

Advanced Computational Physics Lab

– Project 1

Escape of a block copolymer from a micelle

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Copolymers are made up of two different sub chains that interact differently with the environment. This peculiar property can lead to very interesting dynamics.

1 MCMC simulation of a single chain in a spherical micelle

Markov Chain Monte Carlo (MCMC) simulations can be used to sample a statistical ensemble (usually the Boltzmann ensemble). In a MCMC simulation one proposes simulation step – which is usually a small local change – that than is either accepted or rejected. The acceptance rate can be chosen in a few different ways, but the one most commonly used is the so-called Metropolis acceptance rate. The Metropolis acceptance rate α of a proposed step from configuration $\{r\}_i$ to configuration $\{r\}_j$ is given by

$$\alpha = \min \left(1, \exp \left(\beta (H(\{r\}_i) - H(\{r\}_j)) \right) \right).$$

It is directly connected to another important concept: The concept of detailed balance. The MCMC simulation fulfills detailed balance if

$$P(\{r\}_i) = \frac{t(\{r\}_j | \{r\}_i)}{t(\{r\}_i | \{r\}_j)} P(\{r\}_j),$$

where $t(\{r\}_j | \{r\}_i)$ is the probability to transition from state i to state j . Choosing the acceptance rate in the Boltzmann ensemble like above ensures that this holds. The acceptance rate is probed numerically by proposing a random number between zero and one. If the proposed number is smaller than α the step is accepted, otherwise rejected.

In this project we look at the ensemble of a polymer mad up of two sub chains. The polymer is embedded in two external fields – where one chain of the polymer interacts with only one field, respectively. This description has been derived from a collection of copolymers where the same sub chains are attracting each other while opposite sub chains are repelling one another. Collectively the copolymers form a micelle, where the shorter sub chains are on the inside. Ultimately we want to find the escape rate for a single copolymer to leave the micelle using MCMC techniques.

1.1 Homopolymer simulations

1.1.1 End-to-End vector

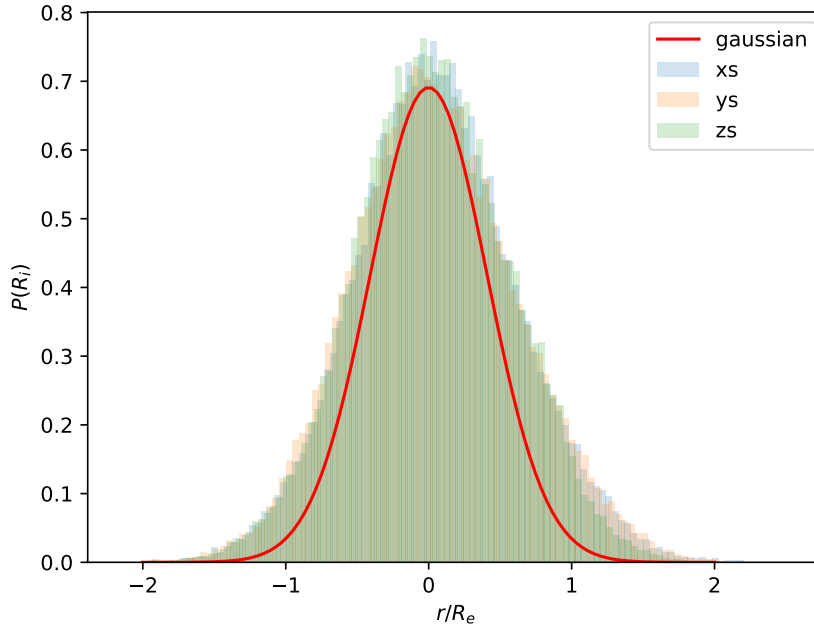


Figure 1: Distribution of coordinate components for the end-to-end vector of the free homopolymer obtained from a MCMC simulation. The simulation was executed for a total of 10^6 sweeps – discarding the first 10^5 to ensure equilibrium dynamics.

To ensure that the result of our MCMC simulation is correct we verify it by looking at the case without any external fields (the case of a homopolymer). About this system we can make exact predictions from the Rouse-Model that we can use to verify our simulation technique. The Rouse-Model makes predictions about the distribution of the end-to-end vector \mathbf{R} of the polymer

(distance between first and last bead of the polymer). Specifically, it predicts that the distribution is gaussian with $\langle \mathbf{R} \rangle = \mathbf{0}$ and $\langle \mathbf{R}^2 \rangle = R_e^2$.

In Figure 1 we can see the overlaid distributions of the components of \mathbf{R} . We can clearly see that the distribution has very gaussian-like features and the means of the individual components x/y/z ($0.0574 R_e$, $0.0446 R_e$ and $0.0263 R_e$) also correspond correctly to the predictions of the Rouse-Model. From the rules of gaussian error propagation we can see that summing the individual variances of components yields the total variance of \mathbf{R}^2 . Such, looking at the variances of the individual components ($0.3225 R_e^2$, $0.3359 R_e^2$ and $0.2915 R_e^2$) we can also verify that the prediction for $\langle \mathbf{R}^2 \rangle$ holds.

1.1.2 Mean Square Deviation and Diffusion

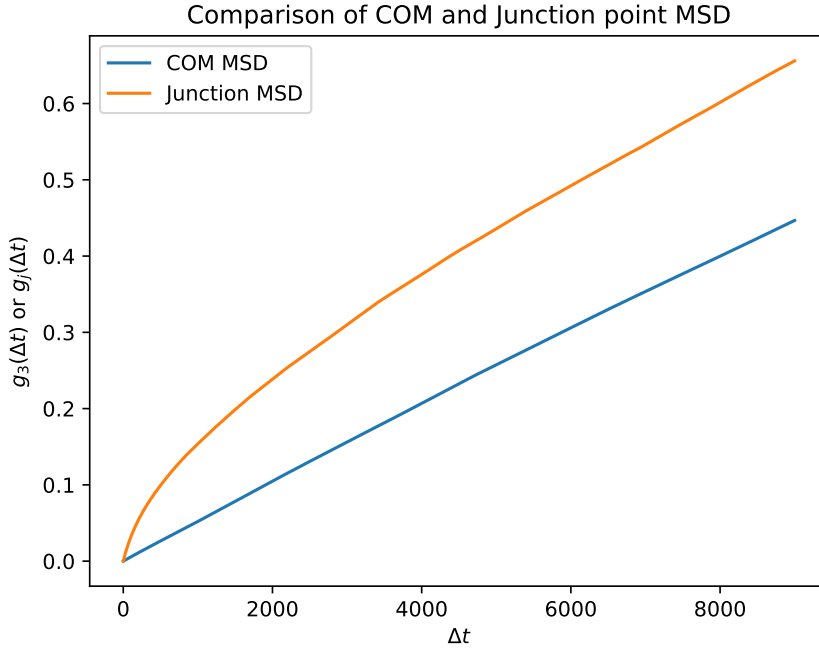


Figure 2: Comparison of the MSD of the COM and the MSD of the junction point of a homopolymer. COM/junction point MSD (g_r/g_j) is plotted against the difference in time measured in MC sweeps. Simulation data was obtained from the same simulation as in Figure 1.

Another property we can investigate in the homopolymer is its self-diffusion behavior. For this we can calculate the Mean Square Deviation (MSD) of the Center of Mass (COM) of the homopolymer. Alternatively we can also calculate the MSD of the junction point which we define as the middle between the connected beads of the subchains of a copolymer. Note we are

still dealing with the homopolymer here, but we take the junction point such that it corresponds to the same point in the homopolymer.

Both MSDs are plotted in Figure 2. We can clearly see that the MSD of both points in the chain asymptotically approach linear growth (also see the linear regressions in the attached jupyter notebook). While we can see that the MSD of the junction point is generally larger than the MSD of the COM, both asymptotically show the same rate of growth. This rate of growth is connected to the self-diffusion coefficient.

To calculate this self-diffusion coefficient we can either use

$$D = \lim_{\Delta t \rightarrow \infty} g(\Delta t)/6\Delta t,$$

or we make a linear fit to get the slope of the asymptote. Doing so we obtain $D = 8.6 \times 10^{-6} R_e^2 \Delta t^{-1}$.

1.2 Copolymer simulations

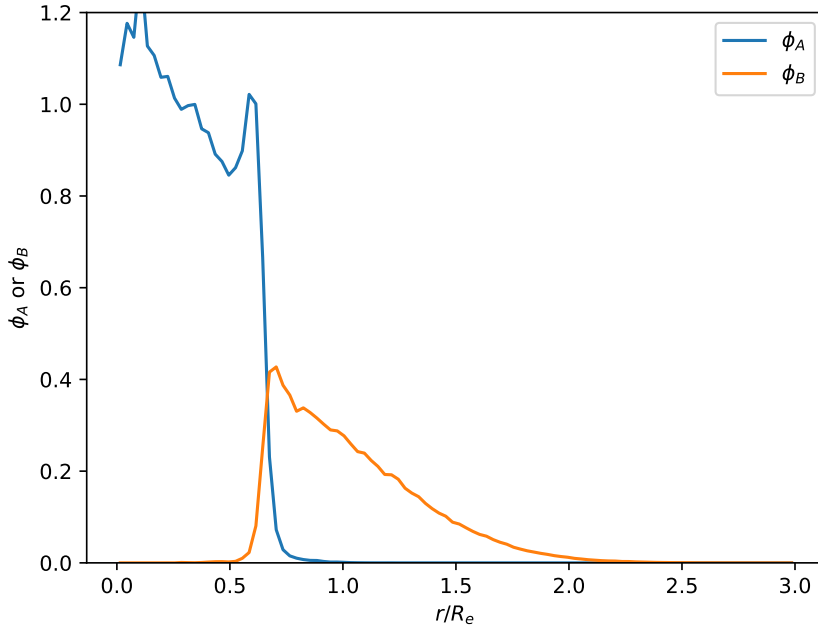


Figure 3: Partial density profile of the two sub chains of the polymer plotted against the radius. Simulations were executed over 10^6 MC sweeps while the first 10^5 were discarded. The configuration's segments were weighted as if we were only looking at a singular thread leaving the micelle.

To verify the correctness of the simulation of a copolymer (external fields switched on) we compare the radial partial density profile of the sub chains

with the results obtained from self-consistent mean-field theory given on the exercise sheet. In Figure 3 we can see the calculated result for the density profile. Note that the domain around $r/R_e = 0$ for the A sub chain is quite ragged because of the radial nature of the plot. As we approach small radii the sampled volume at each bin in the density becomes very small and we don't achieve the necessary accuracy to obtain the correct value for $\phi_A(0)$ (which is 1).

1.3 Free Energy from Umbrella potential

To calculate the Free Energy landscape of the system we first need to do some analytical preparation. We can add an umbrella potential to the Hamiltonian of our system to sample the system at a particular point in our landscape. Afterwards we can remove that umbrella potential again from the correct value of the Free Energy to obtain the correct local values for the Free Energy.

To do so we calculate

$$\begin{aligned}
\frac{dF}{dr} &= \frac{d}{dr} \lim_{k \rightarrow \infty} -\frac{1}{\beta} \ln \sum_{\{\mathbf{r}_i\}} \sqrt{\frac{k}{2\pi R_e^2}} \exp(-\beta \mathcal{H}(\{\mathbf{r}_i\} | r)) \\
&= -\frac{1}{\beta} \lim_{k \rightarrow \infty} \frac{\sum_{\{\mathbf{r}_i\}} \sqrt{\frac{k}{2\pi R_e^2}} \frac{d}{dr} \exp(-\beta \mathcal{H}(\{\mathbf{r}_i\} | r))}{\sum_{\{\mathbf{r}_i\}} \sqrt{\frac{k}{2\pi R_e^2}} \exp(-\beta \mathcal{H}(\{\mathbf{r}_i\} | r))} \\
&= -\frac{1}{\beta} \lim_{k \rightarrow \infty} \frac{\sum_{\{\mathbf{r}_i\}} -\beta \mathcal{H}(\{\mathbf{r}_i\} | r) \exp(-\beta \mathcal{H}(\{\mathbf{r}_i\} | r))}{Z_k} \\
&= \left\langle \frac{\partial \mathcal{H}(\{\mathbf{r}_i\} | r)}{\partial r} \right\rangle_k
\end{aligned}$$

But we also know

$$\frac{\partial \mathcal{H}(\{\mathbf{r}_i\} | r)}{\partial r} = \frac{\partial}{\partial r} \left(-k \frac{k_B T}{2R_e^2} (r - r_j)^2 \right) = -k \frac{k_B T}{R_e^2} (r - r_j).$$

This we can use to calculate the local free energies by numerically integrating $\frac{dF}{dr}$.

1.4 Free Energy Barrier

To calculate the free energy profile of the system we can use – as mentioned in the section above – the umbrella sampling at different locations along a suitable reaction coordinate. That suitable reaction coordinate in our case is the junction point of the copolymer. From the results of the previous section

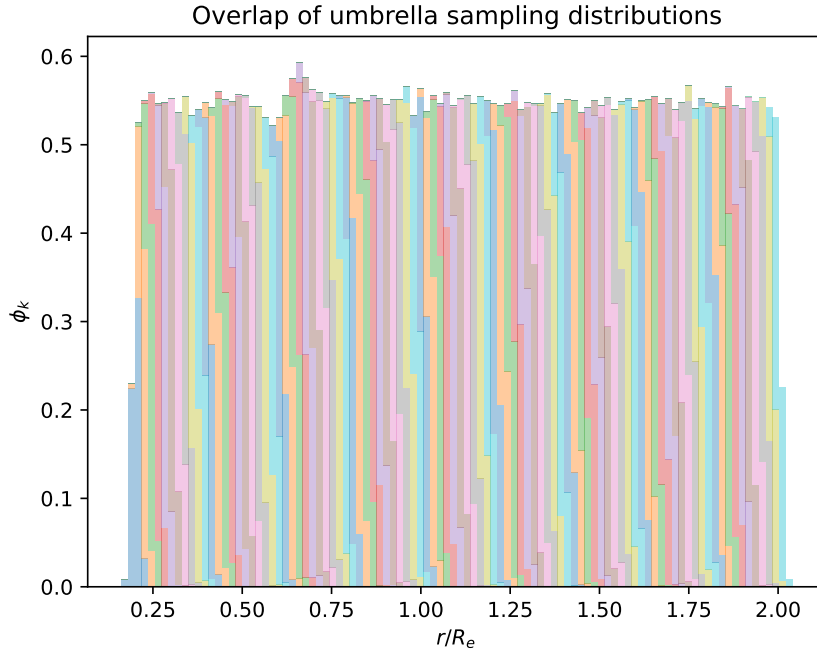


Figure 4: In this graphic we show that our grid of umbrella ensembles generate overlapping distributions in the junction point r_j . Every color corresponds to an independent umbrella ensemble run for 10^6 MC sweeps, discarding the first 10^5 . The constraint for the individual ensembles varies in steps of $2 \times 10^{-2} R_e$ from $0.2 R_e$ to $2 R_e$ and shown are 90 distributions in total.

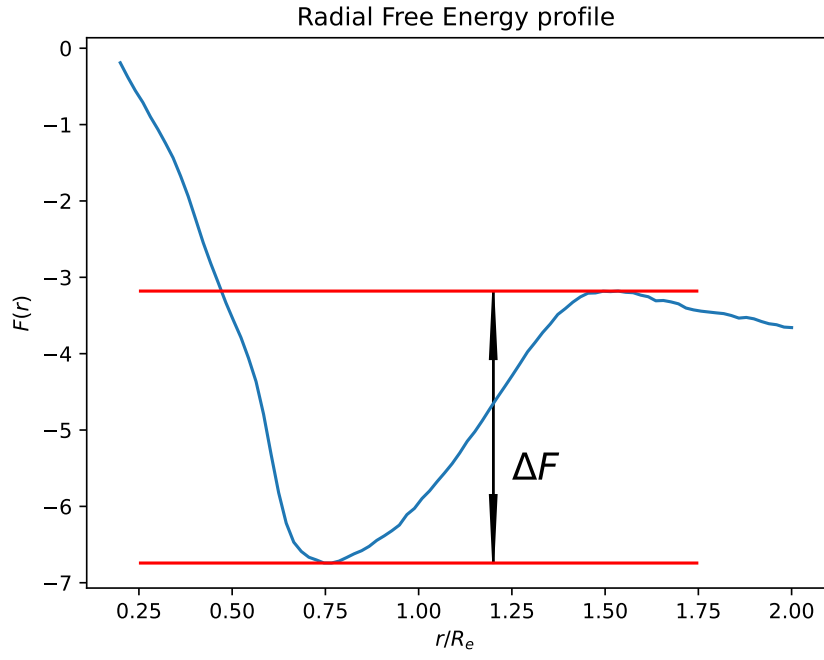


Figure 5: Free Energy profile calculated from the umbrella sampling plotted against the junction point of the copolymer. The bottom of the basin and the top of the barrier are marked by horizontal red lines. ΔF as the difference between these lines is $3.56 k_B T$.

we know that we can calculate the Free energy via the values of the junction point in the umbrella ensemble.

Firstly we need to show that the grid we used for the umbrella sampling is sufficiently small, s. t. the local free energy does not vary too much from site to site on the grid. We can achieve this by checking that the umbrella ensembles generate overlapping distributions in the reaction coordinate. In Figure 4 we can clearly see, that this is the case for our experiment.

Now we can use the umbrella ensembles to calculate the local Free Energy along the reaction coordinate using the formula derived earlier. In Figure 5 we can see the results of these calculations. In the figure the height of the barrier is already marked. It is $\Delta F = 3.56 k_B T$.

2 Markovian Dynamics of the Junction Point r_j ?

If we describe the configurations of our copolymers by their complete set of segment positions we get true continuous time markovian dynamics. This is due to the fact that we don't have any "hidden" variables and as such the future time evolution of the system depends only on the configuration of the current state. Therefore – as long as we ensure detailed balance – we get the characteristic decay of the current configuration over some relaxation time τ_r that is connected to the largest eigenvalue of the transfer matrix.

As we have seen, the junction point can be used as a reaction coordinate that characterizes the escape of the copolymer from the micelle. We can therefore ask ourselves if it would be sufficient to only simulate the reaction coordinate with a detailed balance algorithm to obtain correct dynamics. This would be a severe saving in computational resources and would allow us to study the system much more thoroughly. Unfortunately this is not the case.

If we considered the system's configuration to consist only of the junction point, we would discard the information of the state that corresponds to the sub chains. The problem is easy to spot if one considers that the value of the junction point is symmetric under exchange of the sub chains. Obviously the exchanged sub chains have to lead to different dynamics in the external field. Therefore the future evolution of the system would not only be conditioned on the current configuration and the dynamics are not markovian.

3 Forward Flux Sampling - Transition Rates

To calculate the transition rate of a single copolymer escaping the micelle we can use Forward Flux sampling. Firstly we need to find a good way to define interfaces along the rise of the barrier. We choose to use barriers in distances of around $0.4 k_B T$. Then we fit a linear function to the rise and choose barriers in equal distances along the reaction coordinate such that the largest distance in the Free Energy is $0.4 k_B T$. In Figure 6 the interfaces are embedded into the Free Energy landscape.

The transition rate can thus be calculated as the product of the forward transition rates from one interface to the next. The calculated value is $\eta = 4(1) \times 10^{-6} \Delta t^{-1}$.

4 Kramers Rate

Alternatively to the Forward Flux sampling process we can also estimate the transition rate via the Kramers rate. The formula for the Kramers rate given

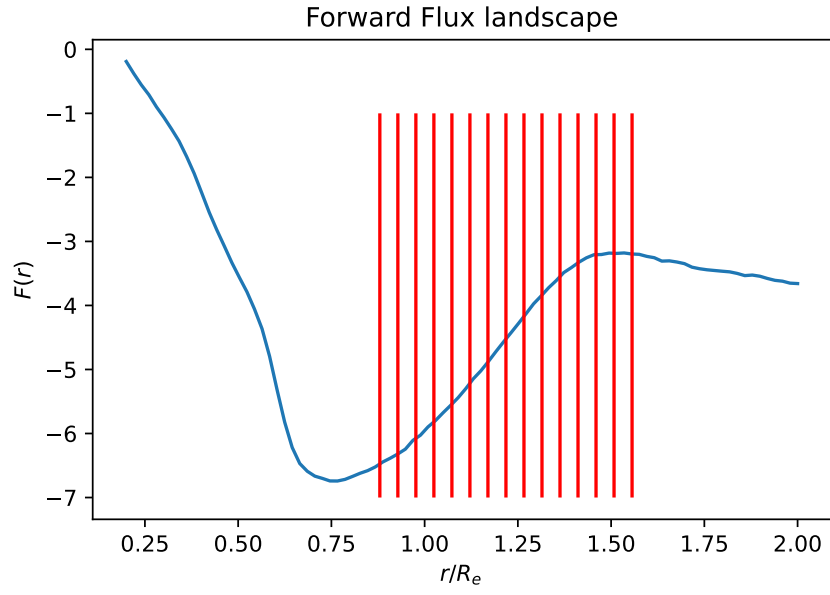


Figure 6: Free Energy profile from Figure 5 but with the chosen Forward Flux interfaces shown as red vertical lines.

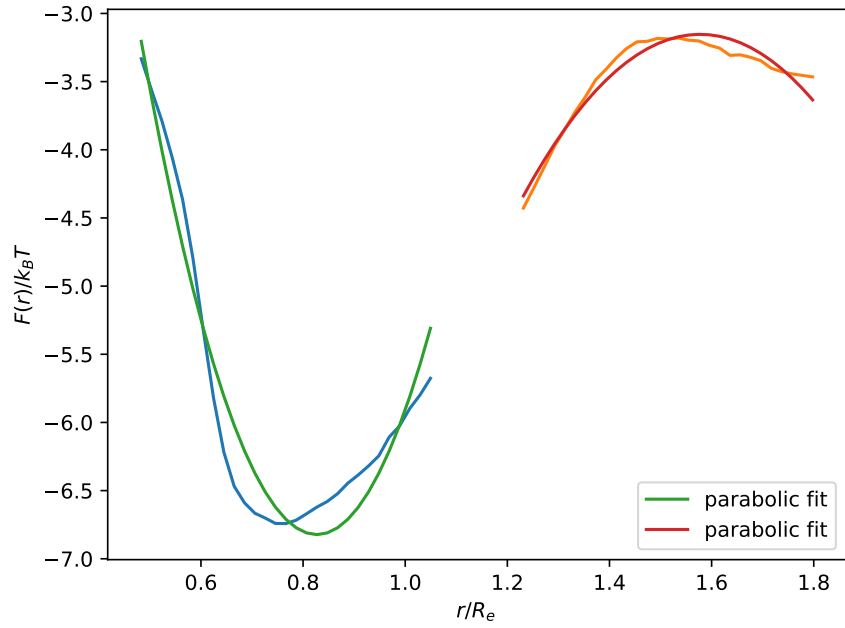


Figure 7: Again plotted the same Free Energy Landscape used like in Figure 5 but only the parts that were used to fit quadratic functions to the extrema are filled in.

is

$$\eta_k = \frac{D}{\pi k_B T} \sqrt{F''_{\max} F''_{\min}} \exp\left(-\frac{\Delta F}{k_B T}\right).$$

Here F''_{\max} and F''_{\min} are the second derivative of the Free Energy at the maximum or minimum respectively. To calculate accurate values for these we can fit a parabola to an selected environment around the minimum. From these calculations and using our results for the diffusion constant D and Δf we obtain $\eta_k = 1.35 \times 10^{-6} \Delta t^{-1}$.