11th i-CoMSE Workshop: Mesoscale Particle-Based Modeling

Mississippi State University
July 21–25, 2025

Session 8: Periodic boundary conditions II (dynamics)

Dynamic Quantities

Time correlation functions:

$X(t)$ = fluctuating variable measured at time t

$\langle X(0)X(t)\rangle$ = autocorrelation function, tells us how correlated $X(t)$ is with $X(0)$

Normalize: $C(t) = \frac{\langle X(0)X(t)\rangle}{\langle X(0)^2\rangle}$ - decays from 1

Decay time ~ τ ("independent sample" can be taken after ~τ)

To improve averaging, multiple "time origins" or windows can be used:
$\langle X(t_0)X(t+t_0)\rangle$

How to compute:
1. FFT (convolution)
2. Manual/brute force

Dynamic Quantities

Fluctuation Dissipation theorem (from linear response theory):

What is the systems' response to a small perturbation?

One can show that:

$$\gamma = \int_0^{\infty} \langle \dot{A}(0)\dot{A}(t)\rangle$$

Green-Kubo formula:
Integral of time (auto-) correlation function

transport coefficient

rate of change of dynamic variable A

Also:

$$\langle [A(t) - A(0)]^2 \rangle = \langle \Delta A(t)^2 \rangle = 2\gamma t \quad \text{for} \quad t \to \infty$$

Fluctuation-Dissipation theorem (Einstein relation)

So:

$$\frac{1}{2} \lim_{t\to\infty} \frac{d}{dt} \langle \Delta A(t)^2 \rangle = \gamma$$

For diffusion: $A = x \quad \dot{A} = v_x.\ \ \gamma = D_x \to \ \ D_x = \frac{1}{2} \lim_{t\to\infty} \frac{d}{dt} \langle \Delta x(t)^2 \rangle$

$$D = \frac{1}{6} \lim_{t\to\infty} \frac{d}{dt} \langle \Delta \vec{r}(t)^2 \rangle$$

*isotropic system

Diffusion

How much is something moving over time?
Measure mean-squared displacement!

$$D = \frac{1}{6} \lim_{t\to\infty} \frac{d}{dt} \langle \Delta\vec{r}(t)^2 \rangle$$

Mean-squared displacement!

Improve measurement by using window approach
Downside: all snapshots must be measured at regular time intervals, smaller times will have better statistics.

$$MSD(t) = \frac{1}{N} \sum_{i=1}^{N} |\vec{r}_i(t) - \vec{r}_i(0)|^2$$

$$MSD(m) = \frac{1}{N_{particles}} \sum_{i=1}^{N_{particles}} \frac{1}{N-m} \sum_{k=0}^{N-m-1} \left(\vec{r}_i(k+m) - \vec{r}_i(k)\right)^2$$

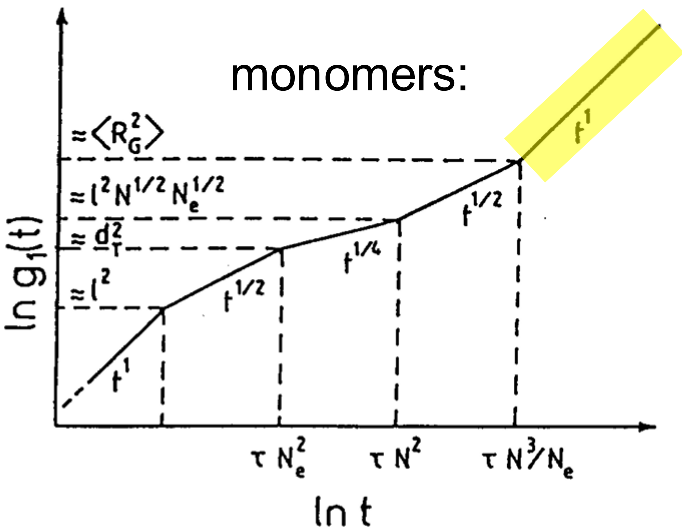
total number of frames

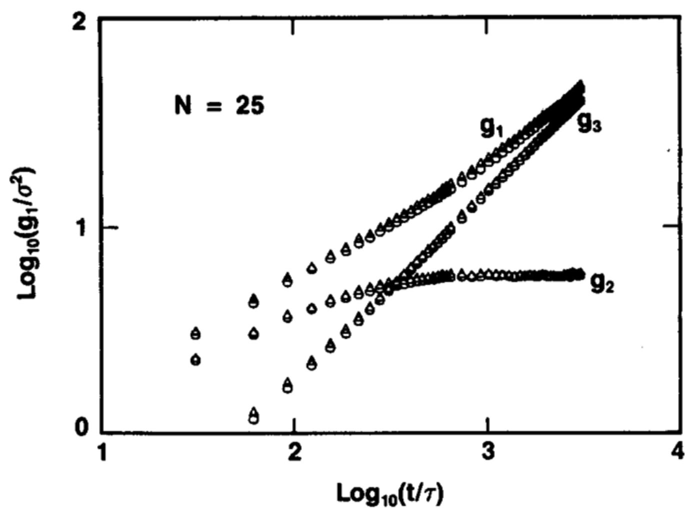
Position of particle *i* in frame *k*

Freud documentation: https://freud.readthedocs.io/en/latest/modules/msd.html

Diffusion of Polymers

- We can look at the monomer g_1, center-of-mass g_3, center-of-mass – monomers g_2, etc. displacements:





$$g_1(t)\sim\begin{cases} t^1, & t<\tau_0 \\ t^{1/2}, & t<\tau_e\sim N_e^2 \\ t^{1/4}, & t<\tau_N\sim N^2 \\ t^{1/2}, & t<\tau_d\sim N^3/N_e \\ t^1, & t>\tau_d \end{cases}$$

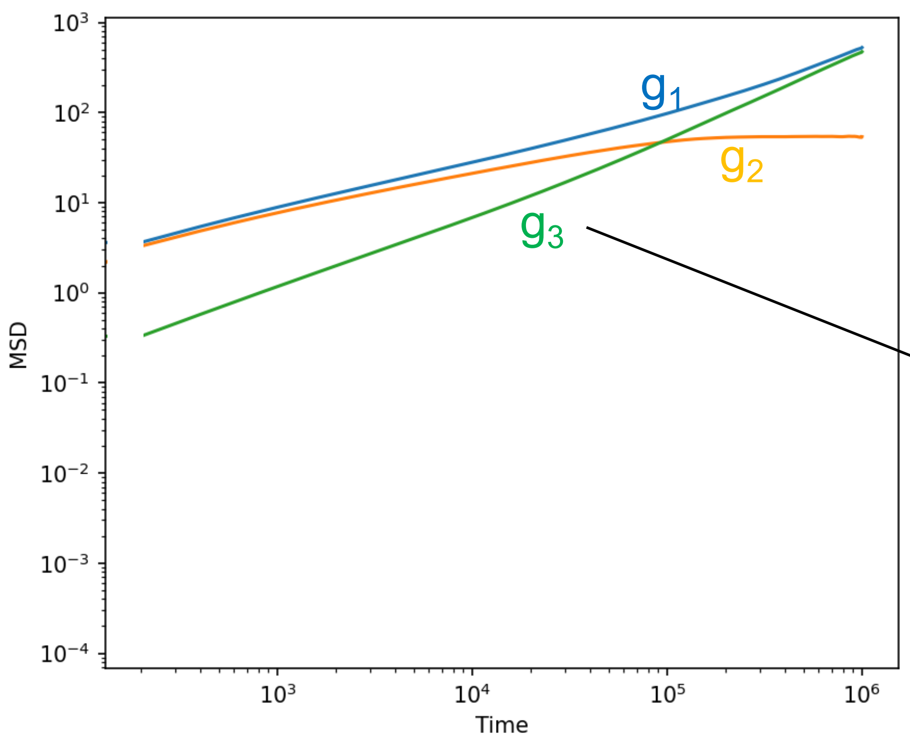
$$g_2(t)\sim\begin{cases} t^1, & t<\tau_0 \\ t^{1/2}, & t<\tau_e \\ t^{1/4}, & t<\tau_N \\ t^0, & t>\tau_N \end{cases}$$

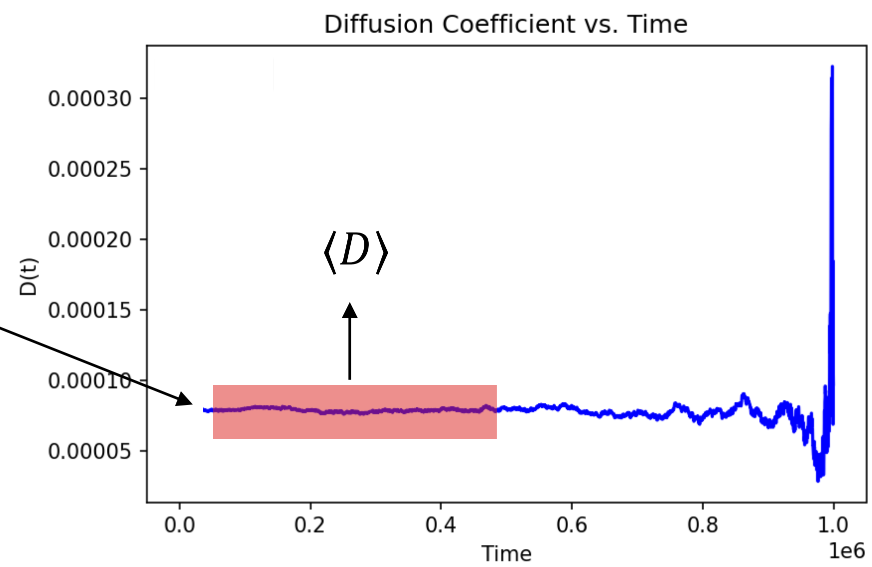
$$g_3(t)\sim\begin{cases} t^1, & t<\tau_e \\ t^{1/2}, & t<\tau_N \\ t^1, & t>\tau_N. \end{cases}$$

Kremer, Grest, JCP, 1990

Diffusion of Polymers

Example:





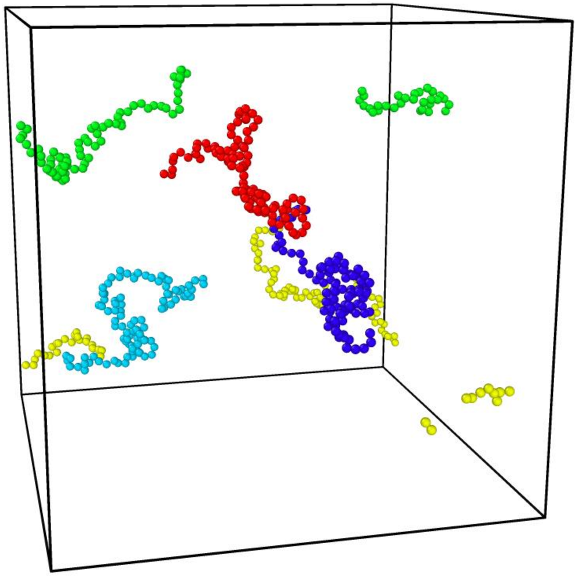
$$D = \frac{1}{6}\lim_{t\to\infty}\frac{d}{dt}MSD$$

Relaxation of Polymers

- There are MANY relaxation times in polymers:
  - Monomer relaxation
  - Segmental relaxation
  - Whole chain relaxation:

$$\tau_R \propto R_g^2/D$$

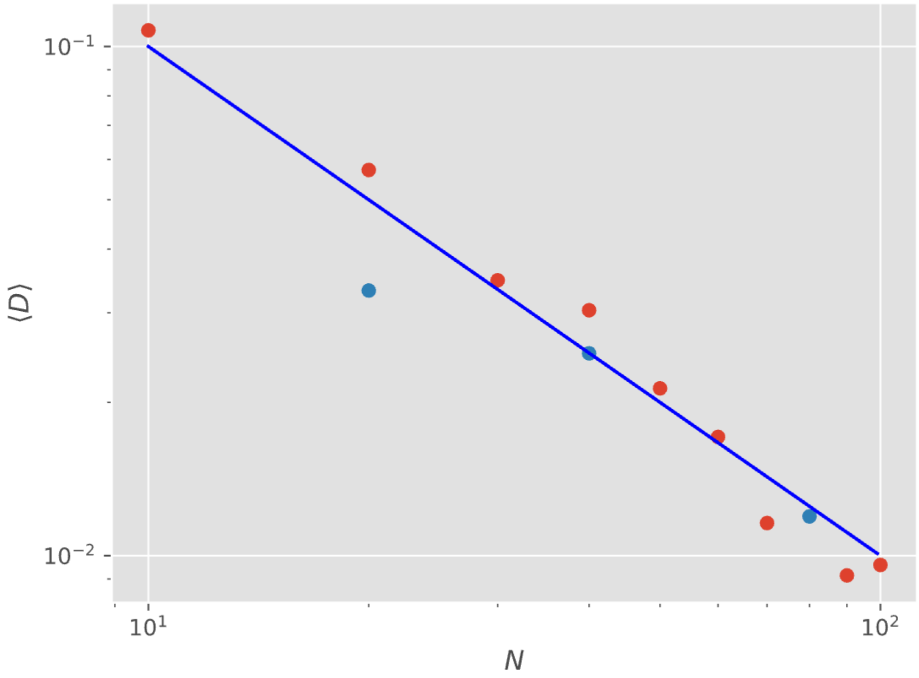
*polymer has relaxed if it has moved its own size



Exercise

Objectives:

- Run simple polymer simulations with varying chain length *N*
- Compute the MSD of the polymers
- Compute the diffusion coefficient as function of *N*
- Confirm that the results match expected scaling behavior



Common Pitfalls

Common pitfalls:

- Initializing the system with polymer crossing PBCs and not accounting for that in the initial images
- Not writing images for unwrapping
- Not excluding initialization/equilibration period
- Not unwrapping the positions (MSD will plateau where it shouldn't)
- Run simulations that are too short
- A lot of things can go wrong, and a log-log plot still might look "OK"