. We hope that the predictions of the renormalization approach concerning the finite-size properties of the problem presented in Section 6 will make easier the comparison with numerical studies. Finally, we would like to stress that the renormalization approach yields not only predictions for averages over the quenched disorder, but also precise predictions sample by sample. For instance, for a given realization of the quenched charges, one may compare the typical configurations of the heteropolymer at equilibrium at temperature T with the blobs structure obtained by the numerical implementation of the renormalization procedure up to scale $\Gamma_{\text{eq}}(T)$. For the case of cyclic chains, one may also test numerically sample by sample the renormalization prediction for the delocalization temperature.

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Appendix A: Imry-Ma argument for the probability distribution of blob lengths

In this appendix, we recall the determination *via* a direct Imry-Ma argument [25] of the asymptotic behavior of the probability distribution of blob lengths in the limit of small lengths, and compare it with the renormalization result.

As noted by Garel and Orland [25], one may extend the usual Imry-Ma argument for the heteropolymer exposed in reference [2] to obtain not only the scaling of the typical length of Imry-Ma domains, but also some information on the probability distribution of the length of domains. The idea is as follows [25]. On one hand, the energy associated

to a blob of length l is the sum of l independent random variables and is thus typically given by

$$E_l = -u\sqrt{2\sigma l}, \quad (\text{A.1})$$

where u is a random variable of order 1, that has at least to be positive since the system tries to use the favorable fluctuations of the disorder to lower its energy. According to [25], the probability distribution for large u is simply given by the Gaussian of the Central Limit Theorem:

$$G(u) \underset{u \rightarrow \infty}{\sim} e^{-u^2/2}. \quad (\text{A.2})$$

The behavior of the distribution $G(u)$ for small u seems however not simple to determine *a priori*, because the small values of u are certainly suppressed with respect to the Gaussian distribution. Indeed, if an Imry-Ma domain corresponds to a small value of u , it is very likely that the heteropolymer will prefer an organization into other Imry-Ma domains. It seems however difficult to write precisely the consequences of this effect on the distribution $G(u)$. On the other hand, the entropy associated to a blob of length l behaves as $(-\frac{3}{2} \ln l)$ (in [2], only powers of l were considered for the symmetric case and thus $\ln l$ was replaced by $l^0 \sim 1$, but here for a better comparison with the renormalization approach, it is more convenient to keep this $\ln l$ dependence). The minimization of the free energy per monomer

$$f(l) \sim -\sqrt{\frac{2\sigma}{l}}u + \frac{3T}{2} \frac{\ln l}{l} \quad (\text{A.3})$$

with respect to l leads to

$$u \sim \frac{3T}{\sqrt{2\sigma}} \frac{\ln l}{\sqrt{l}}. \quad (\text{A.4})$$

The typical blob length l^{typ} corresponding to $u_{\text{typ}} \sim 1$ thus satisfies

$$\frac{\sqrt{l^{\text{typ}}}}{\ln l^{\text{typ}}} \sim \frac{3T}{\sqrt{2\sigma}u_{\text{typ}}}. \quad (\text{A.5})$$

Since within the RG approach $l^{\text{typ}} = \frac{\Gamma_{\text{eq}}^2(T)}{\sigma}$, the above equation corresponds to equation (4.10) with the choice $u_{\text{typ}} \sim \sqrt{2}$ *i.e.* a numerical factor of order 1. Now introducing the rescaled length of Imry-Ma domains

$$\lambda = \frac{l}{l^{\text{typ}}}, \quad (\text{A.6})$$

we find that it is simply related to the random variable u through

$$u \sim \frac{1}{\sqrt{\lambda}}. \quad (\text{A.7})$$

The behavior (A.2) of the distribution $G(u)$ at large u thus corresponds to the following behavior of the distribution $P(\lambda)$ at small λ :

$$P(\lambda) \underset{\lambda \rightarrow 0}{\sim} \frac{1}{\lambda^{3/2}} e^{-\frac{C}{\lambda}} \quad (\text{A.8})$$

where C is a constant of order 1. This asymptotic behavior corresponds exactly to the behavior (4.20) found *via* the renormalization approach. Concerning the behavior of $G(u)$ for small u , we explained above why it is difficult to determine it *a priori*. Using the relation (A.7), the asymptotic behavior (4.19) found *via* the RG approach

$$P_{\text{RG}}(\lambda) \underset{\lambda \rightarrow \infty}{\sim} e^{-\frac{\pi^2}{4}\lambda} \quad (\text{A.9})$$

would correspond to

$$G(u) \underset{u \rightarrow 0}{\sim} \frac{1}{u^3} e^{-\frac{C'}{u^2}} \quad (\text{A.10})$$

i.e. a very strong suppression of small values of u for the energies of Imry-Ma domains.

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