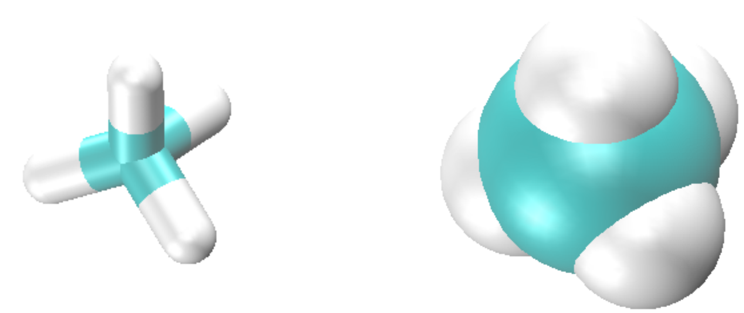
Project 1

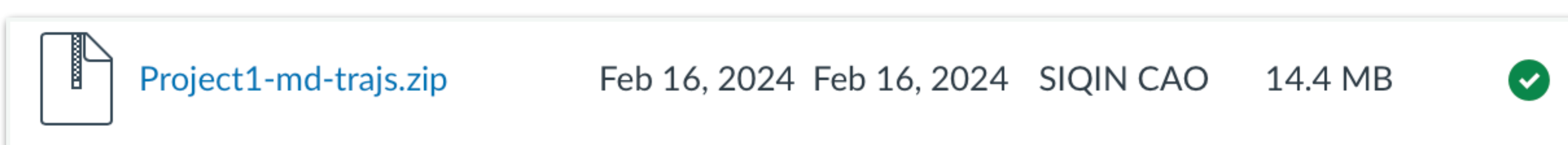
MD simulations and calculations of kinetic properties

Assignments

- Compute the Einstein's diffusion constant
- Compute the velocity autocorrelation function
- Validate the Einstein relation of Langevin dynamics (D and γ) or the fluctuation-dissipation theorem (C_0)



- MD trajectories are available at the canvas page



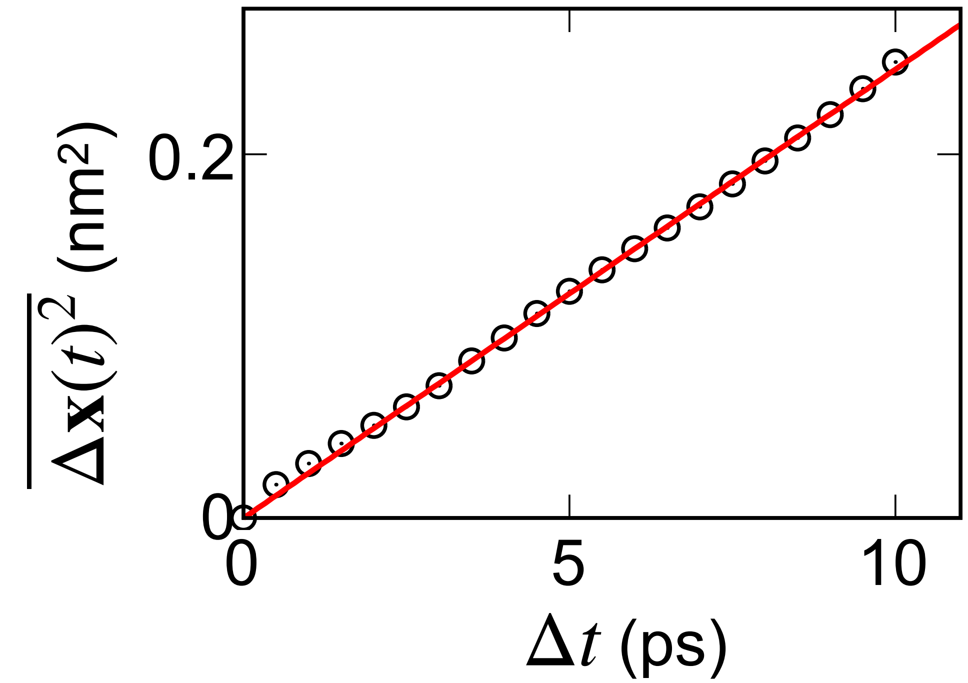
Notes

- Einstein's diffusion coefficient:

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

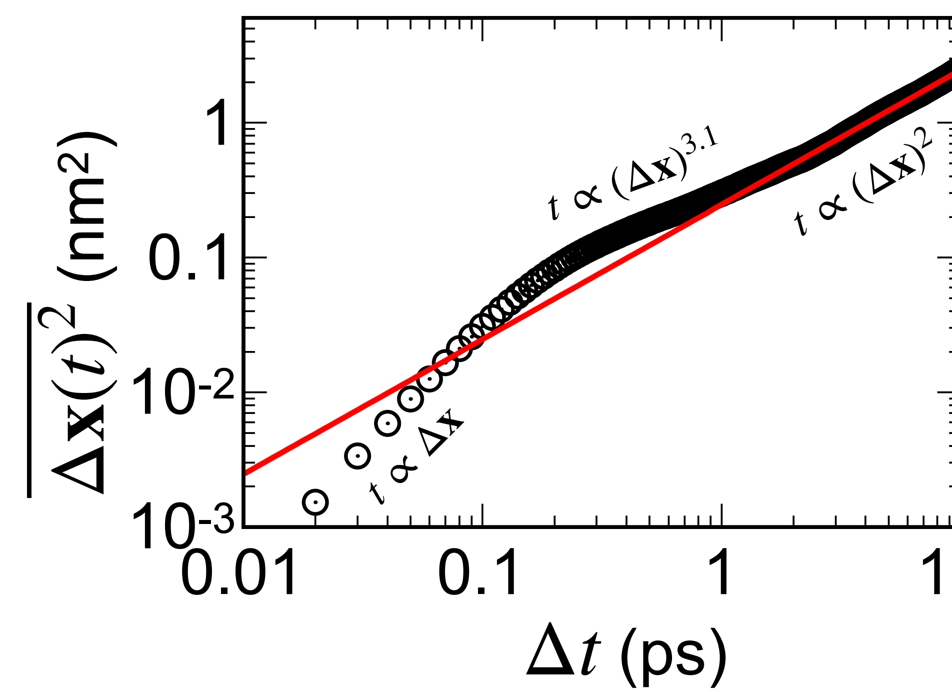
$$\overline{\Delta \mathbf{x}(t)^2} \equiv \overline{\left[\mathbf{x}(t) - \mathbf{x}(0)\right]^2}$$

$$= \sum_{t_0} \left[\mathbf{x}(t_0 + t) - \mathbf{x}(t_0)\right]^2 / \sum_{t_0} 1$$



- 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:

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

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

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

Notes

- The Langevin's equation and velocity autocorrelation function

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

$$\mathbf{v}(t) = \mathbf{v}(t_0)e^{-\gamma(t-t_0)} + \int_{t_0}^{t}\frac{\mathbf{F}(t')}{m}e^{-\gamma(t-t')}dt' = \int_{-\infty}^{t}\frac{\mathbf{F}(t')}{m}e^{-\gamma(t-t')}dt'$$

$$\overline{\mathbf{v}(t)\cdot\mathbf{v}(0)} = \overline{\ \mathbf{v}(0)\ }^{2}e^{-\gamma t} + \int_{0}^{t}\frac{\overline{\mathbf{v}(0)\cdot\mathbf{F}(t')}}{m}e^{-\gamma(t-t')}dt'$$

$$= \overline{\ \mathbf{v}(0)\ }^{2}e^{-\gamma t} + 0$$

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

** the velocity-force correlation

$$\overline{\mathbf{v}(t)\mathbf{F}(s<t)} = \frac{C_0}{m}e^{-\gamma(t-s)}$$

$$-\infty < s < t$$

$$\overline{\mathbf{v}(t)\cdot\mathbf{F}(s<t)} = \int_{-\infty}^{t}\frac{\overline{\mathbf{F}(t')\cdot\mathbf{F}(s)}}{m}e^{-\gamma(t-t')}dt' = \int_{-\infty}^{t}\frac{C_0\delta(t'-s)}{m}e^{-\gamma(t-t')}dt' = \frac{C_0}{m}e^{-\gamma(t-s)}$$

$$\overline{\mathbf{v}(t)\mathbf{F}(s>t)} = 0$$

$$-\infty < t < s \Rightarrow \delta(t-s) = 0$$

Proof:

$$\overline{\mathbf{v}(t)\cdot\mathbf{F}(s>t)} = \int_{-\infty}^{t}\frac{\overline{\mathbf{F}(t')\cdot\mathbf{F}(s)}}{m}e^{-\gamma(t-t')}dt' = \int_{-\infty}^{t}\frac{C_0\delta(t'-s)}{m}e^{-\gamma(t-t')}dt' = 0$$

Alternative proof:

$$\overline{\mathbf{v}(t_1)\cdot\mathbf{F}(t<s<t_1)} = \overline{\mathbf{v}(t)\cdot\mathbf{F}(s)}e^{-\gamma(t_1-t)} + \int_{t}^{t_1}\frac{\overline{\mathbf{F}(t')\cdot\mathbf{F}(s)}}{m}e^{-\gamma(t_1-t')}dt'$$

$$\cancel{\frac{C_0}{m}e^{-\gamma(t-s)}} \qquad \overline{\mathbf{v}(t)\cdot\mathbf{F}(s)}e^{-\gamma(t_1-t)} + \cancel{\frac{C_0}{m}e^{-\gamma(t-s)}} \qquad \Rightarrow \qquad 0 = \overline{\mathbf{v}(t)\cdot\mathbf{F}(s)}e^{-\gamma(t_1-t)}$$

- Origin of the above weird conclusion: the Langevin equation breaks the CPT symmetry CPT: the most fundamental symmetry in physics that never breaks

$$m\frac{d}{dt}\mathbf{v}(t) = -m\gamma\mathbf{v}(t) + \mathbf{F}(t) \qquad -m\frac{d}{dt'}\mathbf{v}'(t) = -m\gamma\mathbf{v}'(t) - \mathbf{F}'(t)$$

Space-parity (P): $x' = -x$; Time-reverse (T): $t' = -t$; Thus: $v' = v$, $F' = -\nabla' U' = -\nabla' U = -F$

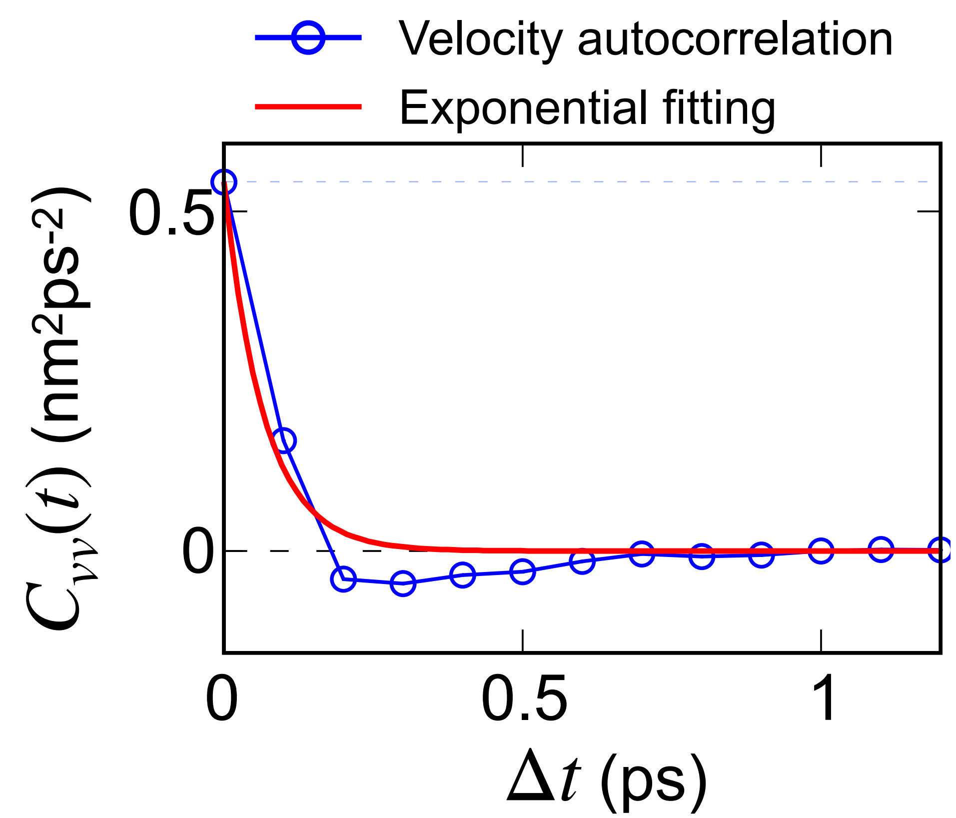
Notes

- The dissipation coefficient γ:

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

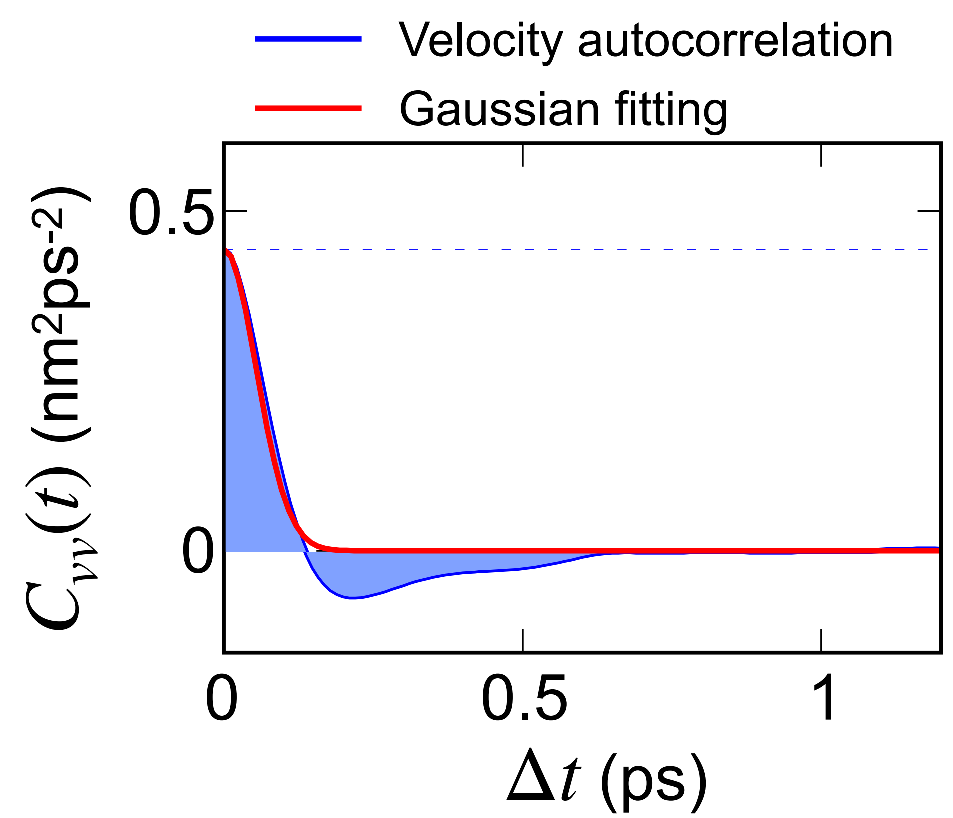
$$C_{vv}(t) = \overline{\mathbf{v}(t)\cdot\mathbf{v}(0)} = C_{vv}(0)e^{-\gamma t}$$

Compute γ by exponential fitting.



- Boon-Yip's integral:

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



Notes

- The Langevin's equation and velocity autocorrelation function

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

$$\mathbf{v}(t) = \mathbf{v}(t_0)e^{-\gamma(t-t_0)} + \int_{t_0}^{t}\frac{\mathbf{F}(t')}{m}e^{-\gamma(t-t')}dt' = \int_{-\infty}^{t}\frac{\mathbf{F}(t')}{m}e^{-\gamma(t-t')}dt'$$

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

$$= \int_{-\infty}^{t}dt_1\int_{-\infty}^{0}dt_2\frac{C_0\delta(t_1-t_2)}{m^2}e^{-\gamma(t-t_1-t_2)} \qquad \boxed{\overline{\mathbf{F}(t_1)\cdot\mathbf{F}(t_2)} = C_0\delta(t_1-t_2)}$$

$$C_{vv}(t) = \overline{\mathbf{v}(t)\cdot\mathbf{v}(0)} = \boxed{\frac{C_0}{2m^2\gamma}e^{-\gamma t} = C_{vv}(0)e^{-\gamma t}}$$

Notes

- Validate the fluctuation-dissipation theorem

$$\boxed{\frac{C_0}{2m^2\gamma} = C_{vv}(0) = \frac{3kT}{m}}$$

$$C_{vv}(t) = \frac{C_0}{2m^2\gamma}e^{-\gamma t} = C_{vv}(0)e^{-\gamma t}$$

$$C_{vv}(0) = \overline{\mathbf{v}(t)\cdot\mathbf{v}(t)} = \frac{3kT}{m}$$

How to compute C_0 from Einstein's diffusion coefficient:

$$\overline{\Delta\mathbf{x}(t)^2} = \iint_0^t dt_1 dt_2 \overline{\mathbf{v}(t_1)\cdot\mathbf{v}(t_2)}$$

$$\Delta\mathbf{x}(t) = \int_0^t dt_1 \mathbf{v}(t_1)$$

$$= \iint_0^t dt_1 dt_2 \frac{C_0}{2m^2\gamma}e^{-\gamma |t_1 - t_2|} = \frac{C_0}{m^2\gamma^2}\left(t - \frac{1-e^{-\gamma t}}{\gamma}\right)$$

$$\overline{\Delta\mathbf{x}(t)^2} \approx \frac{C_0}{m^2\gamma^2}t = 2Dt$$

$$\boxed{C_0 = 2Dm^2\gamma^2}$$

Thus according to the fluctuation-dissipation theorem:

$D = kT/m\gamma$ (Einstein's relation)

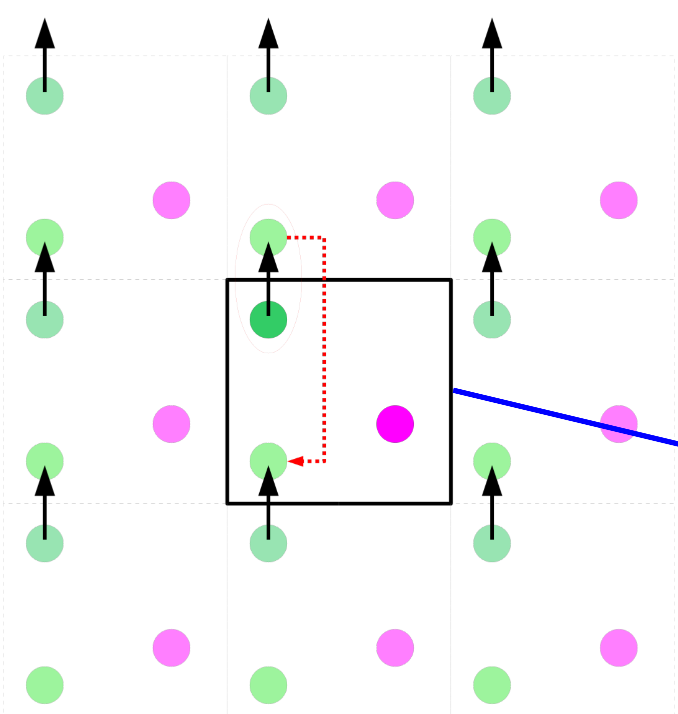
Notes about trajectories

- Time unit: picoseconds; length unit: nanometer; velocity unit: nm•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±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)
- Note:
  - Please re-compute the temperature in the NVE ensemble. It is not 298K.