Localization Transition of a Random Polymer at an Interface

by

Venkatraghavan Ganesan


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Author ........................................................................

Department of Chemical Engineering

July 10, 1999

Certified by ........................................................

Howard Brenner

Willard H. Dow Professor of Chemical Engineering

Thesis Supervisor

Accepted by ........................................................

Robert Cohen

St. Laurent Professor of Chemical Engineering

Chairman, Committee for Graduate Students
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Abstract

An analysis is presented of the phase transitions arising from the presence of a random heteropolymer (RHP) at a flat interface between two fluids which possess competing physicochemical interactions with the different monomers comprising the chain. The analysis specifically probes the low temperature adsorbed regime. Utilizing a Martin-Siggia-Rose generating functional formulation within a Hartree approximation we derive the dynamical equations governing the correlation functions. The long-time limit of the dynamical equations indicate a possible ergodicity-breaking transition of the polymer, corresponding to the localization transition. However, in contradiction to the previous studies postulating scaling arguments for the occurrence of this transition, we predict that this phenomenon occurs at a finite temperature. This result contrasts with the behavior that might be intuitively expected from analogies to results of studies on two dimensional directed polymers in random media (DPRM), and resembles the behavior of a \( d+1 \) directed polymer in random media for \( d > 2 \). Further, we present transfer matrix simulations corroborating our analytical conclusions.

Thesis Supervisor: Howard Brenner
Title: Willard H. Dow Professor of Chemical Engineering
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Chapter 1

Introduction

Studies of the equilibrium and dynamical properties of polymers and fluctuating surfaces are gaining increasing importance especially in the context of biological and technological applications [1]. The realization that the chemical constituents of the macromolecules can exert a profound influence on the observed physical behavior of the polymer, has led to a search for novel techniques to manipulate the behavior by appropriately tuning the chemical composition of the macromolecule. Consequently, an imperative need has arisen for achieving a complete understanding of the physical and thermodynamic properties of the constituent building blocks employed in applications envisaging utilization of macromolecules. In this regard, a recent surge of interest has arisen in studying the phase transitions exhibited by random heteropolymers (RHP) in relation to their behavioral similarities with biological protein molecules [2]. Despite the fact that the constituents of a protein can hardly be termed ‘random,’ remarkable similarities in the mesoscale equilibrium and nonequilibrium behaviors exhibited by a RHP and a protein have suggested the utilization of RHP’s as tractable analytical models for studying some of the universal behavioral patterns displayed by proteins [2, 3].

Explicitly, our work outlined in this thesis is devoted to investigating the nature of the thermodynamic phase behavior that accompanies the presence of a RHP at an interface between water and a nonpolar solvent, e.g. an oil. The random heteropolymer is envisioned to be constituted by a random combination of hydrophilic
and hydrophobic components. In the presence of the mixture of a polar and a nonpolar solvent, the RHP functions like a surfactant and tries to adopt conformations such that the hydrophilic part is in contact with the polar solvent and the hydrophobic part with the non-polar solvent. However, while this self-attuning of conformations proves energetically valuable, the constrained polymer incurs an entropic penalty due to the restricted conformational accessibility entailed in the localized state. This interplay between the competing energetic and entropic components is expected to manifest in a thermodynamic phase transition, the explicit study of which is effected in this thesis. Further, at a fundamental level, random systems such as RHPs, which possess random interactions arising from quenched-in disorder have been shown to possess nontrivial, counter intuitive equilibrium and nonequilibrium properties [4]. Such predictions deem additional motivation to probe the possible implications of quenched random interactions within the context of the localization transition.

Practical motivations for our study is provided by the potential biological implications relating to behavior of proteins in such systems. Furthermore, our analysis constitutes a potential precursor to understanding the more complex interactions existing between a RHP (as a model for a protein) and absorbed surfactants at the interface.

1.1 Physical Description of the Model

To focus upon the essence of the envisioned situation, we consider the simplest scenario wherein the random polymer is neutrally attracted to the interface. Such a constraint requires that the random hydrophilic-hydrophobic components comprising the polymer are present in equal number. Such an assumption precludes asymmetric interactions with either of the solvents constituting the different phases, thereby enabling us treat both the solvents on equal footing. Further, we assume that the interaction strength of the monomers are Gaussian distributed random numbers with a mean zero (signifying the symmetrical interactions) and spread $V \sigma$. $V$ represents the characteristic interaction strength of the monomers and $\sigma$ a nondimensional char-
acterization of the spread of random distribution. Further, we ignore considerations arising from the presence of excluded volume interactions within the polymer. While the presence of excluded volume interactions can be expected to lead to new and interesting features, however in the interest of focusing on the primary effects of randomness, we eschew such intra-polymeric interactions, and rather concentrate on the polymer-solvent interactions.

A similar model has been explored in a pioneering article by Garel et al. [5]. Their study predicted the occurrence of a localization (or adsorption) transition of the RHP onto the interface. Beyond this localization transition the RHP is confined to a layer of finite width around the interface. Furthermore, for the case of a neutrally attracted polymer, their results predict that the localization temperature $T_{loc} = \infty$, i.e., for any finite temperature the energetic advantage of localizing overwhelms the entropic penalty.

In this work, we re-examine their calculations employing a novel formalism to uncover effects which were presumably overlooked in their analysis. Specifically, we argue that the scaling arguments and the mean field concepts proposed in their work invokes suspicion for our system, which, as a result of the competing nature of the random interactions might possess a nontrivial phase space structure for the energy landscape. Therefore, we employ a dynamical formalism (which unearths such non-trivial features) [6] to probe the phase behavior of the RHP. Our arguments lead us to conclude that the localization transition occurs at a lower, finite temperature. This result suggests that at high temperatures the entropic penalty does overcome the energetic gain arising from the localization. Concomitantly, our results elucidate some of the unique, nontrivial characteristics possessed by systems possessing random interactions.

### 1.2 Scaling Arguments

Despite the contradiction between the mean-field scaling results and our analytical and numerical results outlined in the subsequent chapters, it is nevertheless illustra-
tive to recapitulate the scaling arguments of Garel et al. [5] to thereby provide a physicomathematical interpretation of the localization phenomena. In this section, we briefly review the scaling arguments postulated by Garel et al. [5] suggesting the existence of a localization transition at $T_{loc} = \infty$. This discussion serves to underline the physics of the localization transition, simultaneously enabling us to thereby point up the features contrasting a quenched random system and an annealed random system.

Refer fig. (1-1) for the notation employed in this section. The mathematical constraints posed by the presence of symmetric interactions also require that the localization of the polymer occurs in a symmetric, unbiased manner with respect to the two solvents. The occurrence of the localization transition is probed by envisioning a localized state of the polymer [characterized by a finite width $w$ of the polymer — cf. Fig. (1-1)], and subsequently optimizing the localized width to minimize the free energy in localized state. As expounded earlier in the text, the free energy of the localized state possesses both an energetic and an entropic component, each of which can be easily estimated as follows (cf. deGennes [7] for a pedagogical introduction to the scaling concepts employed below):

(i) The functional form of the entropy loss arising from the localization can be estimated by recognizing that this quantity should be an extensive function, and therefore should be proportional to the number of monomers constituting the polymer (denoted as $N$). Further, the localization of the polymer presents an additional lengthscale, namely the width of the adsorbed layer $w$ in addition to the transverse radius of gyration of the polymer $R_\parallel$. Employing dimensional considerations we obtain

$$\delta S \sim f\left(\frac{w}{R_\parallel}\right),$$

wherein “$f$” denotes a scaling function. In postulating eq. (1.1) we have utilized the fact that entropy, is dimensionless.) Note that for an ideal or phantom polymeric chain, namely one wherein the excluded volume interactions are neglected, the radius of gyration of the polymer exhibits a functional form identical to that of an unbiased
Figure 1-1: Pictorial representation of the localized polymer. The symbols I and II denote the polar and non polar solvents respectively. The shaded monomers express a proclivity for the polar solvents. The localized polymer is characterized by a width $w$ comprising $t$ monomers.

random walk and therefore scales as $N^{1/2}$.

When the width of the adsorbed layer $w$ is much smaller than the radius of gyration $R_{||}$, we expect that the functional form of $f$ to exhibit a self-similar power law scaling behavior. Therefore

$$\delta S \sim \left(\frac{w}{R_{||}}\right)^b$$ for $w \ll R_{||}$, \hspace{1cm} (1.2)

wherein $b$ denotes the scaling exponent. Utilizing the above functional form for the loss in entropy in conjunction with the scaling property $R_{||} \sim N^{1/2}$ and the fact that the entropy loss is required to be extensive, posits $b = -2$. Thus, the functional scaling form for the entropy loss $\delta S$ can be quantified as

$$\delta S \sim \frac{R_{||}^2}{w^2}.$$ \hspace{1cm} (1.3)

The above expression can also be rewritten in terms of the total number of monomers
$N$ and the number of monomers in the adsorbed layer $l$

$$\delta S \sim \frac{N}{l}. \quad (1.4)$$

(ii) The energetic gain achieved by the polymer in localizing at the interface can be estimated by employing the central limit theorem. The adsorption of $l$ monomers on either side of the interface leads to an energetic favorability quantified by the sum of $l$ random numbers which are Gaussian distributed with a mean zero and a variance of $V\sigma$. Utilizing central limit theorem, we thereby identify that the energies of the adsorbed loops to be Gaussian distributed and characterized by a mean zero and a spread $V\sigma\sqrt{l}$. The total energetic gain achieved by localization is then estimated as the product of the characteristic energy gain of a loop, namely $V\sigma\sqrt{l}$ and the number of such loops, $N/l$. Thereby we obtain

$$\delta E \sim V\sigma\sqrt{l} \times \frac{N}{l} = \frac{V\sigma N}{\sqrt{l}}. \quad (1.5)$$

Utilizing eqs. (1.4) and (1.5), we obtain the following scaling functional form for the free energy change $\delta F$ arising from the localization of the polymer,

$$\delta F = -T\frac{N}{l} + \frac{V\sigma N}{\sqrt{l}}. \quad (1.6)$$

Minimizing the above expression by treating the size of the loop $l$ as a variational parameter yields

$$l \sim \left(\frac{T}{V\sigma}\right)^2. \quad (1.7)$$

The onset of the localization transition can now be identified by examining the above expression to discern the temperature below which the polymer is confined to a finite width around the interface. Such an exercise indicates that for any temperature $T < T_{loc} = \infty$ the polymer is localized with a finite width ($l < \infty$) at the interface.

The above conclusion summarizes the main result of Garel et al. [5] which postu-
lated the existence of a localization transition at $T = \infty$. It is pertinent to note the inherently mean field nature of the above scaling arguments. Such a spirit is embodied in the utilization of the central limit theorem to estimate the energy gain arising from the localization process. Scenarios can be envisioned wherein the mean-field results break down. For instance, a nonergodic sampling of configurations, possibly arising from the presence of glassy phases, would invalidate such mean field results [8]. It is pertinent to note that glassy phases typically exemplify the presence of random competing interactions — features underlining our problem. Therefore, we might treat the mean-field results of [5] to be a bit suspicious for our problem especially when accounting for the possible presence of glassy phases. The occurrence of such a phenomenon would also invalidate the more rigorous replica symmetric analysis presented in Garel et al. [5], and would necessitate the use of a a replica symmetry breaking ansatz.

The above arguments therefore point towards a reexamination of the mean field scaling analysis (and replica symmetric analysis) to identify the effect of the quenched random interactions. Such an exercise is undertaken in the subsequent chapters.

### 1.3 Outline

In this thesis we employ a Martin-Siggia-Rose (MSR) formulation of equilibrium dynamics to study the nature of the phase transitions accompanying the interaction of a RHP with a polar-nonpolar solvent system. Utilization of a dynamical formulation (in lieu of other methods, like for instance, the replica method or cavity method) for quenched random systems has yielded new insights into the dynamical freezing transitions\(^1\) encountered in such systems. For instance, Thirumalai et al. [9] predicted the existence of a scale-dependent freezing transition for the random hydrophilic-hydrophobic copolymer — in contrast to a mean-field replica analysis, which fails to uncover the existence of such a transition. (However, a replica analysis based on

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\(^1\)In this thesis, the term “freezing” is used to indicate an ergodicity breaking transition. It is not to be confused with the liquid-solid phase transition.
the variational formulation does yield results identical to that obtained through a
dynamical formulation [10].) As expounded earlier, excluded volume effects of the
polymer are ignored in this work to thereby focus attention exclusively on the physics
of polymer-solvent interactions.

Our analytical study presented in the following chapter reveals the possible exis-
tence of a finite temperature localization transition. This result contrasts with the
scaling and mean-field replica symmetric analysis presented in [5]. Our results also
point out in an unequivocal manner, the differences to be expected when the quenched
randomness is inherent to the system rather than being external to it. Subsequently,
in Chapter 3 we corroborate our analytical conclusions by simple transfer matrix
simulations (which represents a convenient nondynamical method to probe possible
phase transitions). Overall conclusions are detailed in Chapter 4.
References


Chapter 2

Localization Transition

In this chapter we present the details of the dynamical formulation employed to analyze the phase transitions of a random heteropolymer (RHP) near an interface. Explicitly, we employ a Martin-Siggia-Rose (MSR) generating functional formulation [1] to rewrite the Langevin equation governing the dynamics of the polymer. This formulation enables averaging over the quenched randomness without explicitly invoking the replica method [2]. Since the formal procedures for breaking replica symmetry is as yet to be firmly established, “nonreplica” procedures such as those employed in this thesis possesses definite advantages over methods which invokes replicas. Further, since the fundamental basis for the replica method and the dynamical formulations are completely distinct, our analysis provides a framework by which potentially an independent verification of our quantitative predictions can be accomplished by utilizing the replica method.

Subsequent to the deriving the generating functional formulation, we utilize a Hartree approximation [3] to decouple the nonlocal terms in the dynamical equations. Such a procedure (along with the use of fluctuation-dissipation theorem) enables the derivation of the corresponding equation for the temporal evolution of the correlation and response functions of the polymer. The long time functional behavior of these quantities provides us an indication of the ergodicity properties of the thermodynamic phases of the system. Within the context of our problem, the implementation of such a procedure suggests the presence of a finite temperature $T_{loc}$ at which the dynamics
of the polymer becomes nonergodic. While the localization transition itself need not necessarily be characterized by nonergodic dynamics, the absence of alternative mechanisms for a phase transition lead us to conclude that this ergodic-nonergodic transition corresponds to the localization transition. Further, in the next chapter we provide numerical support to corroborate this conclusion.

2.1 MSR Functional

In this section we embody the dynamical equation of the RHP within a Langevin formulation to thereby utilize the MSR generating functional method. We adopt a simplistic mathematical framework to model the dynamics of the RHP. The interactions of the RHP is assumed to be characterized by a single quenched random variable \( \theta(n) \) (\( n \) representing the coordinates of the monomer along the polymeric chain, with the total number of monomers being denoted as \( N \)), which is assumed to be Gaussian distributed with a mean \( \langle \theta \rangle \) and a variance \( \sigma \) [4].

\[
\langle \theta(n) \rangle = \langle \theta \rangle \tag{2.1}
\]

\[
\langle \theta(n)\theta(n') \rangle = 2\sigma \delta(n - n') \tag{2.2}
\]

Of interest is the specific case wherein the polymer is neutrally attractive, i.e. \( \langle \theta \rangle = 0 \). The interaction strength between the polymer and the solvent is modeled as an algebraically-signed value proportional to \( \theta(n) \), with the sign depending on the location of the particular monomer with respect to the interface.

The Hamiltonian describing the polymer-solvent system possesses two independent parts characterizing the energetic modes of the RHP

\[
\beta \mathcal{H} = \beta \mathcal{H}_{elastic} + \beta \mathcal{H}_{interactions}. \tag{2.3}
\]

The distinct energetic contributions present in the above equations can be individually
quantified as follows:

(i) The term $H_{\text{elastic}}$ denotes the energetic contribution arising from the elasticity of the polymer. We adopt the Edwards formulation [5] to quantify this specific component of the Hamiltonian. Within such a framework,

$$
\beta H_{\text{elastic}} = \frac{3}{2l^2} \int_0^N dn \left( \frac{\partial \rho}{\partial n} \right)^2,
$$

where $\rho(n)$ represents the spatial coordinate of the $n^{\text{th}}$ monomer and $l$ denotes the Kuhn segment length of the polymer (not to be confused with the notation employed in the preceding chapter wherein $l$ denoted the number of monomers in the localized state).

(ii) If we assume that the $z$-axis characterizes the direction normal to the interface, then the expression for the interaction between the monomers and solvent can be represented utilizing the random variable $\theta(n)$ as [6]

$$
\beta H_{\text{interactions}} = -\beta V \int_0^N dn \theta(n) \text{sign}[\rho_z(n)],
$$

wherein $\rho_z(n)$ denotes the $z$ coordinate of the $n^{\text{th}}$ monomer. Additionally, $V$ characterizes the strength of the interaction between the polymer and the solvents.

Utilizing equations (2.3) - (2.5) we obtain:

$$
-\beta H = -\frac{3}{2l^2} \int_0^N dn \left( \frac{\partial \rho}{\partial n} \right)^2 + \beta V \int_0^N dn \theta(n) \text{sign}[\rho_z(n)].
$$

In the above equation, the term corresponding to $\text{sign}[\rho_z(n)]$ can be replaced by the sum of a Heaviside function $H[\rho_z(n)]$ and an irrelevant constant term.

The dynamics of the polymer in the polymer-solvent system is assumed to be governed by a Langevin-type equation of the form:

$$
\frac{1}{\Gamma_1} \frac{\partial \rho}{\partial t} = -\beta \frac{\delta H}{\delta \rho} + \zeta_1(n,t),
$$

where $\Gamma_1$ denotes the mobility coefficient of the polymer, which also serves to fix
the time-scale. Since our interest centers upon the long time limit behavior of the polymer (corresponding to equilibrium), the precise value and the functionality of the mobility coefficient $\Gamma_1$ proves irrelevant in our analysis. Further, $\zeta_1(n, t)$ represents a Gaussian-correlated thermal noise contribution. Employing the expression (2.6) for the Hamiltonian $\mathcal{H}$ in equation (2.7) we obtain,

$$\frac{1}{\Gamma_1} \frac{\partial \rho}{\partial t} = \frac{3}{l^2} \frac{\partial^2 \rho}{\partial n^2} + \beta V \theta(n) \delta[\rho_z(n, t)] + \zeta_1(n, t)$$  \hspace{1cm} (2.8)

The MSR generating functional rewrites the above equation (2.8) in a form especially convenient for extracting the functional form of the correlation and response functions of the quantity whose dynamics is being examined. It utilizes the following property of the delta function

$$\int dx \delta(x) = 1.$$ \hspace{1cm} (2.9)

For the dynamical equation represented by eq. (2.8), the generating functional (denoted as $Z$) can be identified as

$$Z = \int \mathcal{D}\rho(n, t) \delta \left[ \frac{1}{\Gamma_1} \frac{\partial \rho}{\partial t} - \frac{3}{l^2} \frac{\partial^2 \rho}{\partial n^2} - \beta V \theta(n) \delta[\rho_z(n, t)] - \zeta_1(n, t) \right],$$ \hspace{1cm} (2.10)

wherein, we have used the notation $\mathcal{D}$ to denote the functional integrals.

Upon Fourier transforming the above equation (2.10) in the functional space by utilizing an auxiliary function $\hat{\rho}(n, t)$ (quantifying the functional wave vector) to rewrite the functional $\delta$ function we obtain,

$$Z = \int \mathcal{D}\rho(n, t) \int \mathcal{D}\hat{\rho}(n, t) \exp \left[ -i \hat{\rho} \left( \frac{1}{\Gamma_1} \frac{\partial \rho}{\partial t} - \frac{3}{l^2} \frac{\partial^2 \rho}{\partial n^2} - \beta V \theta(n) \delta[\rho_z(n, t)] - \zeta_1(n, t) \right) \right].$$ \hspace{1cm} (2.11)

The form of the generating functional as embodied in equation (2.11) is amenable to implementing the thermal and the quenched averages over the random variables $\zeta_1(n, t)$ and $\theta(n)$. To effect the averages we utilize the following identity relating to
the averages of Gaussian random variables \[7\]:

**Identity 1** For a Gaussian distributed random variable \(x\),

\[
\langle \exp(x) \rangle = \exp\left(\frac{1}{2} \langle x^2 \rangle \right),
\]  

(2.12)

(The proof of the above identity is enabled by an explicit expansion of the expression on the left hand side and subsequently averaging each of the individual terms.)

Upon implementing the averages within the MSR functional we obtain

\[
\mathcal{Z} = \int \mathcal{D}\rho(n,t)\mathcal{D}\tilde{\rho}(n,t) \exp(L_1 + L_2),
\]  

(2.13)

where

\[
L_1 = \int_0^\infty dn \int dt \, i\tilde{\rho} \left[ \frac{1}{\Gamma_1} \frac{\partial \rho}{\partial t} - \frac{3}{i^2} \frac{\partial^2 \rho}{\partial n^2} + \frac{i}{\Gamma_1} \tilde{\rho} \right],
\]  

(2.14)

and

\[
L_2 = \frac{\beta^2 V^2 a^2}{2} \int \, dt_1 \int \, dt_2 \int \frac{dp}{2\pi} \int \frac{dq}{2\pi} \int_0^N \, dn \, B(n, p, q, t_1, t_2),
\]  

(2.15)

with

\[
B(n, p, q, t_1, t_2) = i\tilde{\rho}(n, t_1)i\tilde{\rho}(n, t_2) \exp[i\rho_\sigma(n, t_1) + iq\rho_\sigma(n, t_2)].
\]  

(2.16)

The first term, \(L_1\), describes the dynamics of an ideal, non-interacting (with the solvent) polymer chain. The second term, \(L_2\), represents the manifestation of the quenched disorder.
2.2 Correlation and Response Functions

The correlation and the response functions can be defined in terms of the fields $\rho$ and $\dot{\rho}$ as:

\[
D(n_1, t_1; n_2, t_2) = \langle \rho_z(n_1, t_1) \rho_z(n_2, t_2) \rangle
\] (2.17)

and

\[
M(n_1, t_1; n_2, t_2) = \langle \rho_z(n_1, t_1) i \dot{\rho}_z(n_2, t_2) \rangle
\] (2.18)

Here, $D$ represents the correlation between the $z$ coordinates of the respective monomers $n_1$ and $n_2$ at times $t_1$ and $t_2$. A non-zero value of the function $D$ at long times $t_1 - t_2$ would imply a nontrivial ordering phenomena corresponding to a freezing transition. This order parameter is analogous to that used in spin-glass physics to describe the ergodicity-breaking transition encountered therein [2, 8].

We employ a Hartree approximation in equation (2.13) to obtain the dynamical equation governing $D$. Hartree approximation involves replacing the MSR functional by a Gaussian functional of all bilinear combinations of $\rho$ and $\dot{\rho}$ coupled to self-consistent averages of the same. In the high-temperature phase which we are investigating, the fluctuation-dissipation theorem and time-translational invariance can be expected to hold. Furthermore, we also assume that translational invariance along the polymer chain holds. Thus,

\[
M(n_1, t_1; n_2, t_2) = M(n_1 - n_2; t_1 - t_2) = \begin{cases} 
\beta \frac{\partial D(n_1 - n_2; t_1 - t_2)}{\partial t_2} & t_1 > t_2 \\
0 & t_1 < t_2.
\end{cases}
\]

The dynamical equation obtained from such an analysis for the Rouse mode repre-
sentation of $D(n, t)$ (denoted as $D(s, t)$) is

$$\frac{1}{\Gamma_1} \frac{\partial D(s, t)}{\partial t} + \frac{3s^2}{t^2} D(s, t) - \beta^3 V^2 \sigma^2 \int \frac{dp}{2\pi} \int \frac{dq}{2\pi} \left\{ \frac{(p + q)^2}{2pq} D(s, t) \exp\left[ -\frac{(p + q)^2}{2w^2} \right] \right. $$

$$+ \left. \int_0^t dt_1 \frac{\partial D(s, t_1)}{\partial t_1} \exp\left[ -\frac{p^2 + q^2}{2w^2} - pq \int ds D(s, t-t_1) \right] \right\} = 0. \quad (2.19)$$

In the above equation, the equal time correlation $\langle \mu^2(n, t) \rangle$ is denoted as $w$. By definition it represents the (temperature dependent) width of the localized layer.

### 2.3 Long-time Limit and Ergodicity Breaking

To analyze the possible freezing of the modes we need to consider the long-time limit of equation (2.19). In order to achieve this objective we define a normalized ergodicity-breaking parameter $h(s)$ such that

$$\frac{D(s, t)}{D_{st}(s)} = \phi(s, t) + h(s). \quad (2.20)$$

In the above, $D_{st}(s) \equiv D(s, 0)$ denotes the static or equal time correlation, whereas $\phi(s, t)$ represents the regular part of $D(s, t)$ and vanishes as $t \to \infty$.

Upon defining

$$H = \int ds D_{st}(s) h(s),$$

and considering the long-time limit of equation (2.19), we obtain

$$h(s) = \frac{I_1}{I_1 + I_2 - 3s^2/t^2}, \quad (2.21)$$

where

$$I_1 = \beta^3 V^2 \sigma^2 \int \frac{dp}{2\pi} \int \frac{dq}{2\pi} \exp\left[ -\frac{p^2 + q^2}{2w^2} - Hpq \right] \quad (2.22)$$
and

\[ I_2 = \frac{\beta^3 V^2 \sigma^2}{2} \int \frac{dp}{2\pi} \int \frac{dq}{2\pi} \frac{(p + q)^2}{pq} \exp\left[-\frac{(p + q)^2}{2}w^2\right]. \]  \hspace{1cm} (2.23)

Equation (2.21) is a highly nonlinear integral equation, obviating the possibility of obtaining a closed-form analytical solution. Below, we outline some of the qualitative features of the solution of eq. (2.21) and discuss the implications of these on the physics of the problem at hand.

Examination of eq. (2.21) in the limit \( \beta \to 0 \) and \( \beta \to \infty \) reveals that as \( \beta \to 0 \) \((T \to \infty)\) the only possible solution of (2.21) is \( h(s) = 0 \). In contrast, in the limit \( \beta \to \infty \) \((T \to 0)\), one can infer the existence of another solution viz., \( h(s) = 1 \). The behavior of \( h(s) \) as \( T \to \infty \) and \( T \to 0 \) suggests that there exists a low temperature phase which exhibits nontrivial ordering phenomena characteristic of glassy dynamics.

A similar ergodic-nonergodic behavior has also been predicted in analytical studies of directed polymers in random media [9]. In fact, a 1+1 dimensional directed polymer can be exactly mapped onto a self-avoiding polymer (cf. Chapter 3 for a pictorial representation of the equivalence between a phantom polymeric chain and a directed polymer). It might therefore be speculated that the behavior of our system can be mapped onto the corresponding 1+1 dimensional directed polymer in random media [9]. However, our system corresponds to the physical situation wherein the randomness is inherent to the system rather than being external to it as in the case of a DPRM. Such a physical feature also reflects in the phase behavior predicted in the above analysis. While a DPRM has been predicted to exhibit an ergodicity breaking transition at a temperature \( T = \infty \), in contrast, we can prove the existence of a finite temperature phase transition in our system by deriving an upper bound on the localization temperature \( T_{\text{loc}} \). Such a bound is derived by noting that since \( I_2 > 0, 0 < h(s) < 1 \) requires that \( I_2 > 3s^2/l^2 \forall s \ (s = 1 \cdots \infty) \). Evaluating \( I_2 \) in spherical coordinates (imposing the appropriate cutoffs dictated by the Kuhn segment length \( l \)), and using as a first approximation the Imry-Ma scaling relation between the width and the temperature, we obtain \( T_{\text{loc}} < 0.9V\sigma \). [The numerical prefactor is to be
construed as being very approximate. More accurately, we can say that \( T_{\text{loc}} \approx AV\sigma \), where \( A \) is an \( O(1) \) quantity. This bound on \( T_{\text{loc}} \) distinguishes our problem from 1+1 DPRM wherein the low temperature phase persists for all temperatures until \( T = \infty \). This result, predicting the existence of a finite temperature phase transition, is the primary result of this thesis.

The ergodicity breaking freezing transition predicted above might in fact correspond to a phase transition beyond the simple localization transition to a spin glass like localized phase. However, in the absence of excluded volume interactions, the system does not appear to be frustrated [10] and hence we claim on physical grounds that this phase transition should in fact correspond to the localization transition predicted in [6]. The existence of a finite temperature localization transition contradicts the earlier result of Garel et al. [6], and suggests that above \( T_{\text{loc}} \) the quenched disorder is irrelevant and that thermal fluctuations destroy the localized phase. This particularly significant result also underlines the differences that can arise when the quenched randomness is inherent to the system (as in our example) rather than being external to it (as in DPRM).

Since \( H \) involves coupling of all the modes \( h(s) \), the freezing transition predicted above would involve the simultaneous freezing of all modes. This freezing transition is analogous to the one predicted by Takada et al. [11] for a self-interacting random polymer and contrasts with the scale- (or “\( s \)”)-dependent freezing transition predicted for self-interacting copolymers [8, 12]. Beyond this freezing transition the polymer sacrifices entropy to sample a few energetically dominant conformations. Physically, such a transition occurs at low temperatures (corresponding to a dense adsorbed state) wherein the polymer achieves a frozen state (corresponding to sampling a few energetically dominant conformations) so as to avoid the unfavorable polymer-solvent interactions resulting from the random nature of the polymer.
2.4 Conclusions

In this chapter we presented an analytical study of the phase behavior of a hydrophobic-hydrophilic random heteropolymer near an interface between a polar and nonpolar solvent. Explicitly, we formulated the analysis within a dynamical framework to thereby use a Martin-Siggia-Rose formulation of the generating functional. Such a procedure enables a rigorous treatment of the quenched disorder by avoiding any need to invoke an arbitrary mechanism of replica symmetry breaking. Subsequently we employed a Hartree approximation to discern the dynamical equations satisfied by the correlation and the response functions. Examination of the long time limit of the equations typically provides insights into the phase behavior of the polymer. Such an exercise led us to the recognition of the existence of a finite temperature ergodicity breaking freezing transition. Further, we claimed that as a consequence of the physics of the situation, this freezing transition should in fact correspond to the localization transition.

Despite our plausible analytical demonstration concerning the existence of a finite temperature localization transition, the physical mechanism which forces such a scenario is still unclear. Further, while an examination of the physical situation enabled us to claim that the finite temperature freezing transition was indeed the localization transition, we have been as yet unable to provide a concrete evidence of our claim. An alternative physical mechanism which might lead to such a scenario would be the presence of a finite temperature ergodicity breaking transition subsequent to the infinite temperature localization transition. Within the context of a replica analysis, the occurrence of such a phase transition would be indicated by the onset of an instability within a stability analysis of the replica symmetric solution. Such an analysis has been initiated in a recent work (which appeared in print subsequent to the publication of the article embodying this thesis), and the results derived there seem to lend support to the two-transition scenario. However, the analysis presented therein is restricted to the first step of a replica symmetry breaking, and therefore the result should be construed as preliminary and requiring further confirmation.
In the next chapter we provide numerical evidence corroborating our analytical conclusions presented in this chapter. Explicitly, we employ a nondynamical transfer matrix simulation framework to discern the phase behavior of the polymer. The results of such an exercise suggests the presence of a finite temperature ergodicity breaking transition. Furthermore, the density of the adsorbed segments display a steep increase at the onset of the localization transition, thereby lending support for our physically based claim regarding the coincidence of the localization transition and the ergodicity breaking transition.
References


[10] We are grateful to Prof. M. Kardar for pointing out this feature.


Chapter 3

Transfer Matrix Simulations

In this chapter we employ a numerical framework to address the phase transition corresponding to the localization behavior of the polymer. Specifically, we present the results discerned from the implementation of a transfer matrix algorithm. This procedure embodies an exact enumeration of the Boltzmann weights of the different conformations of the polymer to thereby identify possible phase transitions in the system [1]. The results of these simulations confirm and corroborate the analytical predictions outlined in the preceding chapter. Explicitly, we discern the presence of a finite temperature ergodicity breaking transition (monitored numerically via an appropriate order parameter). Furthermore, the density of the adsorbed chains display a steep increase at the onset of this freezing transition, thereby suggesting that this phase transition should indeed correspond to the localization transition of the polymer.

We commence our exposition in this chapter by briefly reviewing the principles underlying the transfer matrix simulation technique. Subsequently, we outline and interpret the results of the simulations as applied to our problem. Finally, we conclude by reiterating our analytical predictions within the context of our numerical simulations.
3.1 Lattice Formulation

The implementation of transfer matrix (TM) simulation techniques to our problem owes to the exact mapping achievable between the phantom polymeric chain and the directed polymer (DP). The discrete version of such a mapping enables the utilization of transfer matrix simulation techniques. The simulation algorithm for the finite temperature DP in random media has been developed extensively by Kardar and coworkers [1]. The details of the simulation method utilized in the following analysis is adapted from the same sources.

The implementation of the TM simulation technique requires the utilization of a lattice formulation for the random polymer. Fig. (3-1) details the manner in which the conformation of a phantom polymeric chain (i.e. a polymer wherein the excluded volume constraints are ignored) can be mapped onto a 1 + 1 dimensional directed polymer [2]. In view of this exact mapping, we address the statistical mechanics of the directed random walk on such a discrete “triangular” (for a d-dimensional polymeric surface, the corresponding structure is hyperpyramidal) network. For each random walk configuration described on the lattice, a random energy of magnitude \( \theta(n') \text{sign}(z') \) is incurred depending on the location \( z' \) of the monomer \( n' \). The random walk corresponding to the conformation of the polymeric chain is assumed to commence at \( z(n = 1) = 0 \), with its path at each step being constrained by the condition

\[ |z(n) - z(n + 1)| = 0 \text{ or } 1. \]

Further, an elastic energy penalty quantified by a parameter \( \Gamma \) is employed for each bend undertaken during the random walk (i.e. \( |z(n) - z(n + 1)| = 1 \)).

Interest is centered upon the evaluation of the partition function \( Z^*(z^*, N) \) of a random walk\(^1\) embodying a given configuration of monomers [i.e. a specified sequence \( \theta(n) \)] and ending at the position \( z^* \). The transfer matrix algorithm renders the eval-

\(^1\)In this chapter we use \( Z \) to denote the partition function of the random walk statistics. Despite identical notation, the partition function is distinct from the generating functional evaluated in the previous chapter.
Figure 3-1: Pictorial representation of the mapping between a phantom chain and a directed polymer on a lattice: (a) depicts a phantom chain wherein the monomers are labeled explicitly; (b) displays the same phantom chain, however with the axes plotted in a different fashion. With the constraint of each walk being restricted to a step length of a single unit, the maximum extent of $z$ coordinates at the $n^{\text{th}}$ step satisfies the condition $-n \leq z \leq n$, and thereby endows the lattice a triangular structure.
evaluation of the partition function $Z^*(z^*, N)$ a recursive procedure. For instance, the total Boltzmann weight of random walk of $n$ steps ending at the position $z$ is evaluated by summing the energetically weighted partition functions of the random walks which reached the positions $z, z - 1$ and $z + 1$ at the end of $n - 1$ steps. Within a mathematical framework,

$$
Z^*(z, n) = Z^*(z, n - 1) \exp \left( -\frac{\theta(n - 1)\text{sign}(z)}{T} \right) + Z^*(z - 1, n - 1) \exp \left( -\frac{\theta(n - 1)\text{sign}(z - 1) + \Gamma}{T} \right)
+ Z^*(z + 1, n - 1) \exp \left( -\frac{\theta(n - 1)\text{sign}(z + 1) + \Gamma}{T} \right).
$$

(3.1)

In the above equation $T$ denotes the temperature.\(^2\) The recursive implementation of the above equation (3.1) in conjunction with the initial condition $z(n = 1) = 0$ enables the numerical determination of the partition function $Z^*(z^*, N)$.

Subsequent to obtaining the Boltzmann weight of the random walks which end at $z^*$, the partition function of the given polymer [with a specified sequence $\theta(n)$] $Z(N)$ can be obtained by summing over all possible end locations of the random walk, i.e.

$$
Z(N) = \sum_{z^*} Z^*(z^*, N).
$$

(3.2)

The free energy of the polymer can then be evaluated by utilizing the statistical mechanical identity, $F(N) = -T \ln Z(N)$. Further, evaluation of the partition function also permits the calculations of the average values of conformation dependent physical variables, like for instance, the mean displacement of the random walk $\langle z^*(N) \rangle$. For a generic function denoted $A(z^*)$, the thermal average $\langle A \rangle$ can be defined as

$$
\langle A \rangle = \frac{\sum_{z^*} A(z^*) Z(z^*, N)}{Z^*(N)}.
$$

(3.3)

It is to be borne in mind that the above formulation and the averages are defined for a specified sequence of monomers [specified by $\theta(n), n = 1 \cdots N$]. To evaluate the thermodynamic properties of the system, the above quantities need to be averaged

---

\(^2\)We have set the Boltzmann constant $k_B$ to be identically equal to unity to avoid unnecessary numerical factors.
over different realizations of the sequences to thereby determine the sample averaged physical quantities. Such a procedure requires implementation of the above recursive algorithm for different sequences of the monomers, subsequent to which an average of the resulting thermal averages can be determined.

3.2 Results

In our simulation we set the energy cost for each bend of the polymeric chain $\Gamma$ to be identically equal to 1.0. The interaction energy of the polymer, accounted by random variables $\theta(n)$ were obtained from a Gaussian distribution with zero mean and variance $\sigma = 1.0$. The simulations are then repeated for different chain lengths, and for different realizations of the random polymer.

To analyze the possibility of a finite temperature freezing transition, we have monitored the quantity $x = 1 - \frac{1}{n} \sum P_i^2 [3, 4]$, where $P_i$ refers to the probability of a particular conformation of the polymer and $\cdots$ denotes the sample average. When the polymer samples a multitude of conformations, this quantity is asymptotically expected to equal 1. Whereas, in the phase wherein the polymer samples only a few conformations (corresponding to the frozen or glassy phase), this quantity acquires a value different from 1 (and asymptotically attains a value 0 at $T = 0$). Fig. (3-2) depicting the variation of this quantity as a function of a temperature clearly indicates a phase transition around $T/\sigma \sim 10$ at which $x$ acquires a non zero value. This constitutes a numerical proof of our earlier analytical result predicting the existence of a finite temperature freezing transition.

While the $x$ values suggests the possibility of a finite temperature freezing transition, it does not exclude the scenario of a second phase transition following the $T = \infty$ localization transition. We have also depicted in Fig. (3-2) the variation of the density of the chains on the interface $z = 0$ (denoted as $p$ in the figure). From the behavior of $N = 500, 1000, 2000$ chains we observe a sharp adsorption transition (from an asymptotic $p = 0$ to a finite value of $p$) occurring around the same temperature where $x$ first acquires a non zero value. This result lends support to our earlier claim.
Figure 3-2: Variation of the order parameter $x$, and the density of adsorbed chains $p$ as a function of temperature.
(based on physical reasoning) that the finite temperature freezing transition should in fact correspond to the localization transition.

The numerical results presented in this section corroborate the theoretical analysis presented in the previous chapter, and hence serve to further confirm the presence of a finite temperature freezing/localization transition.

3.3 Conclusions

In this chapter we presented the numerical results of transfer matrix simulations to corroborate our analytical predictions outlined in the preceding chapter. Restricting our considerations to a phantom chain allowed us to map the statistical mechanics of the polymer to that of a directed random walk. The partition function of directed random walk could be evaluated in a polynomial time by use of the recursive algorithm based on transfer matrix method. Subsequent to obtaining the partition function, the thermal and the sample averaged values of various thermodynamic functions can be constructed. We utilized such a procedure to monitor the ergodicity breaking order parameter $x$ as well as the density of the chains at the interface $p$. The behavior of the ergodicity breaking parameter $x$ demonstrates the existence of a finite temperature at which a freezing or an ergodicity breaking transition occurs. Concomitantly, the density of the chains adsorbed at the interface also registers a steep rise, thereby suggesting that this phase transition corresponds to the localization transition. However, we have not monitored the finite size effects (which could be significant for problems such as this involving the presence of intrinsically quenched randomness) on the above results.\(^3\)

\(^3\)The evaluation of finite size effects can be accomplished explicitly by the use of finite size scaling techniques. We have taken refuge to the consistency our numerical results with our analytical predictions to thereby explicitly avoid performing the finite size scaling analysis.
References


Chapter 4

Conclusions

This thesis outlines our studies on the possible thermodynamic and dynamic phase transitions resulting from the interaction between a random polymer and an immiscible polar-nonpolar solvent system. The interaction between the polymer and the pair of solvents was modeled via a random potential with attractive and repulsive components depending upon the location of the monomer with respect to the interface. MSR formalism was used to derive the dynamical equations governing the correlation functions. Examination of the long-time limit of the resulting equations suggested the possibility of a finite temperature freezing transition of the polymer. These conclusions were however gleaned in an indirect manner by examining the high and low temperature limits of the equations. This prediction was also corroborated by the results of finite-temperature transfer matrix simulations. Furthermore, based on physical reasoning accompanying this scenario, we claimed that this phase transition should correspond to the localization transition predicted in [1]. Results from the transfer matrix simulations seem to lend credence to such a claim. Independent confirmation could probably also be achieved by studying the same problem within the framework of a (static) Gaussian variational approach [2].

While a localization transition at \( T = \infty \) was predicted in [1], the existence of a finite temperature localization transition (thereby revealing the dominance of thermal fluctuations at high temperatures) is a new result which appears hitherto not to have been suggested before. Furthermore, the results for our system contrast with those
obtained for 1+1 DPRM, wherein the polymer is expected to exist in a glassy phase for all temperatures $T < \infty$ [3]. This contrast serves to highlight the differences to be expected in systems wherein the quenched disorder is inherent to the system rather than being external to it. The difference seems to be particularly significant, since most theories of the dynamics of random systems seems to have focused upon the latter case. This raises the question of the applicability of the results obtained in those theories to the systems considered herein.

In the above analysis the interface was assumed to be a flat surface serving to separate the two solvents. However, realistically, the interface also experiences thermal fluctuations due to the finite nature of its stiffness. The adsorption of a polymer chain onto fluctuating interfaces and membranes has been analyzed in [4]. To study the effects of a fluctuating interface, one can incorporate a second Langevin-type dynamical equation of the form

$$\frac{1}{\Gamma_2} \frac{\partial h}{\partial t} = -\beta \frac{\delta H}{\delta h} + \zeta_2(x, t),$$

where $h \equiv h(x, t)$ represents the interfacial fluctuations in height, with $\Gamma_2$ and $\zeta_2(x, t)$ respectively representing the mobility and thermal noise. The discontinuity in the force experienced by the polymer lying on the two sides of the interface is manifested in the coupling between the dynamics of the RHP and the interface. Preliminary results indicate a scale-dependent freezing transition of the interface following the phase transition of the polymer.

Our investigation outlined in the preceding chapters of this thesis highlights the manner in which the behavior of proteins at interfaces can be modeled, while pointing up some of the novel features expected to arise in such systems. It is also possible to extend the analysis presented herein so as to incorporate the dynamics in the low temperature phase characterized by novel phenomena like aging etc. [5]. Furthermore, our study may be regarded as a precursor to a comparable study of RHP-surfactant systems, wherein the surfactant can reside in both bulk and the interfacial phases.
References


