Dynamics of a tagged monomer: Effects of elastic pinning and harmonic absorption

Shamik Gupta

Laboratoire de Physique Théorique et Modèles Statistiques, Université Paris-Sud, France

Joint work with

Alberto Rosso
Christophe Texier

Bounds on human demeanour.
Upper bound: To bring in happiness wherever you go.
Upper bound: To bring in happiness *wherever* you go.
Lower bound: To bring in happiness *whenever* you go.
• Upper bound: To bring in happiness *wherever* you go.
• Lower bound: To bring in happiness *whenever* you go.
Upper bound: To bring in happiness *wherever* you go.
Lower bound: To bring in happiness *whenever* you go.

\[ 2433 \ldots \]
Upper bound: To bring in happiness wherever you go.
Lower bound: To bring in happiness whenever you go.

2433 email exchanges and chats since 2009 (and still counting)!!

Shamik Gupta  
Dynamics of a tagged monomer
The model

1. Rouse polymer of $L$ monomers immersed in a solvent:
The model

1. Rouse polymer of $L$ monomers immersed in a solvent:

2. $h_i$: displacement of the $i$-th monomer from equilibrium.
The model

1. Rouse polymer of $L$ monomers immersed in a solvent:

2. $h_i$: displacement of the $i$-th monomer from equilibrium.

3. Elastic energy $E_{el} = (1/2) \sum_i (h_{i+1} - h_i)^2$. 
The model

1. Rouse polymer of $L$ monomers immersed in a solvent:

2. $h_i$: displacement of the $i$-th monomer from equilibrium.

3. Elastic energy $E_{el} = \frac{1}{2} \sum_i (h_{i+1} - h_i)^2$.

4. Langevin Dynamics: $\frac{\partial h_i(t)}{\partial t} = -\frac{\partial E_{el}}{\partial h_i} + \eta_i(t) = \sum_j \Delta_{ij} h_j(t) + \eta_i(t)$.
The model

1. Rouse polymer of $L$ monomers immersed in a solvent:

2. $h_i$: displacement of the $i$-th monomer from equilibrium.

3. Elastic energy $E_{el} = \frac{1}{2} \sum_i (h_{i+1} - h_i)^2$.

4. Langevin Dynamics: \[
\frac{\partial h_i(t)}{\partial t} = -\frac{\partial E_{el}}{\partial h_i} + \eta_i(t) = \sum_j \Delta_{ij} h_j(t) + \eta_i(t).
\]

5. $\Delta$: discrete Laplacian, \[
\{\eta_i(t)\} \rightarrow \text{independent Gaussian white noise:}
\]
\[
\langle \eta_i(t) \rangle = 0, \quad \langle \eta_i(t) \eta_j(t') \rangle = 2T \delta_{i,j} \delta(t - t').
\]
The model

1. Rouse polymer of $L$ monomers immersed in a solvent $≡ L$-dim. discrete Edwards-Wilkinson interface

2. $h_i$: displacement of the $i$-th monomer from equilibrium.

3. Elastic energy $E_{el} = \frac{1}{2} \sum_i (h_{i+1} - h_i)^2$.

4. Langevin Dynamics: $\frac{\partial h_i(t)}{\partial t} = -\frac{\partial E_{el}}{\partial h_i} + \eta_i(t) = \sum_j \Delta_{ij} h_j(t) + \eta_i(t)$.

5. $\Delta$: discrete Laplacian, 
   
   $\{\eta_i(t)\} \rightarrow$ independent Gaussian white noise: 
   
   $\langle \eta_i(t) \rangle = 0$, $\langle \eta_i(t) \eta_j(t') \rangle = 2T \delta_{i,j} \delta(t - t')$. 

Shamik Gupta 
Dynamics of a tagged monomer
The model

1. Rouse polymer of $L$ monomers immersed in a solvent $\equiv L$-dim. discrete Edwards-Wilkinson interface

2. $h_i$: displacement of the $i$-th monomer from equilibrium.

3. Elastic energy $E_{el} = (1/2) \sum_i (h_{i+1} - h_i)^2$.

4. **Langevin Dynamics:**
   \[
   \frac{\partial h_i(t)}{\partial t} = -\frac{\partial E_{el}}{\partial h_i} + \eta_i(t) = \sum_j \Delta_{ij} h_j(t) + \eta_i(t).
   \]

5. $\Delta$: discrete Laplacian,
   \[
   \{\eta_i(t)\} \rightarrow \text{independent Gaussian white noise:}
   \]
   \[
   \langle \eta_i(t) \rangle = 0, \quad \langle \eta_i(t)\eta_j(t') \rangle = 2T \delta_{i,j} \delta(t - t').
   \]


Shamik Gupta  
Dynamics of a tagged monomer
$L$-dim. discrete Edwards-Wilkinson interface:
1. $L$-dim. discrete Edwards-Wilkinson interface:

2. Centre of mass $(1/L) \sum_{i=1}^{L} h_i(t) \rightarrow$ Markovian dynamics, normal diffusion:

$$\text{Mean-squared displacement } \sim 2(1/L)t.$$
1. $L$-dim. discrete Edwards-Wilkinson interface:

2. Tagged monomer $\rightarrow$ Non-Markovian dynamics, anomalous diffusion:
   Mean-squared displacement $\sim \sqrt{\frac{2}{\pi}} b_0 \sqrt{t}$. 

Shamik Gupta  
Dynamics of a tagged monomer
Tagged monomer Mean-squared displacement $\sim \sqrt{\frac{2}{\pi}} b_0 \sqrt{t}$. 
Tagged monomer Mean-squared displacement $\sim \sqrt{\frac{2}{\pi}} b_0 \sqrt{t}$.

- $b_0$ encodes memory of polymer configuration at $t = 0$.
- Equilibrium at $t = 0$
  - Tagged monomer exhibits fractional Brownian motion (correlated increments), $b_0 = \sqrt{2}$.
- Out of equilibrium flat configuration at $t = 0$
  - Correlated increments drawn from a Gaussian distribution with a time-dependent variance, $b_0 = 1$ (Krug et al. (1997)).
What we are after....

- Two specific situations of practical relevance:
What we are after....

- Two specific situations of practical relevance:
  1. Elastic pinning of the tagged monomer (cf. optical tweezers).

![Diagram](image.png)
Two specific situations of practical relevance:

1. Elastic pinning of the tagged monomer (cf. optical tweezers).

2. Absorption of the tagged monomer on an interval. Example: Reactant attached to a monomer encounters an external reactive site fixed in space.
What we are after....

- Two specific situations of practical relevance:
  1. Elastic pinning of the the tagged monomer.
  2. Absorption of the tagged monomer in an interval.
What we are after....

Two specific situations of practical relevance:
1. Elastic pinning of the tagged monomer.
2. Absorption of the tagged monomer in an interval.

Questions:
- Dynamics of the tagged monomer,
- Steady state,
- Approach to the steady state,
- Memory of the initial condition.

Shamik Gupta
Dynamics of a tagged monomer
What we are after....

- Two specific situations of practical relevance:
  1. Elastic pinning of the tagged monomer.
  2. Absorption of the tagged monomer in an interval.

- Questions:
  Dynamics of the tagged monomer,
  Steady state,
  Approach to the steady state,
  Memory of the initial condition.

- Our work:
  Exact analytical results for elastic pinning and harmonic absorption.
  In particular, strong memory effects in the relaxation to the steady state.
Elastic pinning

\[ \partial \mathcal{W}_t[h|h^0] = \left[ \sum_i \frac{\partial^2}{\partial h_i^2} + \sum_{i,j} \frac{\partial}{\partial h_i} \Lambda_{ij} h_j \right] \mathcal{W}_t[h|h^0]; \]

\[ -\Lambda_{ij} = \Delta_{ij} - \kappa \delta_{i,j} \delta_{i,0}. \]

Langevin approach (Viñales and Despósito (2006,2009), Grebenkov (2011))
Elastic pinning

\[
\frac{\partial \mathcal{W}_t[h|h^0]}{\partial t} = \left[ \sum_i \frac{\partial^2}{\partial h_i^2} + \sum_{i,j} \frac{\partial}{\partial h_i} \Lambda_{ij} h_j \right] \mathcal{W}_t[h|h^0];
\]

\[-\Lambda_{ij} = \Delta_{ij} - \kappa \delta_{i,j} \delta_{i,0}.\]

1 Replace matrix $\Lambda$ by number $\lambda$: 1d Ornstein-Uhlenbeck process.
Elastic pinning

\[ \frac{\partial \mathcal{W}_t[h|h^0]}{\partial t} = \left[ \sum_i \frac{\partial^2}{\partial h_i^2} + \sum_{i,j} \frac{\partial}{\partial h_i} \Lambda_{ij} h_j \right] \mathcal{W}_t[h|h^0]; \]

\[ -\Lambda_{ij} = \Delta_{ij} - \kappa \delta_{i,j} \delta_{i,0}. \]

1. Replace matrix \( \Lambda \) by number \( \lambda \): 1d Ornstein-Uhlenbeck process.

2. \( \mathcal{W}_t[h|h^0] = \sqrt{\det \left( \frac{\Lambda}{2\pi(1-e^{-2\Lambda t})} \right)} \exp \left[ -\frac{1}{2} (h - e^{-\Lambda t} h^0)^T \frac{\Lambda}{1-e^{-2\Lambda t}} (h - e^{-\Lambda t} h^0) \right]. \)
Flat initial condition

$t = 0$:

\[ \text{---} \quad \text{---} \quad \text{---} \quad \text{---} \quad \text{---} \quad \text{---} \quad \text{---} \quad \text{---} \quad \text{---} \quad \text{---} \]

$t > 0 : T = 1 \quad + \quad \text{elastic pinning with spring constant } \kappa.$
Equilibrated initial condition

\[ t = 0 : \text{Equilibrated at temp. } T_0 \]

\[ t > 0 : T = 1 \quad + \quad \text{elastic pinning with spring constant } \kappa. \]
Elastic pinning: Exact results

\[ \langle h_0^2(t) \rangle \approx \frac{1}{\kappa} \left[ 1 + \frac{T_0 - 1}{\kappa} \sqrt{\frac{2}{\pi t}} - \frac{T_0 c_1}{\kappa^2 t} + \cdots \right]. \]

Shamik Gupta  
Dynamics of a tagged monomer
Absorption in an interval

\[ t > 0 : \]

\[ \frac{\partial \mathcal{W}_t[h|h^0]}{\partial t} = \left[ \sum_i \frac{\partial^2}{\partial h_i^2} - \sum_{i,j} \left( \frac{\partial}{\partial h_i} \Delta_{ij} h_j \right) \right] \mathcal{W}_t[h|h^0]. \]
Absorption in an interval

\[ t > 0 : \]

\[ \frac{\partial \mathcal{W}_t[h|h^0]}{\partial t} = \left[ \sum_i \frac{\partial^2}{\partial h_i^2} - \sum_{i,j} \left( \frac{\partial}{\partial h_i} \Delta_{ij} h_j \right) \right] \mathcal{W}_t[h|h^0]. \]

- Absorbing boundary conds. for the tagged monomer.
Harmonic absorption

\[ t > 0 : \]

Absorption probability \( \propto \mu h_0^2(t). \)

\[
\frac{\partial \mathcal{W}_t[h|h^0]}{\partial t} = \left[ \sum_i \frac{\partial^2}{\partial h_i^2} - \sum_{i,j} \left( \frac{\partial}{\partial h_i} \Delta_{ij} h_j + h_i A_{ij} h_j \right) \right] \mathcal{W}_t[h|h^0];
\]

\[ A_{ij} = \mu \delta_{i,j} \delta_{i,0}. \]
Harmonic absorption: Exact results

\[ \langle h_0^2(t) \rangle \]

- \( T_0 = 0 \)
- \( T_0 = 1 \)
- \( T_0 = 4 \)

\( L = 200 \)
\( 4\mu = 0.0025 \)

Shamik Gupta
Dynamics of a tagged monomer
Survival probability

$S(t)$: survival probability of an initial configuration $h^0$. 
Survival probability

1. $S(t)$: survival probability of an initial configuration $h^0$.

2. \[
\frac{\partial \mathcal{W}_t[h|h^0]}{\partial t} = \left[ \sum_i \frac{\partial^2}{\partial h_i^2} - \sum_{i,j} \left( \frac{\partial}{\partial h_i} \Delta_{ij} h_j + h_i A_{ij} h_j \right) \right] \mathcal{W}_t[h|h^0].
\]
Survival probability

1. $S(t)$: survival probability of an initial configuration $h^0$.

2. \[
\frac{\partial \mathcal{W}_t[h|h^0]}{\partial t} = \left[ \sum_i \frac{\partial^2}{\partial h_i^2} - \sum_{i,j} \left( \frac{\partial}{\partial h_i} \Delta_{ij} h_j + h_i A_{ij} h_j \right) \right] \mathcal{W}_t[h|h^0].
\]

3. \[
\partial_t S(t) = -\mu \langle h_0^2(t) \rangle S(t).
\]
Survival probability

1. $S(t)$: survival probability of an initial configuration $h^0$.
2. \[
\frac{\partial \mathcal{W}_t[h|h^0]}{\partial t} = \left[ \sum_i \frac{\partial^2}{\partial h_i^2} - \sum_{i,j} \left( \frac{\partial}{\partial h_i} \Delta_{ij} h_j + h_i A_{ij} h_j \right) \right] \mathcal{W}_t[h|h^0].
\]
3. $\partial_t S(t) = -\mu \langle h_0^2(t) \rangle S(t)$.
4. $S(t) = \exp \left( -\mu \int_0^t d\tau \langle h_0^2(\tau) \rangle \right)$.

Consistent with simulations (Kantor and Kardar (2004)).
Conclusions

1. Tagged monomer dynamics under elastic pinning and harmonic absorption: Exact results.
Conclusions

1. Tagged monomer dynamics under elastic pinning and harmonic absorption: Exact results.
2. Strong memory effects:
Conclusions

1. Tagged monomer dynamics under elastic pinning and harmonic absorption: Exact results.

2. Strong memory effects:
   - Pinning case:
     Relaxation as $1/\sqrt{t}$, unless evolution at the same temp. as that of the initial eqibm. when relaxation as $1/t$.
     Non-monotonic relaxation depending on the initial eqibm. temp.
Conclusions

1. Tagged monomer dynamics under elastic pinning and harmonic absorption: Exact results.

2. Strong memory effects:
   - Pinning case:
     Relaxation as $1/\sqrt{t}$, unless evolution at the same temp. as that of the initial eqibm. when relaxation as $1/t$.
     Non-monotonic relaxation depending on the initial eqibm. temp.
   - Absorption case: Relaxation always as $1/t$.
     Non-monotonic relaxation, except for $T_0 = 0$. 

Shamik Gupta
Dynamics of a tagged monomer
Conclusions

1. Tagged monomer dynamics under elastic pinning and harmonic absorption: Exact results.

2. Strong memory effects:
   - Pinning case:
     Relaxation as $1/\sqrt{t}$, unless evolution at the same temp. as that of the initial eqibm. when relaxation as $1/t$.
     Non-monotonic relaxation depending on the initial eqibm. temp.
   - Absorption case: Relaxation always as $1/t$.
     Non-monotonic relaxation, except for $T_0 = 0$.

3. Analysis may be generalized to a Rouse chain in $d$ dimensions or a $d$-dimensional EW interface, by using the corresponding Laplacian matrix in place of $\Delta$. 
Conclusions

1. Tagged monomer dynamics under elastic pinning and harmonic absorption: Exact results.

2. Strong memory effects:
   - Pinning case:
     Relaxation as $1/\sqrt{t}$, unless evolution at the same temp. as that of the initial eqlbm. when relaxation as $1/t$.
     Non-monotonic relaxation depending on the initial eqlbm. temp.
   - Absorption case: Relaxation always as $1/t$.
     Non-monotonic relaxation, except for $T_0 = 0$.

3. Analysis may be generalized to a Rouse chain in $d$ dimensions or a $d$-dimensional EW interface, by using the corresponding Laplacian matrix in place of $\Delta$.

4. Hydrodynamic effects for the chain or long-range elastic interactions for the interface may be included by replacing $\Delta$ with the corresponding fractional Laplacian $-(−\Delta)^{z/2}$.