Dynamics of pinned polymer loop in 1D

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1 Model

Polymer dynamics of bead rod can be mapped to particle hopping model by the coarse grain that rod orientation be either right($+1$) or left(-1). This binary state of rods can be represented by the state of lattice sites which is either occupied by one particle(1) or empty(0). Denote the state of i^{th} rod by z_i and state of i^{th} lattice site by s_i, then we have $s_i = (z_i + 1)/2$.

It is easy to show that the configuration of polymer can be one to one mapped to the configuration of lattices with particles. The dynamics of be polymer then can be investigated in the context of particle hopping process, known as ASEP. Here we consider the case of pinned polymer loop model in an external force field which corresponds to N particles hopping in $2N$ lattices sites with reflecting boundaries. Other models, e.g. free bead rod chain, corresponds to simply different settings of ASEP will be discussed in our future work.

To calibrate dynamics of bead rod and ASEP, we need to know exactly what is the correspondence of a single particle hopping step to left or right. This is illustrated in the sketch Fig. **??**

One single hopping step of a particle affects two neighbouring lattice sites, namely two neighbouring rods orientation. The switch of the site state corresponds to flip of the rod orientation. With this intuition, it is easy to understand that one hopping step of a particle is equivalent to two neighbouring rods rotate for π, i.e. a flip. Notice that a flip of two neighbouring rods means that the shared bead diffuse for a distance of $2a$, where a is the length of rod. We use this to estimate the time scale of the dynamics. Denote τ_0 the time of a particle hopping step, then

$$\tau_0 \propto \frac{4a^2}{2D_0} = \frac{2a^2\xi}{k_B T} \tag{1}$$

where D_0 is the diffusion coefficient of the bead, ξ is friction coefficient, k_B is Boltzmann factor, and T is temperature.

Next, we need to know what is the effect of force exerting on beads to the hopping of particles. Force changes the bias of rod flipping thus the bias of particle hopping. Denote α, β the rate of particle hopping to left and right, respectively. We have

$$\beta/\alpha = \exp(-\frac{\Delta E}{k_B T}) \tag{2}$$

where ΔE is the energy difference between the two configuration before and after hopping. Without lose of generality we assume the constant force F exerting on beads is in the direction of right. So we have $\Delta E = 2Fa$.

On the other hand, the totally rate of hopping is irrelevant with the external force but depends on the temperature. Actually this can be obtained from the hopping time scale Eq. (1). We thus have

$$\alpha + \beta = r_{total} = 1/\tau_0 \tag{3}$$

With Eq. (2) and Eq. (3), we can solve the hopping rates α and β.

$$\alpha = \frac{r_{\text{total}}}{1 + \exp\left(-2Fa/k_B T\right)} \tag{4a}$$

$$\beta = \frac{r_{\text{total}} \exp\left(-2Fa/k_B T\right)}{1 + \exp\left(-2Fa/k_B T\right)} \tag{4b}$$

Now we have a welled defined ASEP model corresponds to the dynamics of pinned bead rod polymer loop in external force field. In order to solve the dynamics, let us discuss more about the *pseudo* particles in the mapped ASEP model. The dynamics of these *pseudo* particles is essentially Brownian particles with constant drift. Without loss of generality, we set the lattice constant which denotes the width of lattice site to 1. Then the diffusivity and drifting velocity of the *pseudo* particle D and μ can be written as

$$D = 1^2/2\tau_0 = \frac{1}{2}(\alpha + \beta) \tag{5a}$$

$$\mu = \alpha - \beta \tag{5b}$$

The dynamical equation of the particle system can be describe by Fokker-Planck Equation

$$\begin{aligned} \frac{\partial p(\mathbf{x}, t|\mathbf{x}_0)}{\partial t} =& D\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \cdots + \frac{\partial^2}{\partial x_N^2}\right) p(\mathbf{x}, t|\mathbf{x}_0) \\ & - \mu\left(\frac{\partial}{\partial x_1} + \frac{\partial}{\partial x_2} + \cdots + \frac{\partial}{\partial x_N}\right) p(\mathbf{x}, t|\mathbf{x}_0) \end{aligned} \tag{6}$$

where $\mathbf{x} = (x_1, x_2, \cdots, x_N)^T$ is the vector denotes the position of each particle and $\mathbf{x_0}$ denotes the initial position of particles. In general case D and μ can depend on time and position. However, what we consider here D and μ are just constants. The reflecting boundary conditions of the ASEP system can be written as

$$\left(D\frac{\partial}{\partial x_1} p(\mathbf{x}, t|\mathbf{x}_0) - \mu p(\mathbf{x}, t|\mathbf{x}_0) \right) \Bigg|_{x_1=0} = 0 \tag{7a}$$

$$\left(D\frac{\partial}{\partial x_N} p(\mathbf{x}, t|\mathbf{x}_0) - \mu p(\mathbf{x}, t|\mathbf{x}_0) \right) \Bigg|_{x_N=L} = 0 \tag{7b}$$

Where $L = 2N$ in our case. Furthermore, notice the exclusive condition which means particle can not overtake each other. This can be formulated as follow

$$\left(\frac{\partial}{\partial x_{i+1}} p(\mathbf{x}, t|\mathbf{x}_0) - \frac{\partial}{\partial x_i} p(\mathbf{x}, t|\mathbf{x}_0) \right) \Bigg|_{x_i=x_{i+1}} = 0 \tag{8}$$

Finally, the initial condition we assume is

$$p(\mathbf{x}, 0|\mathbf{x}_0) = \delta(x_1 - x_{1,0})\delta(x_2 - x_{2,0}) \cdots \delta(x_N - x_{N,0}) \tag{9}$$

2 Solution

The solution of Eq. (6) together with Eq. (7),(8),(9) can be found by coordinate Bethe Ansatz[]. We assume the solution of $p(\mathbf{x}, t|\mathbf{x}_0)$ can be written in the following form

$$p(\mathbf{x}, t|\mathbf{x}_0) = \sum_{\sigma \in S_N} \psi(x_1, x_{\sigma(1)}; t)\psi(x_2, x_{\sigma(2)}; t) \cdots \psi(x_N, x_{\sigma(N)}; t) \tag{10}$$

where σ is a N-permutation of $x_{i,0}$. This means the expanded form of Eq. (10) reads

$$\begin{aligned} p(\mathbf{x}, t|\mathbf{x}_0) =& \psi(x_1, x_{1,0}; t)\psi(x_2, x_{2,0}; t) \cdots \psi(x_N, x_{N,0}; t) + \\ & \psi(x_1, x_{2,0}; t)\psi(x_2, x_{1,0}; t) \cdots \psi(x_N, x_{N,0}; t) + \\ & \text{all other permutations of } \{x_{1,0}, x_{2,0}, \cdots, x_{N,0}\} \end{aligned}$$

After that, it is important to find out the correct $\psi(x_i, x_{\sigma(i)}; t)$. Surprisely, we will show here that $\psi(x_i, x_{\sigma(i)}; t)$ is simply the form of one single Brownian particle with drifting in the reflecting box. But before dive into the derivation, we want to point out Eq. (10) is not a common Bethe Ansatz solution

of a 1D N-particle system, e.g. it is not the solution form when the boundary is periodic or open[]. The key reason it works in this case is rooting from the reflecting boundaries of the system. Because of the reflecting boundaries, the response of particles in the middle or in the periphery will be exactly the same, i.e. reflecting. This leads to a factorized form of the N-particle PDF, i.e. Eq. (10). In other words, Eq. (10) is the solution of the 1D N-particle system as long as the boundary is reflecting, even through the external field is much more complex than the constant one we considered in this work. We will give a proof that can easily extend to more general cases in the following text.

The proof that Eq. (10) is indeed a solution is actually quite simple and straight forward. Notice that $\psi(x_i, x_{j,0}; t)$ is the solution of single particle drifting in the box so that

$$\frac{\partial \psi(x_i, x_{j,0}; t)}{\partial t} = D\frac{\partial^2}{\partial x_i^2}\psi(x_i, x_{j,0}; t) - \mu\frac{\partial}{\partial x_i}\psi(x_i, x_{j,0}; t) \tag{11a}$$

$$\left(D\frac{\partial}{\partial x_i}\psi(x_i, x_{j,0}; t) - \mu\psi(x_i, x_{j,0}; t)\right)\Big|_{x_i=0} = 0 \tag{11b}$$

$$\left(D\frac{\partial}{\partial x_i}\psi(x_i, x_{j,0}; t) - \mu\psi(x_i, x_{j,0}; t)\right)\Big|_{x_i=L} = 0 \tag{11c}$$

$$\psi(x_i, x_{j,0}; 0) = \delta(x_i - x_{j,0}) \tag{11d}$$

We firstly exam that Eq. (10) satisfies the Fokker-Planck equation. Just substitute Eq. (10) into Eq. (6) we obtain

$$\text{lhs} = \sum_{\sigma\in S_N}\sum_{i=1}^{N}\frac{\partial \psi(x_i, x_{\sigma(i)}; t)}{\partial t}\prod_{j\neq i}\psi(x_j, x_{\sigma(j)}; t)$$

$$\text{rhs} = \sum_{\sigma\in S_N}\sum_{i=1}^{N}\left(D\frac{\partial^2\psi(x_i, x_{\sigma(i)}; t)}{\partial x_i^2} - \mu\frac{\partial\psi(x_i, x_{\sigma(i)}; t)}{\partial x_i}\right)\prod_{j\neq i}\psi(x_j, x_{\sigma(j)}; t)$$

It is obvious that *lhs* = *rhs* because of Eq. (11a). And other permutation terms of Eq. (2) can be proved in the same way.

Next, we show that the reflecting boundary conditions is satisfied, again

just plug Eq. (10) into Eq. (7), obtain

$$\begin{aligned}
&\left(D\frac{\partial}{\partial x_1}p(\mathbf{x},t|\mathbf{x}_0)-\mu p(\mathbf{x},t|\mathbf{x}_0)\right)\Bigg|_{x_1=0}\\
&=\sum_{\sigma\in S_N}\left(D\frac{\partial\psi(x_1,x_{\sigma(1)};t)}{\partial x_1}-\mu\psi(x_1,x_{\sigma(1)};t)\right)\prod_{j\neq 1}\psi(x_j,x_{\sigma(j)};t)\Bigg|_{x_1=0}\\
&=0
\end{aligned}$$

Eq. (11b) is ultilized for the last step. Similarly, the boundary condition at $x_N = L$ is also satisfied because of Eq. (11c).

We then show that the exclusive condition Eq. (8) is also true. Take a pair of permutation terms that we can always find in the solution of Eq. (10),

$$\begin{aligned}
\phi =&\psi(x_i,x_{m,0};t)\psi(x_{i+1},x_{n,0};t)\prod_{j\neq i,i+1}\psi(x_j,x_{\sigma(j)};t)\\
&+\psi(x_i,x_{n,0};t)\psi(x_{i+1},x_{m,0};t)\prod_{j\neq i,i+1}\psi(x_j,x_{\sigma(j)};t)
\end{aligned}$$

It is easy to verify that

$$\begin{aligned}
\left(\frac{\partial\phi}{\partial x_{i+1}}-\frac{\partial\phi}{\partial x_i}\right)\Bigg|_{x_i=x_{i+1}} &= \left(\frac{\partial\psi(x_{i+1},x_{m,0};t)}{\partial x_{i+1}}\psi(x_i,x_{n,0};t)+\frac{\partial\psi(x_{i+1},x_{n,0};t)}{\partial x_{i+1}}\psi(x_i,x_{m,0};t)\right.\\
&\quad\left.-\frac{\partial\psi(x_i,x_{m,0};t)}{\partial x_i}\psi(x_{i+1},x_{n,0};t)-\frac{\partial\psi(x_i,x_{n,0};t)}{\partial x_i}\psi(x_{i+1},x_{m,0};t)\right)\\
&\quad\times\prod_{j\neq i,i+1}\psi(x_j,x_{\sigma(j)};t)\Bigg|_{x_i=x_{i+1}}\\
&=0
\end{aligned}$$

And because $p(\mathbf{x},t|\mathbf{x_0})$ can be written as the summation of ϕ, so the exclusive condition Eq. (8) is proved.

Last, we come to the initial condition. Simply plug Eq. (11d) into the solution Eq. (10) we get

$$\begin{aligned}
p(\mathbf{x},0|\mathbf{x}_0) =&\delta(x_1-x_{1,0})\delta(x_2-x_{2,0})\cdots\delta(x_N-x_{N,0})\\
&+\delta(x_1-x_{2,0})\delta(x_2-x_{1,0})\cdots\delta(x_N-x_{N,0})\\
&\text{all other permutations of } \{x_{1,0},x_{2,0},\cdots,x_{N,0}\}
\end{aligned}$$

All the other terms vanish except the first in the above equation because by definition we have $x_1 < x_2 < \cdots < x_N$ and $x_{1,0} < x_{2,0} < \cdots < x_{N,0}$. We thus prove the initial condition Eq. (9). And now we finally proved that Eq. (10) with $\psi(x_i, x_{j,0}; t)$ satisfies Eq. (11) is the solution of our problem. Notice that this procedure of proof is still valid in the case that external field is more complex than just constant.

Now let us come back to the solution Eq. (10). So if we know the exact form of $\psi(x_i, x_{j,0}; t)$ then we have a close form solution of our problem. Luckly, $\psi(x_i, x_{j,0}; t)$ is known thanks to the recent works[]. In our notation, $\psi(x_i, x_{j,0}; t)$ can be written as

$$\psi(x_i, x_{j,0}; t) = \psi_0(x_i) + \sum_{n=1}^{\infty} \exp(-\lambda_n t)\varphi_n(x_i, x_{j,0}) \tag{12}$$

where $\psi_0(x_i)$ is stationary state PDF that irrelevant with time and initial condition. λ_n is the eigenvalue related to n^{th} relaxation mode, $\varphi_n(x_i, x_{j,0})$ is the function relates to initial condition. These terms can be written as following

$$\psi_0(x_i) = \begin{cases} \frac{1}{L} & \text{for} \quad \mu = 0 \\ \frac{\mu}{D}\frac{\exp(\frac{\mu x_i}{D})}{\exp(\frac{\mu L}{D})-1} & \text{for} \quad \mu \neq 0 \end{cases} \tag{13a}$$

$$\lambda_n = \frac{\mu^2}{4D} + \frac{Dn^2\pi^2}{L^2} \tag{13b}$$

$$\varphi_n(x_i, x_{j,0}) = \frac{D\pi^2 \exp(\frac{\mu}{2D}(x_i - x_{j,0}))}{2\lambda_n L} X_n(x_i) X_n(x_{j,0}) \tag{13c}$$

$$X_n(x) = \frac{2n}{L}\cos(\frac{n\pi x}{L}) + \frac{\mu}{D\pi}\sin(\frac{n\pi x}{L}) \tag{13d}$$

Plug Eq. (12)(13) into Eq. (10) we get the close form N-particle PDF. However, it is so lengthy that not clean enough for us to understand the physics. Notice what we usually interested in are the stationary state and the longest relaxation time. So we keep only these two terms after the substitution, obtain

$$p(\mathbf{x}, t|\mathbf{x}_0) = p_0(\mathbf{x}) + p_1(\mathbf{x}, t|\mathbf{x}_0) + p_H(\mathbf{x}, t|\mathbf{x}_0) \tag{14}$$

where p_H is the summation of all higher mode terms $n > 1$, p_0 and p_1 are stationary mode and longest relaxation mode, respectively, which reads

$$p_0(\mathbf{x}) = N!\,\psi_0(x_1) \prod_{i=1}^{N-1} \psi_0(x_{i+1})\Theta(x_{i+1} - x_i) \tag{15a}$$

$$p_1(\mathbf{x}, t|\mathbf{x}_0) = A_1(\mathbf{x}, \mathbf{x}_0) \exp(-\lambda_1 t) \tag{15b}$$

$$A_1(\mathbf{x}, \mathbf{x}_0) = (N-1)! \sum_{i=1}^{N} \psi_0(x_i) \sum_{j\neq i}^{N} \sum_{k=1}^{N} \varphi_1(x_j, x_{k,0}) \tag{15c}$$

$\Theta(x)$ is the Heaviside step function and A_1 is the amplitude of the longest relaxation mode which relates only the position of particles.

3 Pinned Polymer

Now we consider transfer back from ASEP model to the dynamics of pinned polymer.

The position of beads in 1D polymer relates to the rods orientation in the following way

$$r_i = \sum_{j=1}^{i} z_j = 2\sum_{j=1}^{i} s_j - i = 2\sum_{j=1}^{N} \Theta(i - x_j) - i \tag{16}$$

where $\sum_{j=1}^{i} s_j$ is effectively the total number of particles in the range of $[0, i]$. Thus we have

$$r_i(t|\mathbf{x}_0) = 2N \frac{\int_{\Omega_i} p(\mathbf{x}, t|\mathbf{x}_0) d\mathbf{x}}{\int_{\Omega} p(\mathbf{x}, t|\mathbf{x}_0) d\mathbf{x}} - i \tag{17}$$

where Ω is the sample space, notice it is not simply the space of $\Re^N$ because $x_1 < x_2 < \cdots < x_N$. Ω_i denotes the subspace of Ω that $x \leqslant i$ is satisfied for all particles. Substitute Eq. (14) into the above one we arrive at

$$\begin{aligned} r_i(t|\mathbf{x}_0) =& 2N \frac{\int_{\Omega_i} p_0(\mathbf{x}) + p_1(\mathbf{x}, t|\mathbf{x}_0) + p_H(\mathbf{x}, t|\mathbf{x}_0) d\mathbf{x}}{\int_{\Omega} p(\mathbf{x}, t|\mathbf{x}_0) d\mathbf{x}} - i \\ =& \left(2N \frac{\int_{\Omega_i} p_0(\mathbf{x}) d\mathbf{x}}{\int_0^L p(\mathbf{x}, t|\mathbf{x}_0) d\mathbf{x}} - i \right) + \left(2N \frac{\int_{\Omega_i} p_1(\mathbf{x}, t|\mathbf{x}_0) d\mathbf{x}}{\int_{\Omega} p(\mathbf{x}, t|\mathbf{x}_0) d\mathbf{x}} \right) \\ &+ \left(2N \frac{\int_{\Omega_i} p_H(\mathbf{x}, t|\mathbf{x}_0) d\mathbf{x}}{\int_{\Omega} p(\mathbf{x}, t|\mathbf{x}_0) d\mathbf{x}} \right) \\ =& r_i^{eq} + \Delta r_i^{relax} + \Delta r_i^{H} \end{aligned} \tag{18}$$

We only interested in r_i^{eq} and Δr_i^{relax} which we will discuss one by one in the following subsection.

3.1 Relaxation time

Interestingly, it is every easy to solve the relaxation time in our formalism, even simpler than the equilibrium statistics. So we will discuss this part first. The longest relaxation time can directly read from Δr_i^{relax} as following

$$\begin{aligned}\Delta r_i^{relax} =& 2N\frac{\int_{\Omega_i} p_1(\mathbf{x},t|\mathbf{x}_0)d\mathbf{x}}{\int_{\Omega} p(\mathbf{x},t|\mathbf{x}_0)d\mathbf{x}}\\ =& 2N\frac{\int_{\Omega_i} A_1(\mathbf{x},\mathbf{x}_0)d\mathbf{x}}{\int_{\Omega} p(\mathbf{x},t|\mathbf{x}_0)d\mathbf{x}}\times\exp(-\lambda_1 t)\\ =& \Phi(\mathbf{x},\mathbf{x}_0)\exp(-\lambda_1 t)\end{aligned} \tag{19}$$

Notice that $\Phi(\mathbf{x},\mathbf{x}_0)$ is only related to position, so we have the relaxation time

$$\begin{aligned}\tau =& \frac{1}{\lambda_1} = \frac{1}{\frac{\mu^2}{4D}+\frac{D\pi^2}{L^2}}\\ =& \frac{2L^2\tau_0\left(e^{\frac{2Fa}{k_BT}}+1\right)^2}{L^2\left(e^{\frac{2Fa}{k_BT}}-1\right)^2+\pi^2\left(e^{\frac{2Fa}{k_BT}}+1\right)^2}\\ =& \frac{2L^2\tau_0}{\pi^2}-\frac{2L^4\tau_0\left(e^{\frac{2Fa}{k_BT}}-1\right)^2}{\pi^2\left(L^2\left(e^{\frac{2Fa}{k_BT}}-1\right)^2+\pi^2\left(e^{\frac{2Fa}{k_BT}}+1\right)^2\right)}\end{aligned} \tag{20}$$

We can see from Eq. (20) that $\tau > 0$. And the first term in the third line of Eq. (20) is the plateau value of relaxation time when the external force $F \to 0$. The second term is the effect of external force on relaxation time. Notice it is monotonically decrease as increase of force. The theory is compared with 1D ASEP simulation in Fig. 1.

From Eq. (1) we know the estimation of time scale τ_0, but it is not a exact relation. However, we can write $\tau_0 = c\frac{2a^2\xi}{k_BT}$, where c is a constant. Substitute into Eq. (20) and compare the first term with Rouse theory $\tau_{Rouse} = \frac{\xi L^2 a^2}{3k_BT\pi^2}$ [], which correctly describe the dynamics of bead rod polymer when there is no external force, we can obtain $c = \frac{1}{12}$. Resubstitute τ_0 with c into Eq. (20) we obtain

$$\tau = \frac{\xi L^2 a^2}{3\pi^2 k_BT}-\frac{\xi L^4 a^2\left(e^{\frac{2Fa}{k_BT}}-1\right)^2}{3\pi^2 k_BT\left(L^2\left(e^{\frac{2Fa}{k_BT}}-1\right)^2+\pi^2\left(e^{\frac{2Fa}{k_BT}}+1\right)^2\right)} \tag{21}$$

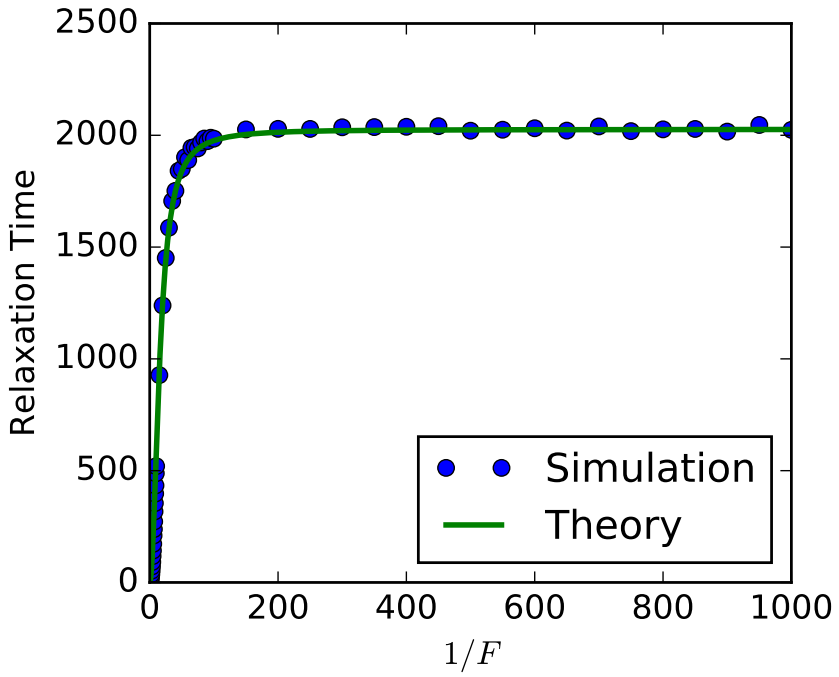

Figure 1: Relaxation time v.s. external force. Simulation result from 1D Kinetic Monte Carlo and Theory from Eq. (20) with the setup of $\tau_0 = 1, a = 1, k_B T = 1$.

This can be compared with the 3D Brownian Dynamics simulation, which is show in Fig. 2. Notice here L is the number of beads.

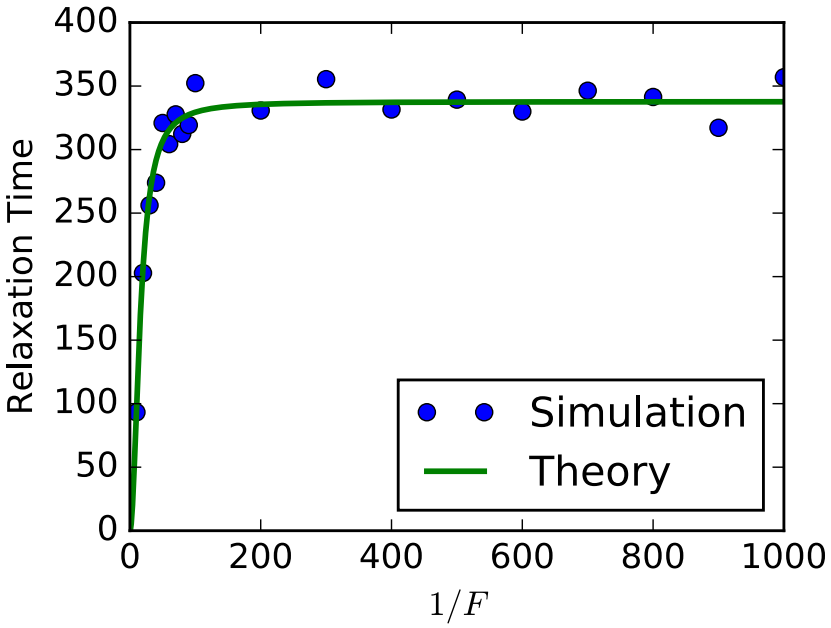

Figure 2: Relaxation time v.s. external force in 3D. Here the relaxation time of simulation is fitting from the z component (force direction) of $\mathbf{r}_d$ (middle bead), theory is from Eq. (21) by set $\xi = 1, a = 1$ and $k_B T = 1$.

In the mean time, we can investigate how relaxation time varies with temperature using Eq. (21). Interestingly, in this case, the non-monotonic behavior is predicted by the theory when external force is strong enough, See in Fig. 3. We don't have the simulation data yet, but will update later on.

3.2 Equilibrium Statistics

Working on it...

References

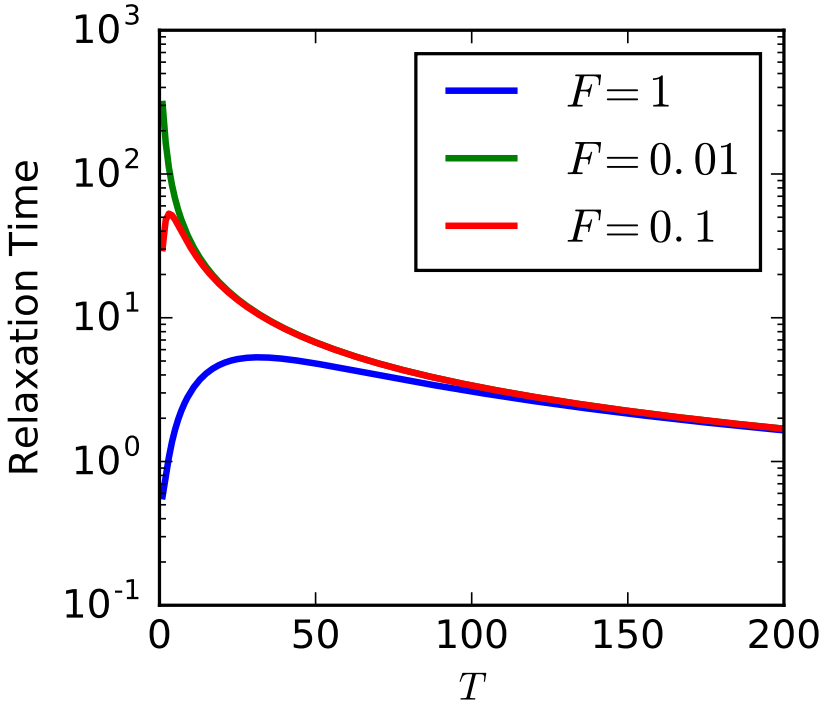

Figure 3: Prediction of of theory from Eq. (21) for how relaxation time varies with temperature.