Localization transition of a random polymer at an interface

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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 whose physicochemical interactions with the different monomers comprising the chain differ from one another. We re-examine the analysis of Garel et al. (Europhys. Lett., 8 (1989) 9) to probe the low temperature adsorbed regime. Utilizing the Martin-Siggia-Rose formulation with 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 predicted in the above-quoted analysis. However, in contradiction to the analysis of Garel et al., we predict that this phenomenon occurs at a finite temperature. This result contrasts with the behavior that might be expected from studies of 1+1 Directed Polymer in Random Media (DPRM), and resembles the behavior of d+1 DPRM for d > 2. Our conclusions are corroborated by transfer matrix simulations.

Studies of the equilibrium and dynamical properties of polymers and fluctuating surfaces are gaining increasing importance, especially in biological and technological contexts [1]. The chemical properties of the constituents of a macromolecule have been observed to possess a profound influence on the statistical behavior of the macromolecule. For instance, macromolecules built from random configurations of hydrophilic and hydrophobic components try to adopt conformations such that the hydrophilic part is in contact with the polar solvent and the hydrophobic part with the nonpolar solvent. In this context, a recent surge of interest has arisen in the phase transitions exhibited by self-interacting random heteropolymers (RHP) in relation to behavioral similarities with proteins [2]. Explicitly, our work is devoted to investigating the nature of the phase transitions that accompany a RHP residing at an interface between water and another nonpolar solvent, e.g. an oil. Motivation for such studies 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 and absorbed surfactants at the interface.

A similar problem has been explored in a pioneering article by Garel et al. [3]. Their study predicts the existence of a localization transition of the RHP onto the interface. Beyond this...
In this work we use the Martin-Siggia-Rose (MSR) formulation of equilibrium dynamics (in the Hartree approximation) \[4,5\] to study the phase transitions accompanying the interaction of a RHP with a polar-nonpolar solvent system. Utilization of a dynamical formulation (instead of replicas) for quenched random systems has yielded new insights into the freezing transitions encountered in such systems. For instance, Thirumalai et al. \[5\] predict the existence of a scale-dependent freezing transition for the random hydrophilic-hydrophobic copolymer—in contrast to a mean-field replica analysis, which does not predict such a transition. Excluded-volume effects of the polymer are ignored in this work so as to focus attention exclusively on the physics of polymer-solvent interactions. Our analytical study reveals the possible existence of a finite-temperature localization transition. This result contrasts with the results predicted in \[3\], as well as those relating to the 1+1 DPRM studies \[6\], but does, however, resemble the phase behavior of \(d+1\) DPRM for \(d > 2\). This conclusion is especially striking in view of the exact mapping that can be achieved between a 1+1 DP (Directed Polymer) and a self-intersecting polymer. Our results point out in an unequivocal manner, and for the first time, the differences to be expected when the quenched randomness is inherent to the system rather than being external to it. We corroborate our conclusions by simple transfer matrix simulations.

**MSR Functional.** — 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 \(\sigma\) \[2\]. Of interest is the case where 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 is given by \[3\]

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

In the above, \(\rho(n)\) and \(\rho_z(n)\) represent, respectively, the vector coordinate and the \(z\)-coordinate position of the monomer \(n\). Additionally, \(V\) characterizes the strength of the interaction between the polymer and the solvents. The term corresponding to \(\text{sign}\[\rho_z(n)]\) can be replaced by a Heaviside function \(H[\rho_z(n)]\) plus a constant term which is irrelevant to the ensuing analysis. The dynamics of the polymer in the polymer-solvent system is assumed to be governed by a Langevin-type equation of the form

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

where \(\Gamma_1\) denotes the mobility coefficient of the polymer, which serves to fix the time-scale. \(\zeta_1(n,t)\) represents a Gaussian-correlated thermal noise contribution. The MSR generating functional for this system can be written in the form

\[
Z = \int \mathcal{D}\rho(n,t) \delta \left[ \frac{1}{\Gamma_1} \frac{\partial \rho}{\partial t} - \frac{3}{l^2} \frac{\partial^2 \rho}{\partial n^2} - \beta V \theta(n) \delta[\rho_z(n,t)] - \zeta_1(n,t) \right].
\]
Upon employing standard techniques involving the use of auxiliary fields \( \hat{\rho}(n,t) \) to rewrite the \( \delta \)-function, followed by subsequent averaging over the thermal noises \( \zeta_1 \) as well as the sequence disorder \( \theta(n) \), we obtain

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

where

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

and

\[
L_2 = \frac{\beta^2 V_2 \sigma^2}{2} \int dt_1 \int dt_2 \int \frac{dp}{2\pi} \int \frac{dq}{2\pi} \int_0^N d\rho B(n,p,q,t_1,t_2),
\]

with

\[
B(n,p,q,t_1,t_2) = i\hat{\rho}(n,t_1)i\hat{\rho}(n,t_2)\exp[ip\rho_z(n,t_1) + iq\rho_z(n,t_2)].
\]

The first term, \( L_1 \), describes the dynamics of an ideal, noninteracting (with the solvent) polymer chain. The second term, \( L_2 \), represents the manifestation of the quenched disorder.

**Correlation and response functions.** – The correlation and the response functions can be defined in terms of the fields \( \rho \) and \( \hat{\rho} \) as

\[
D(n_1,t_1;n_2,t_2) = \langle \rho_z(n_1,t_1)\rho_z(n_2,t_2) \rangle; \quad M(n_1,t_1;n_2,t_2) = \langle \rho_z(n_1,t_1)i\rho_z(n_2,t_2) \rangle.
\]

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 nonzero 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 [4, 5].

We employ a Hartree approximation in (4) to obtain the dynamical equation governing \( D(n,t) \) (denoted as \( D(s,t) \))

\[
\frac{1}{\Gamma_1} \frac{\partial D(s,t)}{\partial t} + \frac{3s^2}{l^2} D(s,t) - \beta^2 V_2 \sigma^2 \int \frac{dp}{2\pi} \int \frac{dq}{2\pi} \left\{ \frac{(p + q)^2}{2pq} D(s,t) \exp \left[ -\frac{(p + q)^2}{2} \right] \right\} + \int_0^t dt_1 \frac{\partial D(s,t_1)}{\partial t_1} \exp \left[ -\frac{p^2 + q^2}{2} \right] = 0.
\]

In the above equation, the equal time correlation \( \langle \rho_z^2(n,t) \rangle \) is denoted as \( w \). By definition it represents the (temperature dependent) width of the localized layer.
Long-time limit and ergodicity breaking. – To analyze the possible freezing of the modes, we need to consider the long-time limit of eq. (9). In order to achieve this objective we define a normalized ergodicity-breaking parameter $h(s)$ such that

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

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 eq. (9), we obtain

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

where

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

and

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

Equation (12) 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. (12) and discuss the implications of these on the physics of the problem at hand.

Examination of eq. (12) in the limit $\beta \to 0$ and $\beta \to \infty$ reveals that as $\beta \to 0 (T \to \infty)$ the only possible solution of (12) 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. Similar behavior has been predicted in studies of DPRM. It might therefore be speculated that our system can be mapped onto the corresponding 1+1 DPRM. However, in contrast to the phase behavior of 1+1 DPRM, we can prove the existence of a finite-temperature phase transition in our system by deriving an upper bound on the localization temperature $T_{loc}$. 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 $T_{loc} < 0.9V\sigma$. (The numerical prefactor is to be construed as being very approximate. More accurately, we can say that $T_{loc} \approx AV\sigma$, where $A$ is an $O(1)$ quantity). This bound on $T_{loc}$ distinguishes our problem from 1+1 DPRM, wherein the low-temperature phase persists for all temperatures up to $T = \infty$. This result, predicting the existence of a finite-temperature phase transition, is the primary result of our paper.

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 [7] and hence we claim on physical grounds that this phase transition should in fact correspond to the localization transition predicted in [3]. However, the existence of a
finite-temperature localization transition contradicts the earlier result of Garel et al. [3]. Our result 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. [8] for a self-interacting random polymer and contrasts with the scale- (or “$s$”)-dependent freezing transition predicted for self-interacting copolymers [5, 9]. 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.

Transfer matrix simulations. – To corroborate the analytical results presented above, we carried out simplistic transfer matrix simulations for this system. Since the excluded-volume constraint was neglected above, there exists an exact mapping between our system and the directed polymer. The simulation algorithm for the finite-temperature DP in random media has been developed extensively by Kardar and coworkers [6], and will not be detailed here. Implementation of the simulation technique is effected in the following manner: One end of the polymer is fixed at the origin and the different paths are enumerated according to their Boltzmann weights by using the transfer matrix algorithm. An energy cost of $\Gamma$ (set equal to 1.0 in our simulations) is penalized for each bend of the polymeric chain. The interaction energy of the polymer is accounted by $\theta(n)$, where the random variables $\theta(n)$ are 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 $x = 1 - \sum P_i^2$ [2, 10], where $P_i$ refers to the probability of a particular conformation of the polymer and $\sum \cdots$ 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 takes a value different from 1 (and asymptotically attains a value 0 at $T = 0$). Figure 1 depicting the variation of this quantity as a function of temperature clearly indicates a phase transition around $T/\sigma \sim 10$, where the $x$ takes a nonzero 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. 1 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 nonzero value. This result lends support to our earlier claim (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 previous sections, and hence serve to further confirm the presence of a finite-temperature freezing/localization transition.

Conclusions. – To summarize, we have studied the possible 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 as a random potential with an attractive or repulsive component depending on 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 suggests the possibility of a finite-temperature freezing transition of the polymer. These conclusions were arrived at in an indirect manner by examining the high- and low-temperature limits of the equations. This prediction was 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 [3]. 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 [9].

While a localization transition at $T = \infty$ was predicted in [3], 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 $T < \infty$. 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.

Our investigation 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. [11]. 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. We anticipate undertaking such a study in a future contribution.

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Additional Remark. – After submission of this manuscript we learnt of a recent work by Stepanow [12] dealing with the analysis of a similar problem, however, within a variational framework. We recently became aware of the paper by Trovato and Maritan (cond-mat/9812321) wherein the localization transition is predicted to occur at $T = \infty$, and is subsequently followed by a replica symmetry breaking transition. If this were indeed the case, then our results would imply that the ergodicity breaking transition predicted in our model corresponds to this second phase transition—a possibility whose physical origin seems unknown.

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