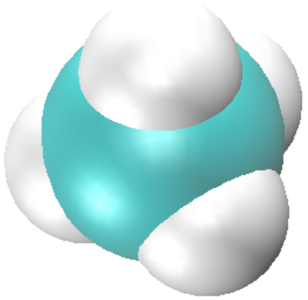
Project 1

MD simulations and calculations of kinetic properties

Assignments

- Compute the Einstein's diffusion constant
- Compute the velocity autocorrelation function
- Validate the Einstein relation of Langevin dynamics (the fluctuation-dissipation theorem)



- MD trajectories are available at box.com

  Random walk of a methane molecule in water: https://uwmadison.box.com/s/wkijstaz6h3ehtkmk2pbwrh7xw7to2t7

Notes

- Einstein's diffusion coefficient:

$$\overline{\Delta\mathbf{x}(t)^2} = 2Dt$$

$$\overline{\Delta\mathbf{x}(t)^2} \equiv \overline{\;\mathbf{x}(t) - \mathbf{x}(0)\;\;^2}$$

$$= \sum_{t_0} \;\mathbf{x}(t_0 + t) - \mathbf{x}(t_0)\;\;^2 / \sum_{t_0} 1$$

- The velocity autocorrelation function:

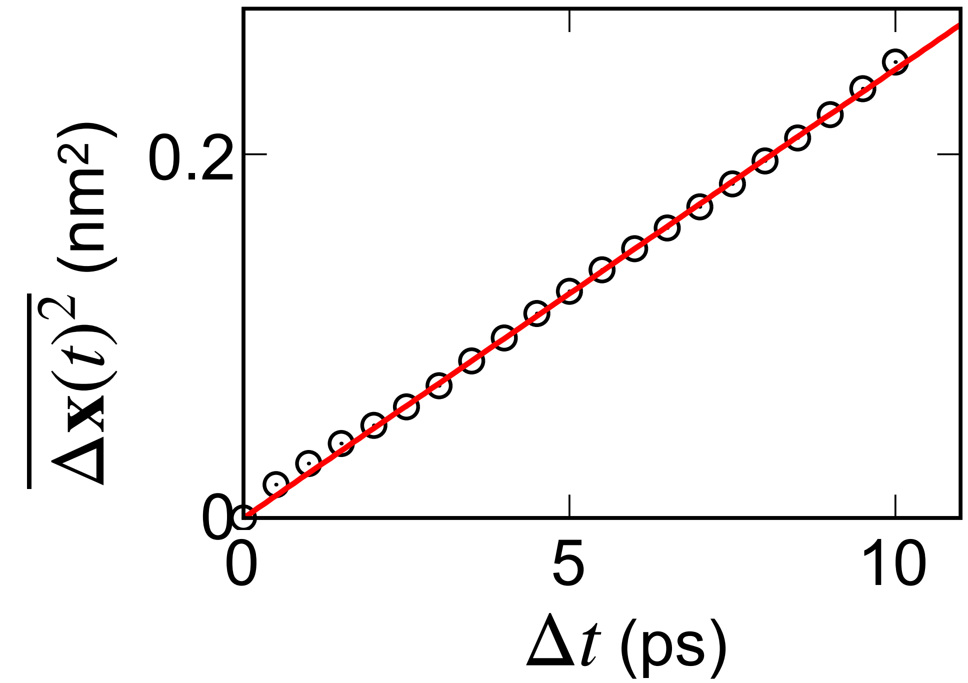
$$C_{vv}(t) = \overline{\mathbf{v}(t)\cdot\mathbf{v}(0)} = \sum_{t_0} \mathbf{v}(t_0 + t)\cdot\mathbf{v}(t_0) / \sum_{t_0} 1$$

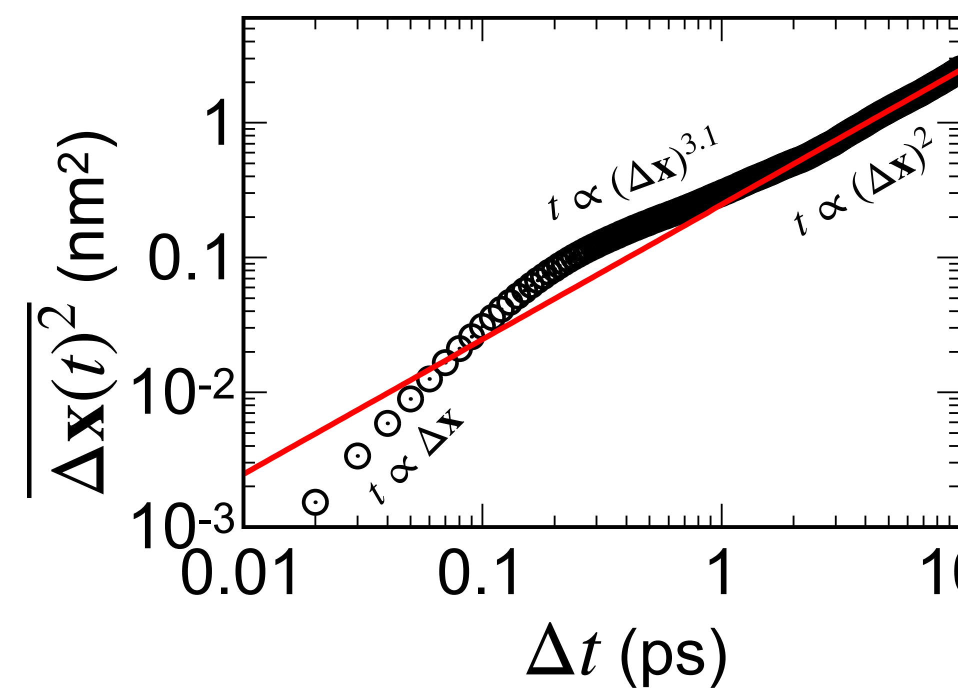
- The equal-partition theorem:

$$\overline{\frac{1}{2}m\mathbf{v}\cdot\mathbf{v}} = \frac{3}{2}kT$$

$$C_{vv}(0) = \frac{3kT}{2m}$$

$$\frac{0.5 \times 16\mathrm{g/mol} \times 0.4608\mathrm{nm^2/ps^2}}{8.3145\mathrm{J/mol/K} \times 295\mathrm{K}} = 1.5$$





Notes

- The Langevin's equation and velocity autocorrelation function

$$m\frac{d}{dt}\mathbf{v}(t) = -m\gamma\mathbf{v}(t) + \mathbf{F}(t) \qquad m\frac{d}{dt}\mathbf{v}(t) = -\overrightarrow{\nabla}U(x) - \gamma\mathbf{v}(t) + \mathbf{F}(t)$$

$$\mathbf{v}(t) = \int_{-\infty}^{t}\frac{F(t')}{m}e^{-\gamma(t-t')}dt'$$

$$\overline{\mathbf{v}(t)\cdot\mathbf{v}(0)} = \int_{-\infty}^{t}dt_1\int_{-\infty}^{0}dt_2\frac{\overline{\mathbf{F}(t_1)\cdot\mathbf{F}(t_2)}}{m^2}e^{-\gamma(t-t_1-t_2)}$$

$$= \int_{-\infty}^{t}dt_1\int_{-\infty}^{0}dt_2\frac{a_F\delta(t_1-t_2)}{m^2}e^{-\gamma(t-t_1-t_2)}$$

$$\overline{\mathbf{F}(t_1)\cdot\mathbf{F}(t_2)} = a_F\delta(t_1-t_2)$$

$$a_F = \overline{\mathbf{F}(t)^2}$$

$$C_{vv}(t) = \overline{\mathbf{v}(t)\cdot\mathbf{v}(0)} = \frac{a_F}{2m^2\gamma}e^{-\gamma t} = C_{vv}(0)e^{-\gamma t}$$

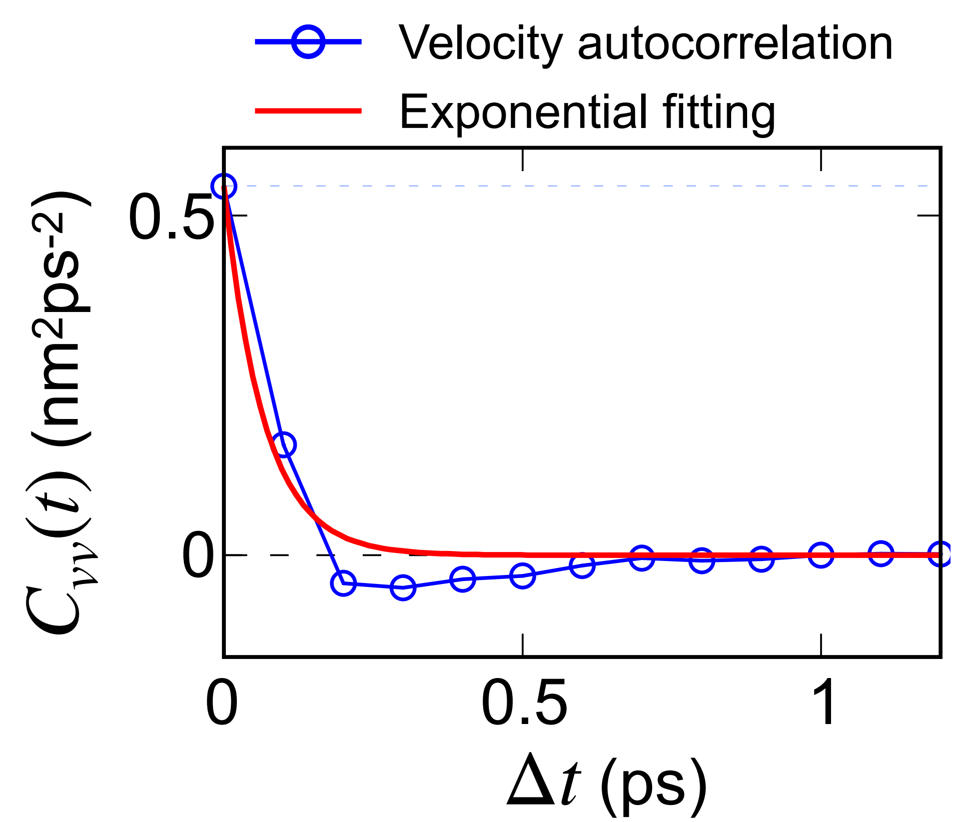
Notes

- The dissipation coefficient γ:

$$m\frac{d}{dt}\mathbf{v}(t) = -m\gamma\mathbf{v}(t) + \mathbf{F}(t)$$

$$C_{vv}(t) = \overline{\mathbf{v}(t)\cdot\mathbf{v}(0)} = C_{vv}(0)e^{-\gamma t}$$

Compute γ by exponential fitting.



- The Einstein relation of Langevin dynamics

  (aka. the fluctuation-dissipation)

$$D = \frac{kT}{m\gamma} \qquad \overline{\Delta\mathbf{x}^2} = 2Dt$$

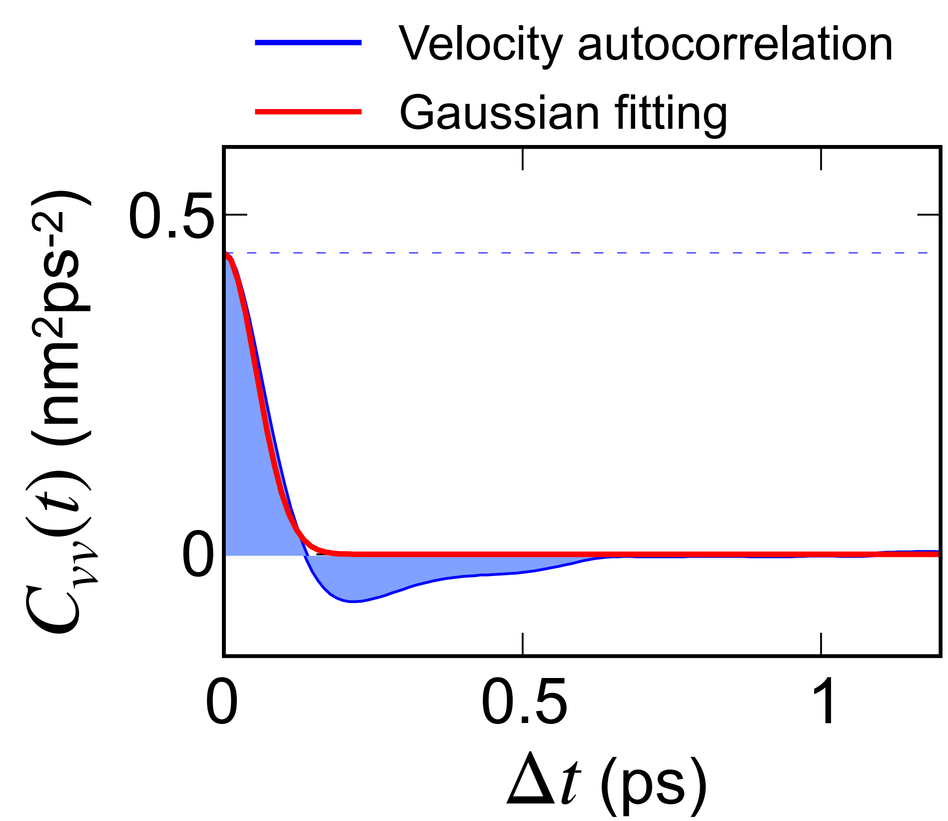
Notes

- Compute γ with Boon-Yip's method:

$$m\frac{d}{dt}\mathbf{v}(t) = -m\gamma\mathbf{v}(t) + \mathbf{F}(t)$$

$$C_{vv}(t) = \overline{\mathbf{v}(t)\cdot\mathbf{v}(0)} = C_{vv}(0)e^{-\gamma t}$$

$$\gamma = \int_0^\infty e^{-\gamma t'}dt' = C_{vv}(0)^{-1}\int_0^\infty C_{vv}(t)dt$$



- The Einstein relation of Langevin dynamics
  (aka. the fluctuation-dissipation)

$$D = \frac{kT}{m\gamma} \qquad \overline{\Delta\mathbf{x}^2} = 2Dt$$

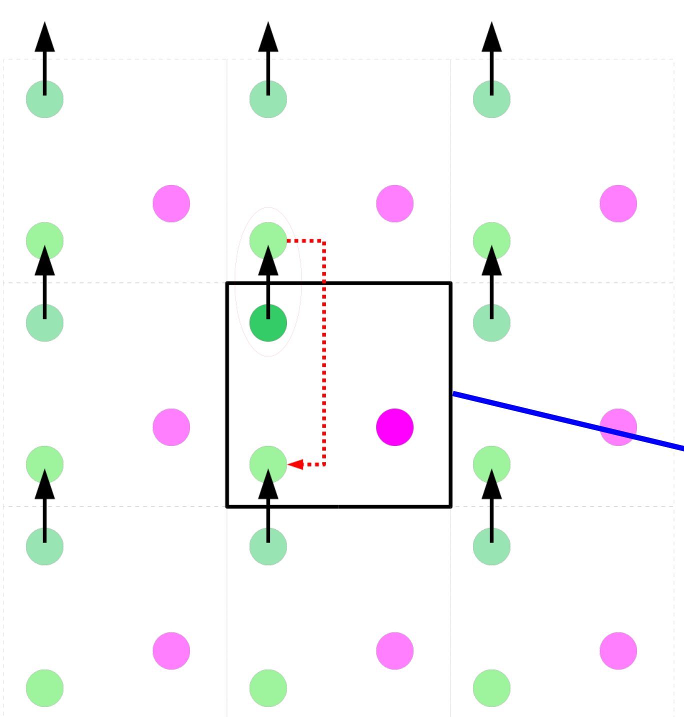
Notes about trajectories

- Time unit: picoseconds; length unit: nanometer; velocity unit: $nm \cdot ps^{-1}$
- File format of GRO:

Time stamp (unit: ps)

Velocities (vx, vy, vz)
unit: nm/ps

```
methane in water t=   0.00000 step= 0
    5
    1MOL     C1    1  1.084   0.171   1.599 -0.6902 -0.2804  0.1925
    1MOL     H1    2  0.996   0.235   1.591 -0.3420  0.3593  1.2614
    1MOL     H2    3  1.044   0.079   1.641  0.5320 -0.3079  1.3658
    1MOL     H3    4  1.127   0.138   1.504 -1.2076 -0.2422 -0.0610
    1MOL     H4    5  1.153   0.222   1.667  0.6313 -0.5384 -0.9108
   2.99601   2.99601   2.99601
methane in water t=   0.01000 step= 5
    5
    1MOL     C1    1  1.076   0.167   1.602 -0.5842 -0.3240  0.3454
    1MOL     H1    2  0.996   0.240   1.589 -0.1792  0.1755  0.5872
    1MOL     H2    3  1.052   0.079   1.662 -0.0691 -0.0585  0.9648
    1MOL     H3    4  1.114   0.151   1.501 -1.9272  0.2084 -0.2576
    1MOL     H4    5  1.163   0.211   1.652  0.4377 -0.2529 -1.4121
   2.99601   2.99601   2.99601
...
```



Dimensions of periodic box
unit: nm

Coordinates (x, y, z)
unit: nm

Notes about trajectories

- MD ensembles:
  - NPT: $T = 298K$, $p = 1$ bar, $V_{box} = 26.87 \pm 0.25\ nm^3$
  - NVT: $T = 298K$, $V_{box} = 26.8924\ nm^3$
  - NVE: $V_{box} = 26.8924\ nm^3$
- Frames:
  - dt = 10fs, 20001 frames (in dt10fs/ folder)
  - dt = 100fs, 2001 frames (in dt100fs/ folder)