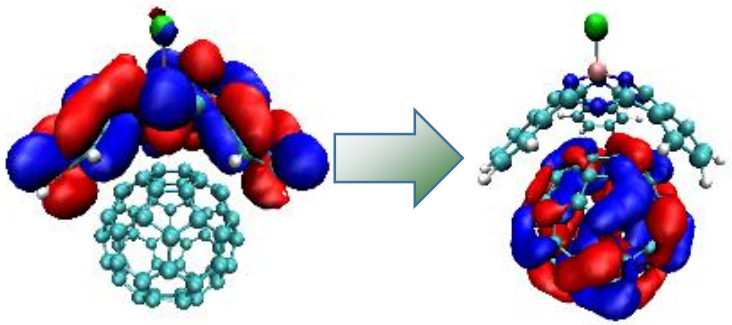
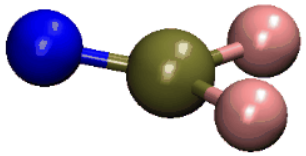
Research in the Akimov group:
Quantum Dynamics in Materials



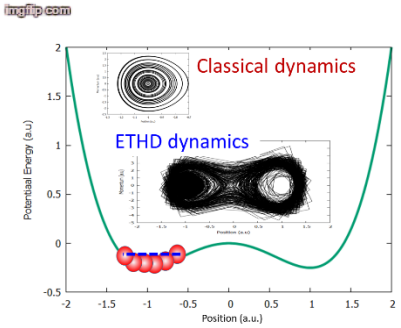


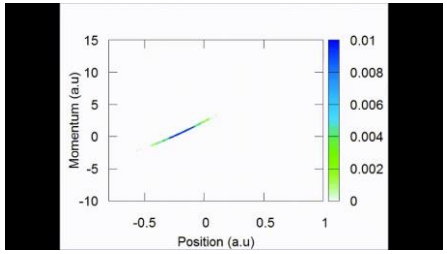
Studies of solar energy materials

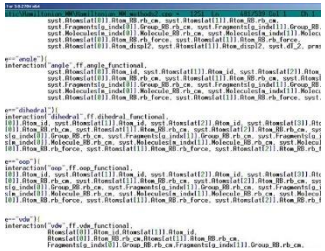
Quantum dots
2D materials/ PV
Perovskites
Organic crystals and biomolecules

Theory of quantum dynamics

- Novel quantum-classical methods
- Non-adiabatic molecular dynamics
- Theory of charge transfer







Methodology development and implementation

- Electron and energy transfer
- Photoinduced molecular dynamics
- Methods for large-scale systems
- Software development

Computational Materials Theory and Methods

Lecture 1:
Classical Molecular Dynamics

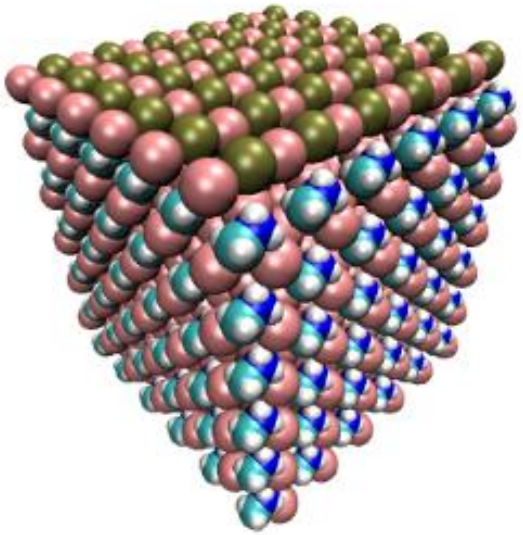
Alexey V. Akimov
University at Buffalo, SUNY

Outline

- Modeling relies on statistical thermodynamics. Gibbs ensembles. Ensemble averages.
- Connection of statistical thermodynamics and MD. Ergodic hypothesis. Time and ensemble averages.
- Hamiltonian dynamics. EOMs and Integration schemes.
- Non-Hamiltonian dynamics. NVT ensemble
- Observables computed from MD simulations.
- MD modeling protocols
- Overview of available software for MD simulations.
- Demonstrations with Libra. Homework #1

Modeling material systems

Atomistic model



Properties

Equilibrium, static:
- Diffusion coefficients, D
- Heat capacity, C_v
- Caloric curves, phase transitions ($E\ vs. T$)
- Radial distribution function (RDF, $g(r)$)

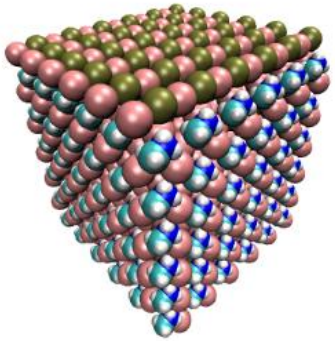
Thermodynamic properties:
- Temperature, T
- Pressure, P
- Kinetic and potential energy, T and U
- Gibbs or Helholtz free energy, G and H

Structural characterization:
- Most stable structure

Dynamical properties:
- Kinetics of phase transitions
- Mechanisms of reactions
- Vibrational spectra, etc.

Modeling realistic systems

Ideal system



"Real" system

Real: all atoms interact with each other

Include all the non-idealities:

- Defects (vacancies, interstitials, dislocations, kinks, dangling bonds, etc.)
- Adsorbates (adatoms, surface dangling bonds passivation, etc.)
- Solvation and counterions
- Phases and grain boundaries

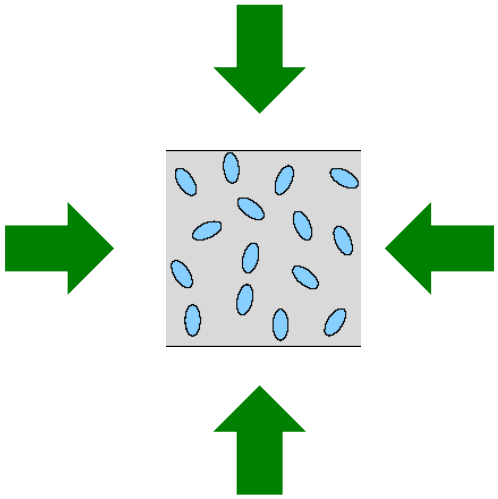
Periodic boundary conditions (PBC)

Real systems = are of N_A size, we can model $1 - 10^6$ atoms, usually around 1000

- Surface/volume ratio is large
- The structure of the surface is different from the bulk

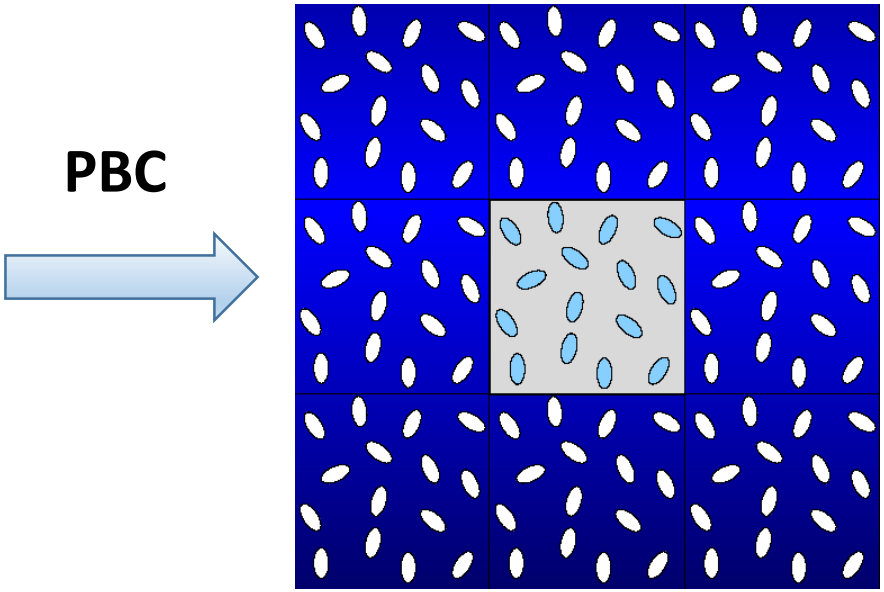
To mitigate these effects:

Use PBC



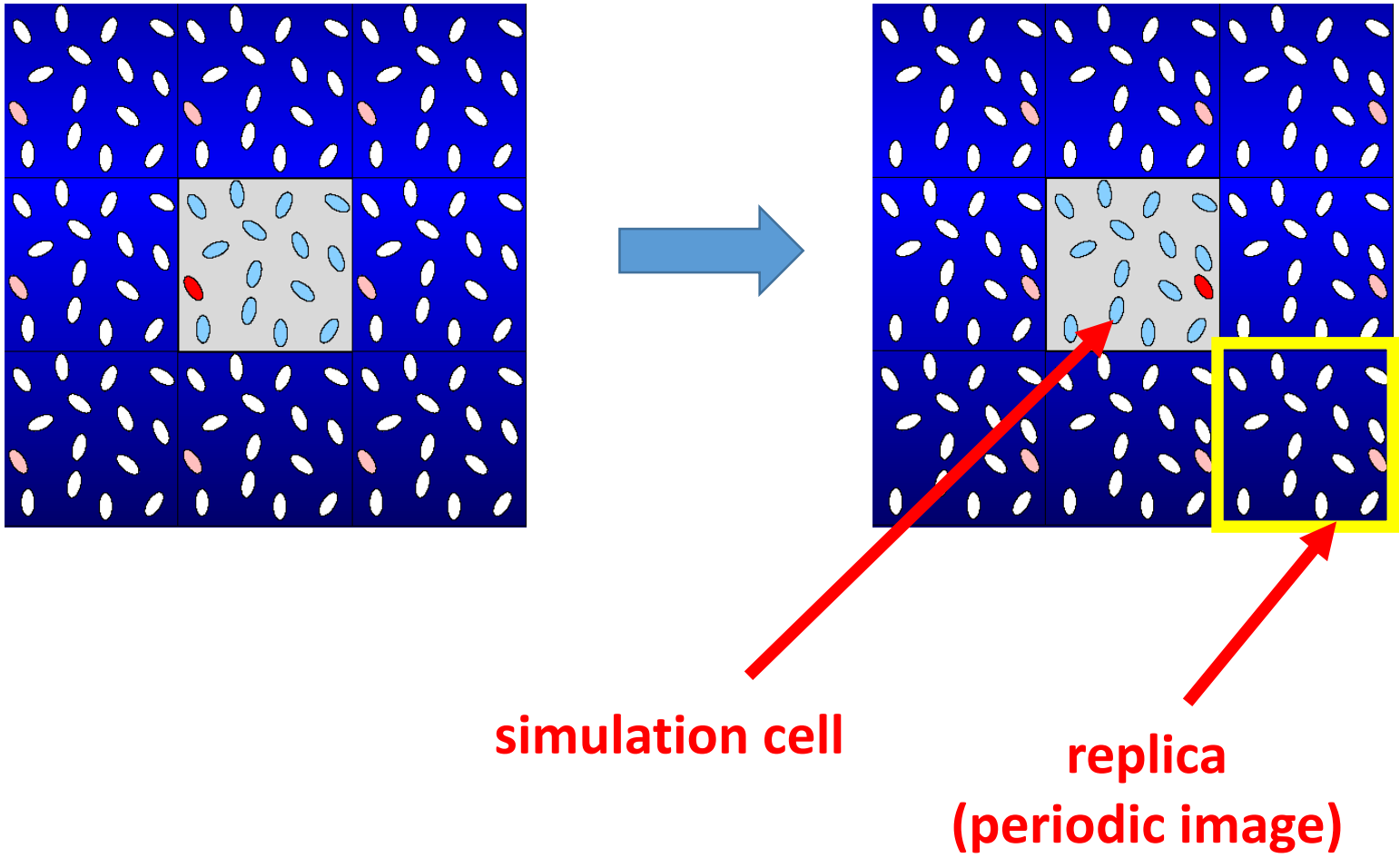
Surface deffects!

PBC



How PBC works

Molecules that exit from the left wall re-enter simulation cell from the right wall



Gibbs Ensemble and phase spaces

Gibbs Ensemble

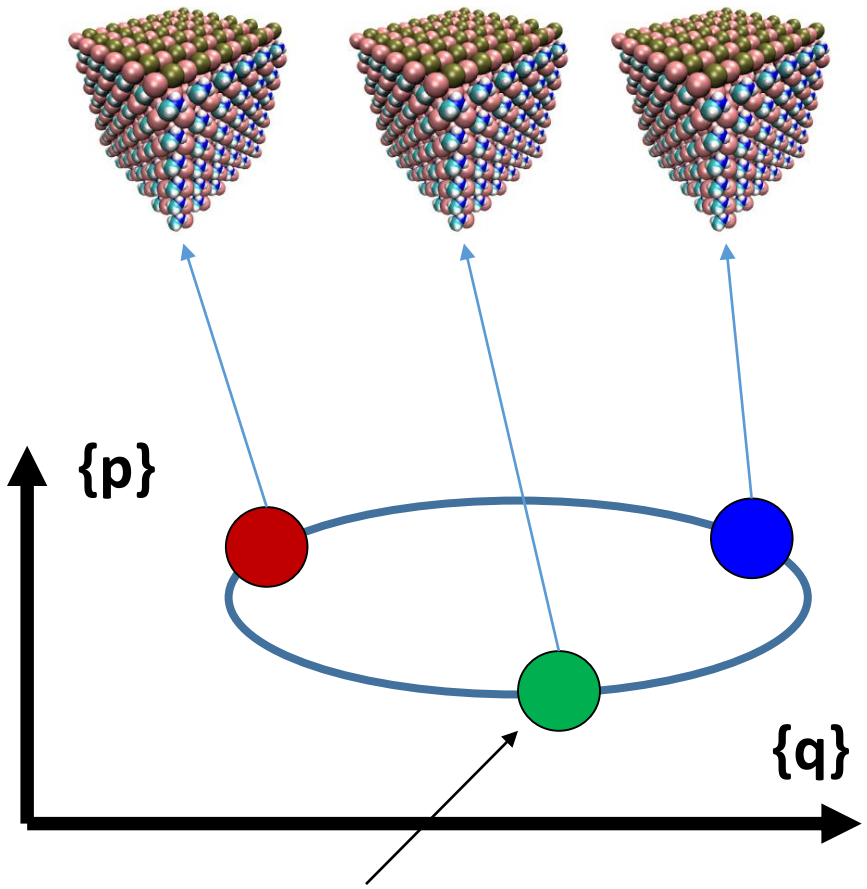
- Non-interacting copies (replicas) of the same “real” system.
- All copies corresponds to the same macroscopic properties (P, T, S, μ) but different microscopic properties (coordinates and velocities of atoms)

Phase Γ-space:

$$\Gamma = \{q, p\}$$

coordinates of a 1 mole of particles

momenta of a 1 mole of particles



Each point is: {3*6*10^{23}; 3*6*10^{23}}

Observed properties are statistical quantities

To compute properties, we compute thermal (ensemble) averages

$$A_{obs} = \langle A \rangle_T = \sum_{\Gamma_i} A(\Gamma_i)\, \omega(\Gamma_i)$$

$\omega(\Gamma_i)$ - a probability to find the system near the point Γ_i in the phase space

$A(\Gamma_i)$ - the value of the property of interest A at the point Γ_i in the phase space

$$A_{obs} = \langle A \rangle_T = \int_{\Gamma} A(\Gamma) d\omega(\Gamma)$$

$$A_{obs} = \langle A \rangle_T = \int_{\Gamma} A(\Gamma) \rho(\Gamma) d\Gamma$$

Ensemble average:

$$A_{obs} = \langle A \rangle_T = \frac{\int_{\Gamma} A(q,p)\rho(q,p) d^{3N}q\, d^{3N}p}{\int_{\Gamma} \rho(q,p) d^{3N}q\, d^{3N}p}$$

All properties are defined by the probability distribution function, $\rho(\mathbf{q}, \mathbf{p})$!

Classification of the Gibbs ensembles

NVE (microcanonical): Constant number of particles (N), volume (V), and total energy (E)

$$\rho_{NVE}(q,p) = \delta(H(q,p) - E)$$

Nothing but the energy conservation requirement to the "regular" (Hamiltonian) dynamics

- If your integrator or system preparation are bad (don't conserve energy) – you do not sample points from the correct NVE distribution function!

NVT (canonical): Constant number of particles (N), volume (V), and temperature (T)

$$\rho_{NVT}(q,p) \sim exp\left(-\frac{H(q,p)}{k_B T}\right)$$

"Thermostatted" MD:
Nose, Nose-Hoover, Andersen thermostats

NPT (isobaric-isothermal): Constant number of particles (N), pressure (P), and temperature (T)

$$\rho_{NVT}(q,p) \sim exp\left(-\frac{H(q,p) + PV}{k_B T}\right)$$

- Closer to real experimental conditions
- Critical to use in high-pressure studies

Examples of the Gibbs ensembles

$$\boldsymbol{H = \frac{p^2}{2m} + \frac{1}{2}kq^2}$$

$$k = 0.1\frac{Ha}{Bohr^2}; m = 100\ a.u.; q_0 = 0.1\ Bohr$$

Run for 25000 a.u.

NVE ensemble:

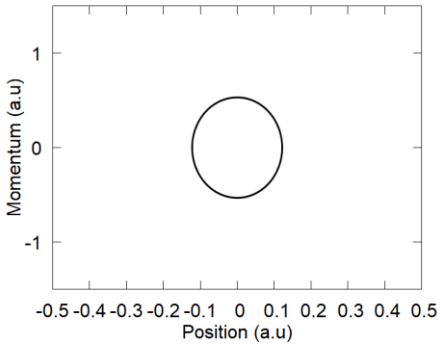
"NVT" ensemble:

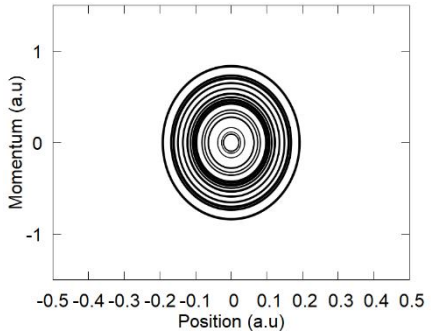
Single trajectory

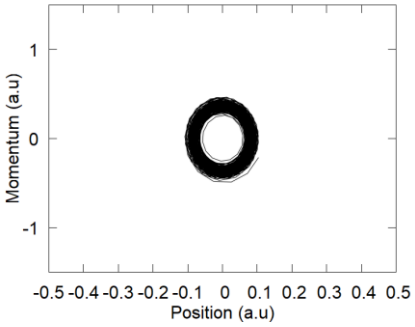
25 trajectories

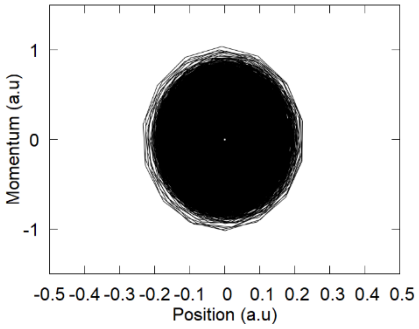
Single trajectory

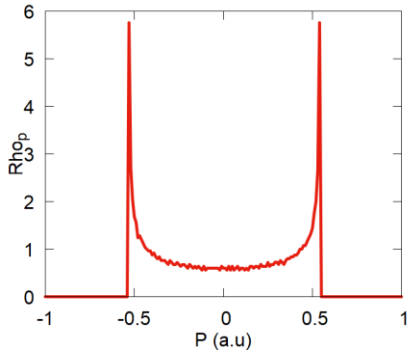
25 trajectories

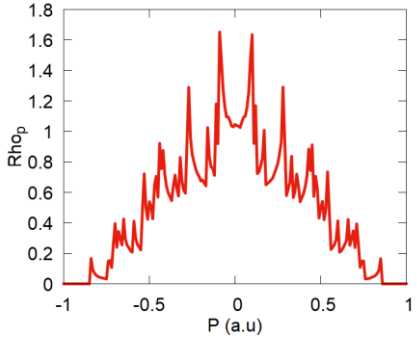


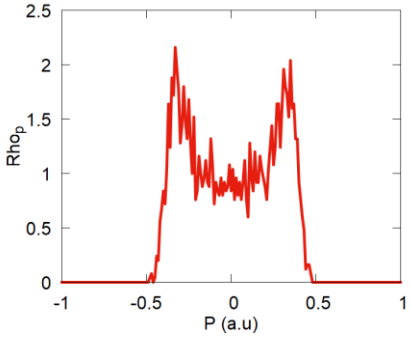


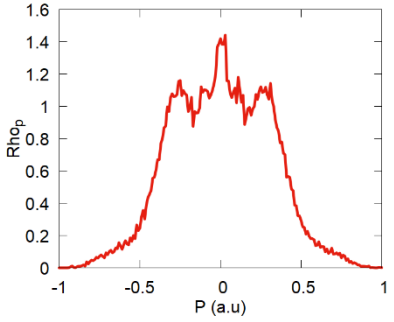












Practical exercises with Libra

Define your potential: in “Hamiltonian.py”

obj.ham_dia.set(0,0, 0.5*k*x*x*(1.0+0.0j))

$$H = \frac{1}{2}kx^2$$

obj.d1ham_dia[i].set(0,0, k*x*(1.0+0.0j))

$$\frac{dH}{dx} = k\text{x}$$

Define your system: in e.g. “nvt.py”

nnucl, ntraj = 1, 25	How many DOFs is per 1 trajectory. How many trajectories
mean_q.set(0,0, 0.1)	The center of the initial distribution. Must specify for each DOF
iM.set(0,0, 1.0/100.0)	The masses of each DOF

Define the simulation parameters : in e.g. “nvt.py”

params["k"]	Harmonic force constant
params[“dt"], params[“nsteps"]	Integration time step (a.u.) and the number of steps

Run the MD : in e.g. “nvt.py”

Q, P = run_nvt(nnucl, ntraj, q, p, iM, compute_model, params)

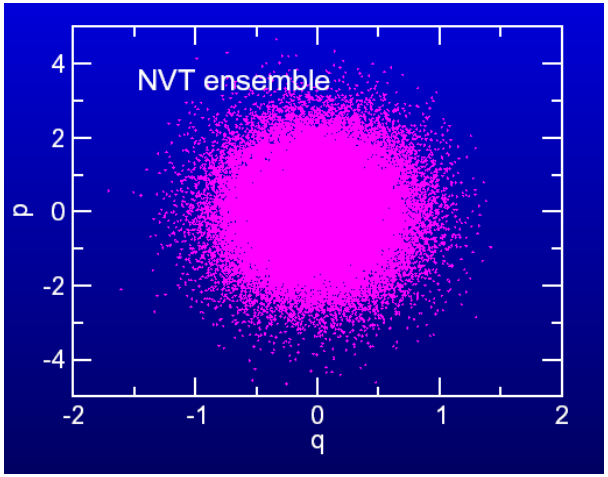
Run the analysis of MD trajectories : in e.g. “nvt.py”

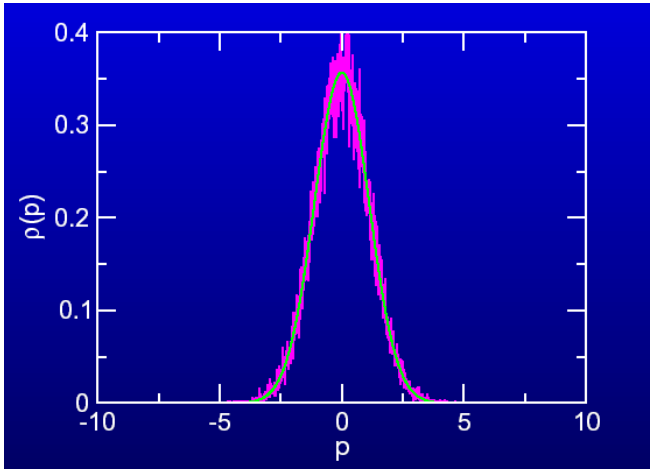
compute_statistics(Q, idof, minx, maxx, dx, "_density_q.txt")

Examples of the Gibbs ensembles

Ideally, in the canonical ensemble we want:

$$\rho_{NVT} \sim \exp\left(-\frac{H(q,p)}{k_B T}\right) \qquad d\omega(p_x) = \frac{1}{\sqrt{2\pi m k_B T}} \exp\left(-\frac{p_x^2}{2 m k_B T}\right) dp_x$$





- This may not happen in reality: **Ergodicity**
- **There are other methods of sampling (e.g. MC)**

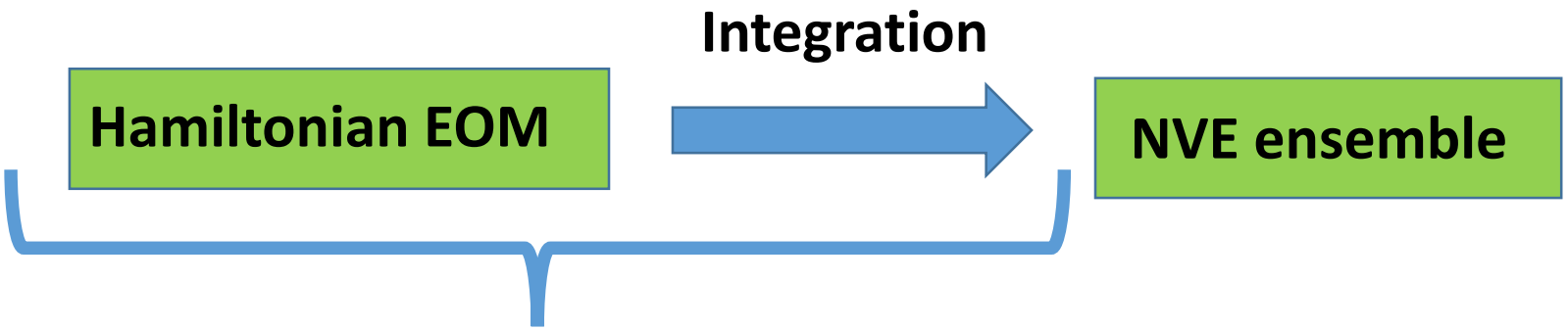
Molecular Dynamics : A way of getting ρ

This is where the statistical thermodynamics is connected to MD!!!

NVE ensemble

Evolution of a point in the phase Γ-space (system) is given by the integrating classical equations of motion (EOM).

The correct integration of the Hamiltonian EOMs ensures the Total energy conservation.



Connection between Stat. Mech. and MD

Ergodic hypothesis

Given an infinite time to evolve, the system will visit all the points of the phase space

$$A_{obs} = \langle A \rangle_{ens} = \langle A \rangle_{time} \equiv \frac{1}{N_T} \sum_{i=1}^{N_T} A(\Gamma(t_i)) = \frac{1}{T} \int_0^T A\big(\Gamma(t)\big) dt$$

The probability density is the distribution of the "sampled" points in the phase space (sampled using method for a given ensemble)

Dealing with the erogodicity

$$A_{obs} = \langle A \rangle_{ens} = \langle A \rangle_{time} \equiv \frac{1}{N_T} \sum_{i=1}^{N_T} A(\Gamma(t_i)) = \frac{1}{T} \int_0^T A\big(\Gamma(t)\big) dt$$

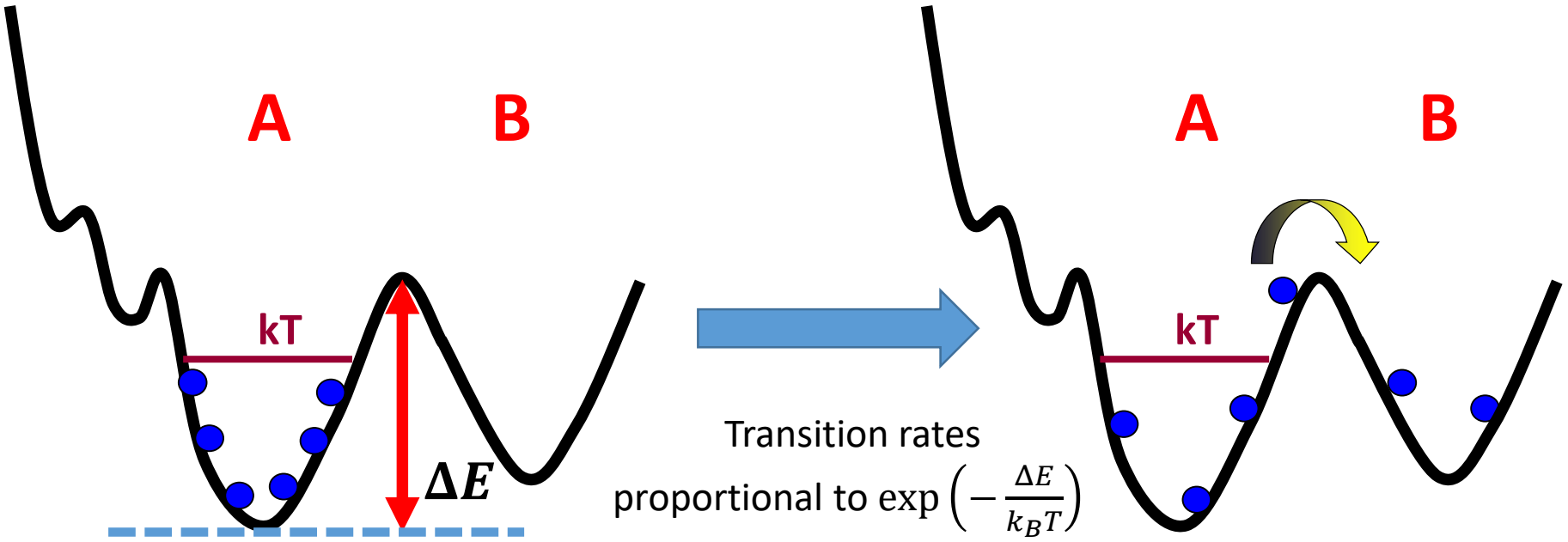
Problem: How to make sure this is true?

Criteria:

- Sufficiently long trajectories
- Starting with many points
- Choosing the right method

Criterion #1: Sufficiently long trajectories

A protein (as well as any material system)
may have two dominant conformations: A and B



If we start in the conformation A, if the barrier ΔE is high, and temperature T is low, we'll have to run a **really long simulation** (beyond the computer capabilities maybe)

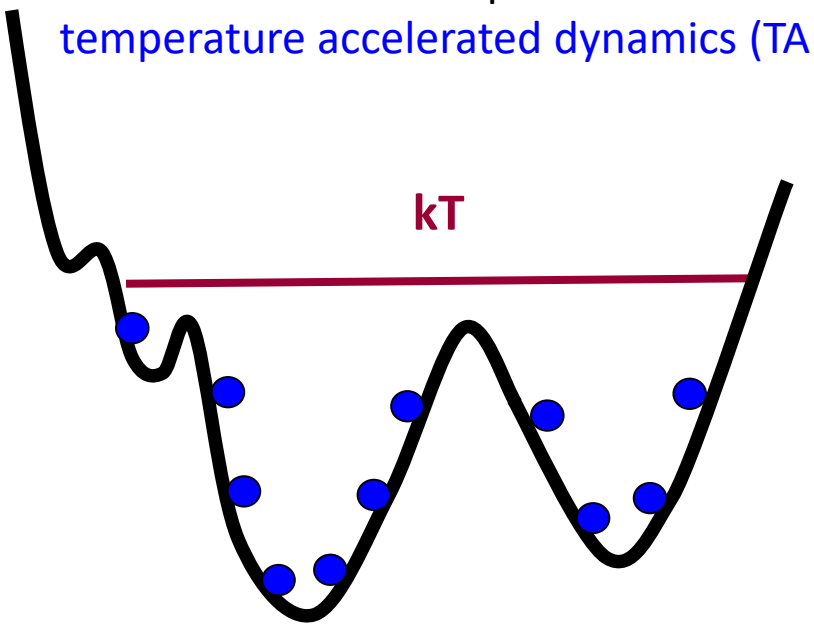
This is fine (to a certain extent!) to study the dynamics of transitions,
but not to compute thermodynamic properties!

Criterion #1: Sufficiently long trajectories (cont.)

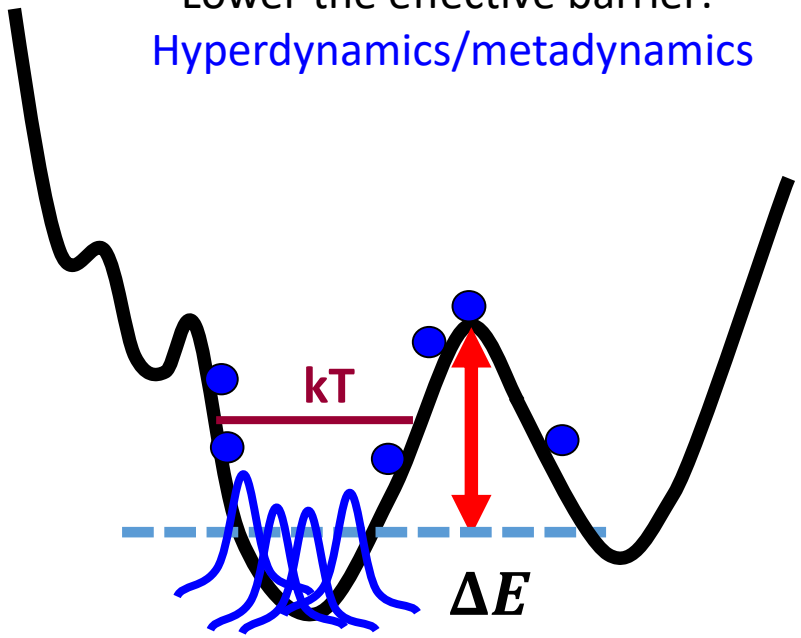
What can we do about it?

$$\exp\left(-\frac{\Delta E}{k_B T}\right)$$

Increase temperature:
temperature accelerated dynamics (TAD)



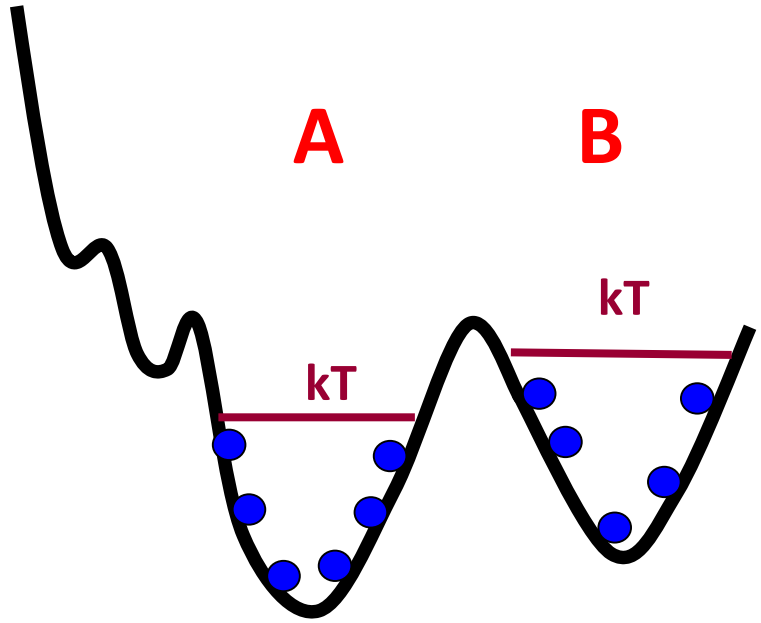
Lower the effective barrier:
Hyperdynamics/metadynamics



- The computed rates must be “rescaled” to the original temperature/barrier
- The dynamics is fictitious

Criterion #2: Starting points

How about if we initialize one fraction of the trajectories to be in the valley A, and the other fraction – to be in the valley B?



- We don't care about slow transitions
- Need to know the relevant regions in advance (e.g. chemical intuition)

Starting point refers not only to initial geometries!

Remember, we work with

$\{q, p\}$

Initial geometries (conformations)

Initial momenta

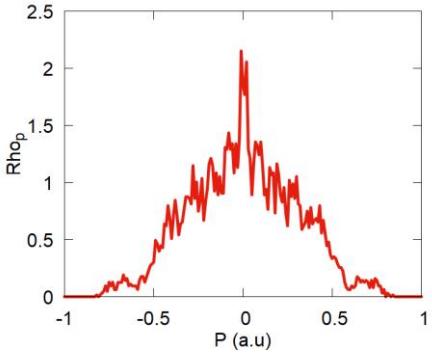
Criteria #1 and #2: Long trajectories & Starting points

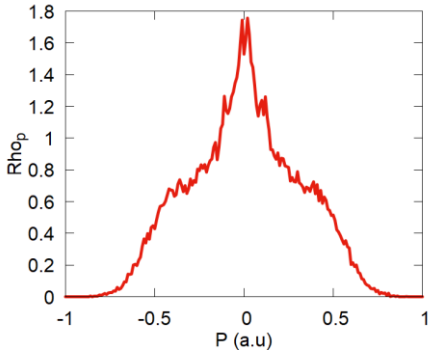
params["nsteps"] = 250

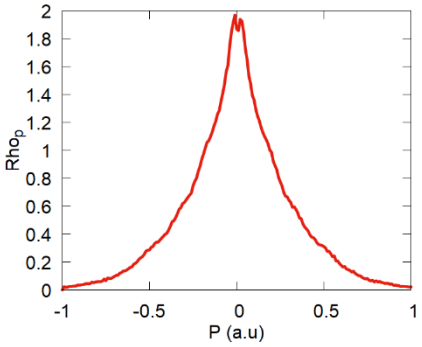
params["nsteps"] = 2500

params["nsteps"] = 25000

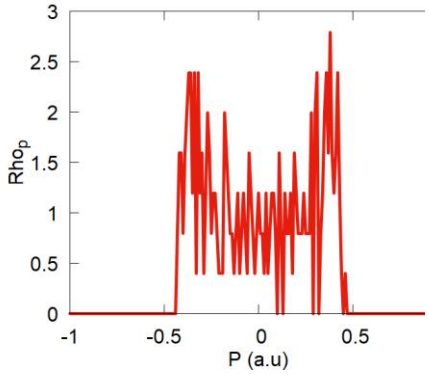
25 trajectories

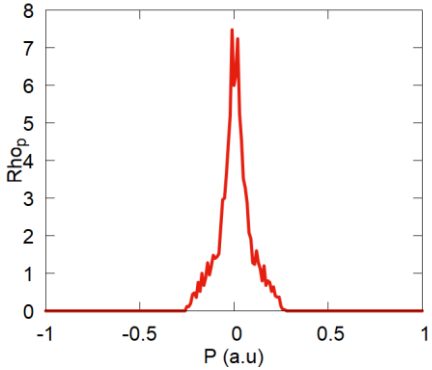


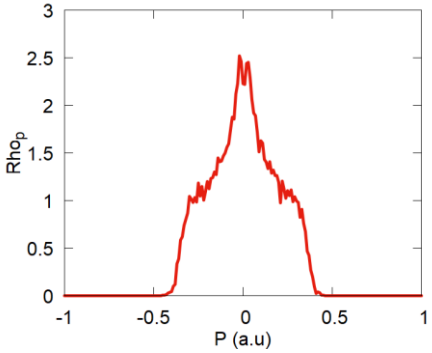




1 trajectory



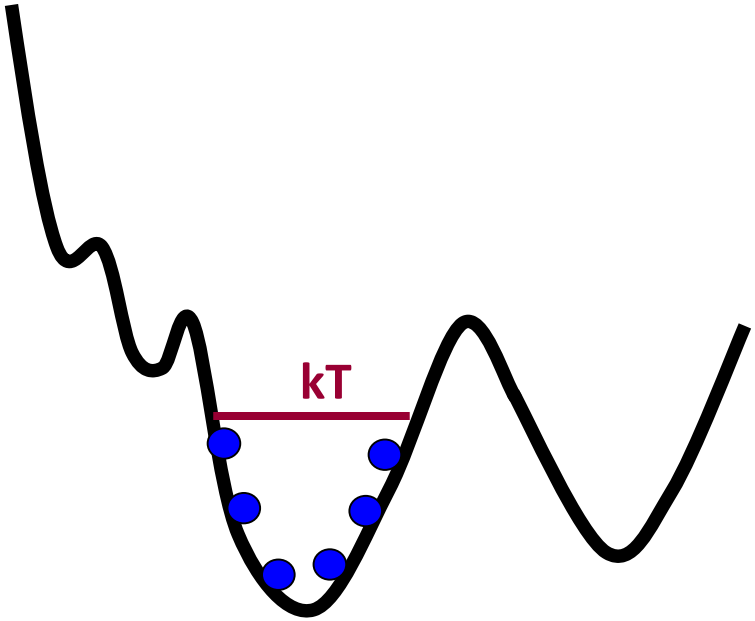




25 trajectories (1 DOF each) coupled to a Nose-Hoover thermostat (“NVT”) ensemble

Criterion #3: Choosing the right method

Not all systems and not all methods lead to ergodicity



In the NVE ensemble (Hamiltonian dynamics): you will stay in this valley forever!

Energy conservation!

Thermodynamic limit ($N \to \infty$):
NVE and NVT ensembles are equivalent

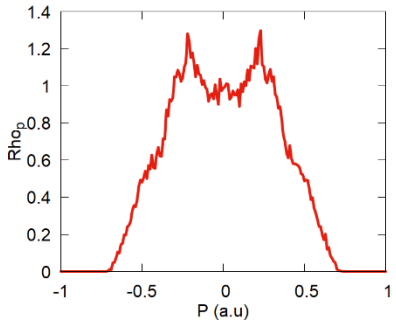
Smaller systems (e.g. Ndof = 1): they are notably different

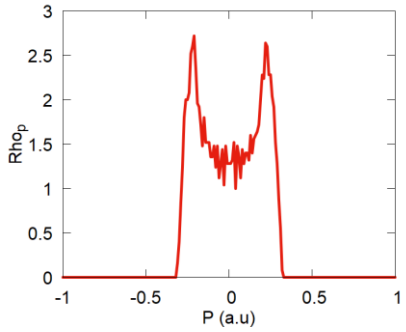
To explore other valleys, we need to utilize NVT simulations!
(non-Hamiltonian dynamics)

The total energy of the system is not conserved!

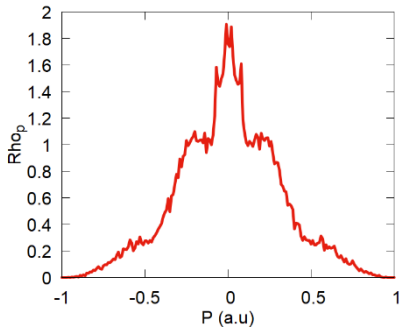
Criterion #3: Using the right method

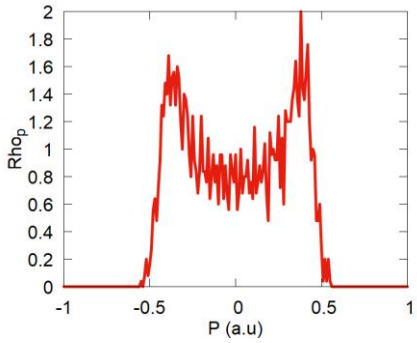
Chain size = 1



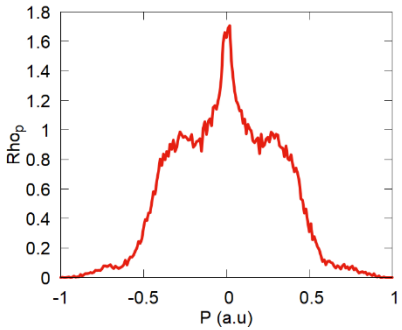


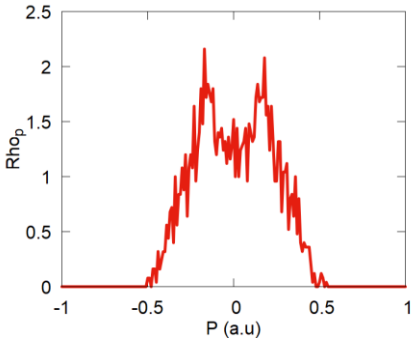
Chain size = 5



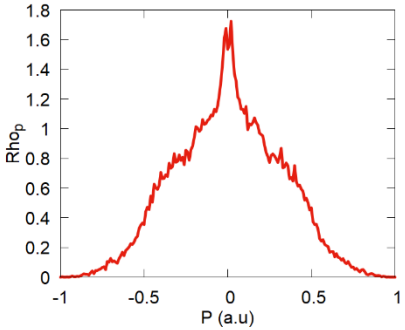


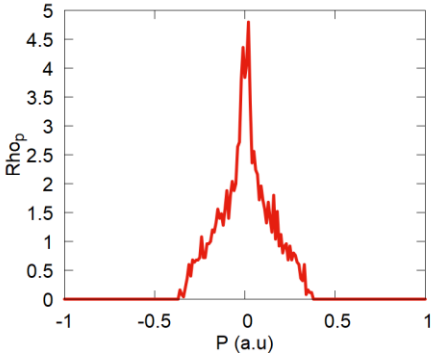
Chain size = 25





Chain size = 250



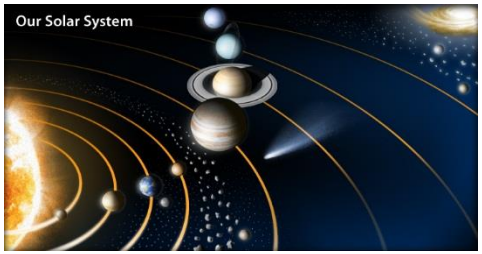


This is not quite the right method: the NVT ensemble doesn't make sense for a system of 1 nuclear DOF

Basic terminology of classical mechanics

Material point: neglect size

What is large? Is the Earth large? Compared to what?



Choice of the coordinates:

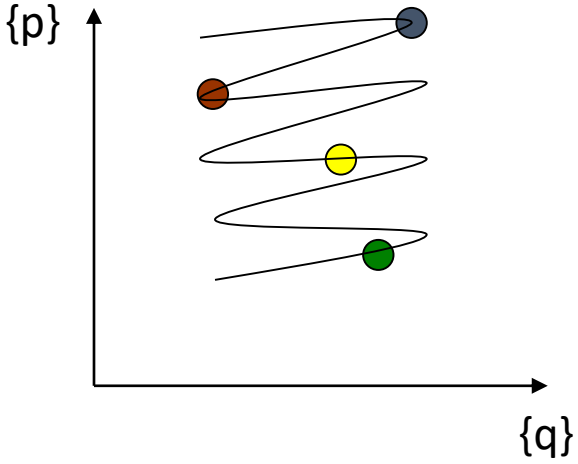
- Cartesian or Internal
- Can be chosen as convenient

Equations of motion(EOM):

$$f(\boldsymbol{r}, \dot{\boldsymbol{r}}, \ddot{\boldsymbol{r}}) = 0$$

This is what we solve by doing MD

Trajectory:



$$\boldsymbol{r}(t) = (x_1(t), y_1(t), z_1(t), x_2(t), y_2(t), z_2(t), \dots)^T$$

$$\boldsymbol{r}(t) = (\boldsymbol{r_1}(t), \boldsymbol{r_2}(t), \dots, \boldsymbol{r_N}(t))^T$$

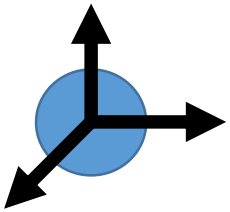
$$\boldsymbol{r_1}(t) = \big(x_1(t), y_1(t), z_1(t)\big)^T = \begin{pmatrix} x_1(t) \\ y_1(t) \\ z_1(t) \end{pmatrix}$$

Degrees of freedom (DOF)

DOF = parameters that fully specify the geometry of a system

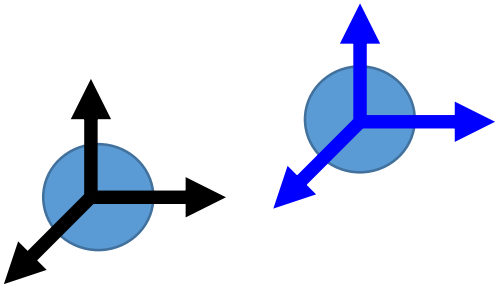
The number of DOFs: 3N – (# of constraints)

An atom: 3*1 = 3 DOFs

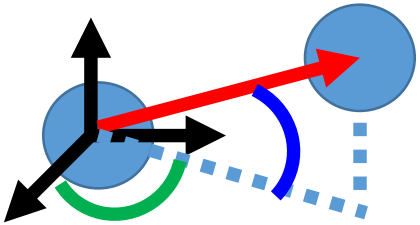


DOFs: x, y, z

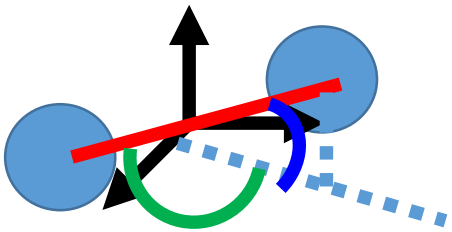
Diatomic molecule: 3*2 = 6 DOFs



DOFs: $x_1, y_1, z_1, x_2, y_2, z_2$ (Cartesian)



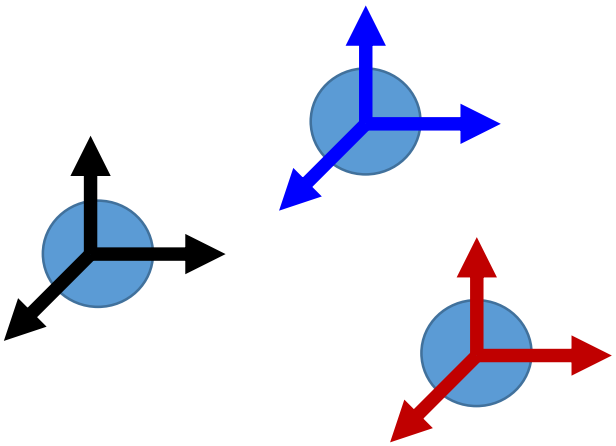
DOFs: $x_1, y_1, z_1, r, \phi, \theta$ (polar)

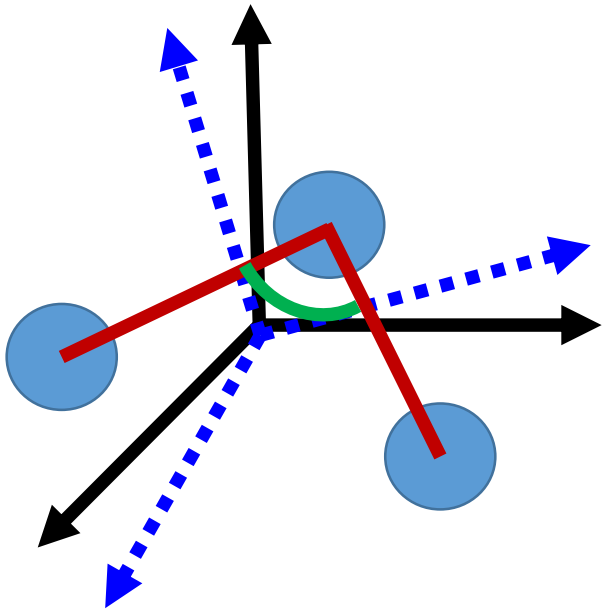


DOFs: X, Y, Z, r, ϕ, θ (internal)

Degrees of freedom (DOF)

Triatomic molecule: 3*3 = 9 DOFs





DOFs: $x_1, y_1, z_1, x_2, y_2, z_2, x_3, y_3, z_3$
(Cartesian)

DOFs (internal):

X, Y, Z – position of the center of mass (COM)

Θ, ϕ, ψ – angles the molecular inertia axes form with the external (Cartesian) coordinate system

r_{12}, r_{23} - interatomic distances

Θ_{123} - an angle between two bonds

Hamiltonian Dynamics

$$H = K + U = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m_i} + U(\{\boldsymbol{q}\}) = \sum_{i=1}^{N} \frac{p_{x,i}^2 + p_{y,i}^2 + p_{z,i}^2}{2m_i} + U(\{q_1, q_2, \ldots q_{3N}\})$$

Total energy (Hamiltonian)

Kinetic energy

Potential energy

Hamiltonian EOM

(generate an NVE ensemble)

$$\dot{q}_i = \frac{\partial H}{\partial p_i}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}$$

In a nutshell: **Newton's second law**

$$v_i = \dot{q}_i = \frac{p_i}{m_i}$$

$$\dot{p}_i = m_i a_i = -\frac{\partial U}{\partial q_i} \equiv F_i$$

Forces in MD

$$\boldsymbol{F} = -\frac{\partial U}{\partial \boldsymbol{q}}$$

what this really means: we compute the x,y, and z components of the forces acting on all particles i just by taking derivatives of the potential energy w.r.t. the corresponding coordinate

More explicitly:

$$F_{1,x} = -\frac{\partial U}{\partial x_1} \qquad F_{1,y} = -\frac{\partial U}{\partial y_1} \qquad F_{1,z} = -\frac{\partial U}{\partial z_1}$$

$$F_{2,x} = -\frac{\partial U}{\partial x_2} \qquad F_{2,y} = -\frac{\partial U}{\partial y_2} \qquad F_{2,z} = -\frac{\partial U}{\partial z_2}$$

$$\dots$$

$$F_{N,x} = -\frac{\partial U}{\partial x_N} \qquad F_{N,y} = -\frac{\partial U}{\partial y_N} \qquad F_{N,z} = -\frac{\partial U}{\partial z_N}$$

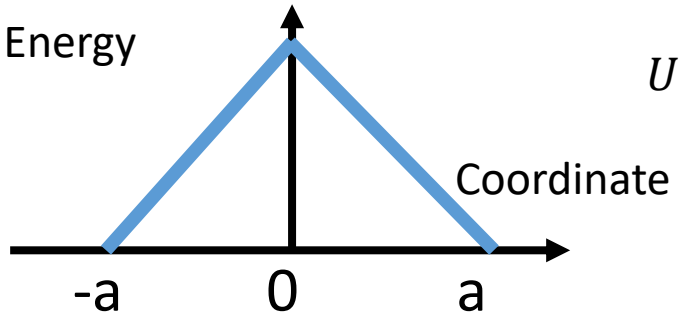
Force and energy evaluations – are the most expensive (time consuming) parts of MD simulations

Where to get U?

- Model Problems (here)
- Force Fields (next)
- Quantum Mechanics (later)

Forces in MD

Forces must be continuous! Or the MD won't be stable (will produce meaningless data)



$$U = \begin{cases} k(x+a), x \in [-a, 0] \\ k(a-x), x \in [0, a] \end{cases} \Rightarrow F = \begin{cases} -k, x \in [-a, 0] \\ k, x \in [0, a] \end{cases}$$

This is gonna be a problematic potential!

Don't forget the sign! Otherwise the system will blow up

Defined in Hamiltonian.py

def compute_model(q, params, full_id):

$H = \frac{1}{2}kx^2$ obj.ham_dia.set(0,0, 0.5*k*x*x*(1.0+0.0j))

$\frac{dH}{dx} = k\text{x}$ obj.d1ham_dia[i].set(0,0, k*x*(1.0+0.0j))

Beware! Here we compute just the derivative, not the force, which is a negative derivative!

Exercises:

- Can you define your Python function for Morse potential?
- Can you define your Harmonic potential for 2 particles connected by a spring in 1 D?

Solving (integrating) the Hamiltonian EOM

Taylor series

$$q_i(t+dt) \approx q_i(t) + \frac{p_i(t)}{m_i}dt + \frac{f_i(t)}{2m_i}dt^2 + O(dt^3) + O(dt^4)$$

$$q_i(t-dt) \approx q_i(t) - \frac{p_i(t)}{m_i}dt + \frac{f_i(t)}{2m_i}dt^2 - O(dt^3) + O(dt^4)$$

$$q_i(t+dt) \approx 2q_i(t) - q_i(t-dt) + \frac{f_i(t)}{m_i}dt^2 + O(dt^4)$$

$$p_i(t) \approx \frac{q_i(t+dt) - q_i(t-dt)}{2dt} + O(dt^3)$$

Verlet algorithm

$$q_i(t+dt) \approx q_i(t) + p_i(t)dt + \frac{dt^2}{2}f_i(t)$$

$$p_i(t+dt) \approx p_i(t) + \frac{dt}{2}[f_i(t) + f_i(t+dt)]$$

velocity Verlet algorithm

More stable!

How to assess the quality of integration scheme?

In the isolated system (NVE),
the following quantities are conserved:

Invariants (integrals) of motion:

$$H = T + U$$ total energy

$$P = \sum_{i}^{N} p_i$$ total momentum

$$L = \sum_{i}^{N} l_i = \sum_{i}^{N} r_i \times p_i$$ total angular momentum

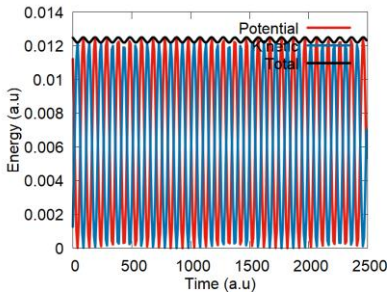
The energy conservation can be affected by:

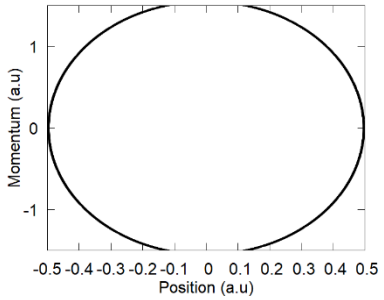
- Integration time step vs. highest frequency $\omega = \sqrt{\frac{k}{m}}$
- Integration algorithm (e.g. Verlet vs. velocity Verlet)
- Force discontinuities
- Total energy of the systems (too "hot" requires smaller dt)

Illustration

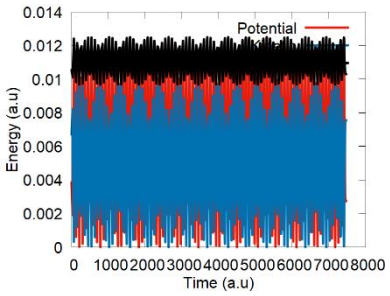
$$k = 0.1, m = 100 \Rightarrow \omega = \sqrt{\frac{0.1}{100}} \approx 0.032\ a.u.^{-1} \Rightarrow dt \sim \frac{1}{0.032} = 31.6$$

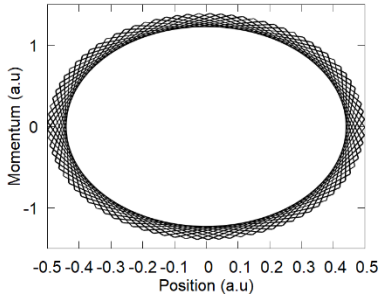
dt = 10



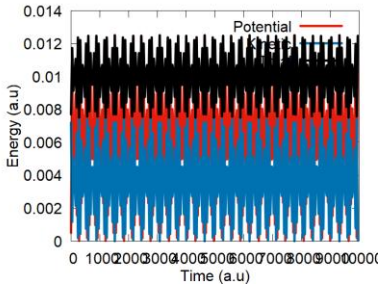


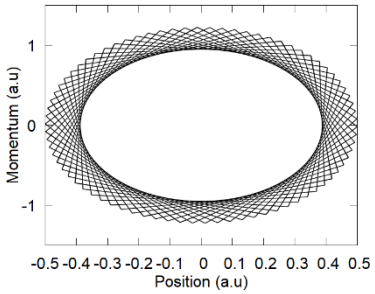
dt = 30



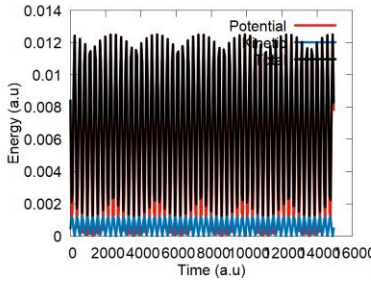


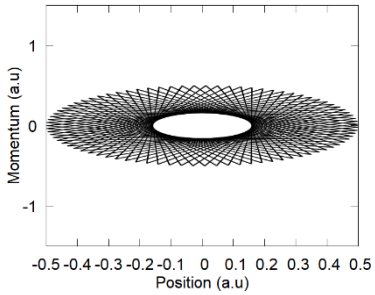
dt = 40





dt = 60





Non-Hamiltonian Dynamics

To generate NVT (and other ensembles) we can:

- rescale velocity to satisfy the temperature T; ➔ incorrect sampling of fluctuations
- add a random force and add a friction (Langevin/Andersen thermostat)
- rescale velocities by a factor not too different from 1.0, but which will eventually lead to the desired average temperature (Berendsen)
- Introduce extended phase space variables such that the integration over extra variables will yield the desired distribution (Nose, Nose-Hoover/chain thermostats, etc.)

$$\delta(H(q,p,s,p_s)-E) \rightarrow \int dsdp_s \delta(H(q,p,s,p_s)-E) = \exp\left(-\frac{H(q,p)}{k_B T}\right)$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i} - \xi p_i$$

There is **no Hamiltonian** from which these equations can be derived.

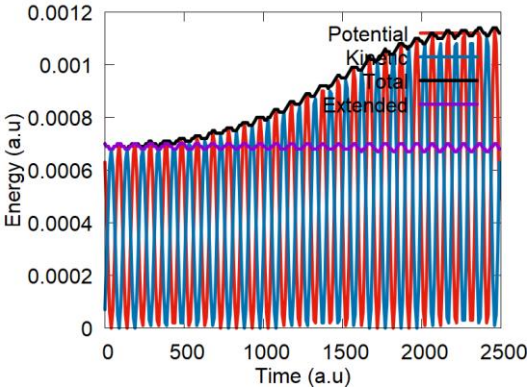
But, there is an extended energy, which is conserved along the motion.

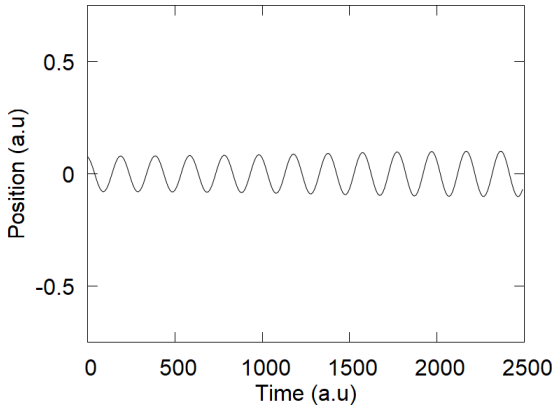
non-Hamiltonian dynamics

An illustration of Non-Hamiltonian Dynamics

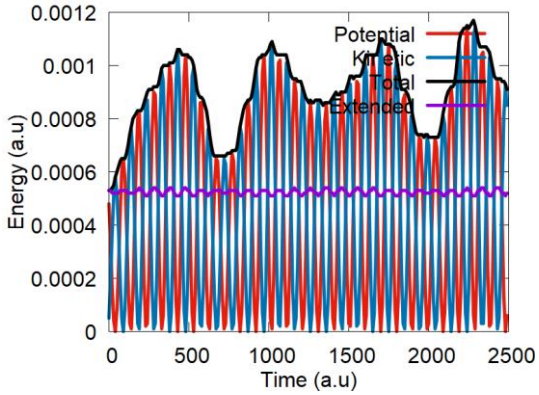
Frequency of system-bath interaction

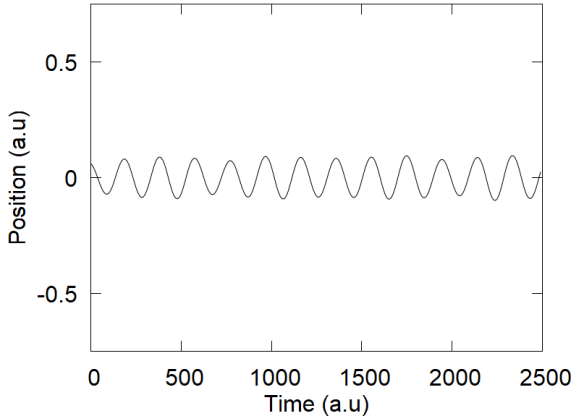
$\nu = 0.001$



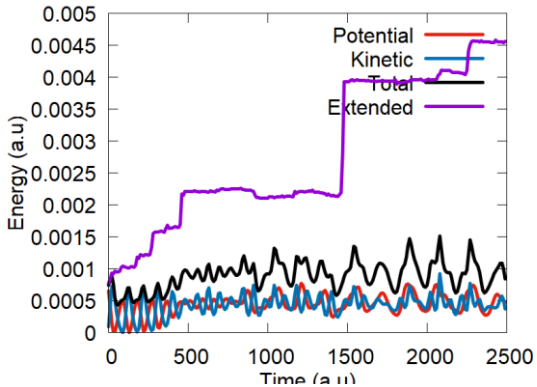


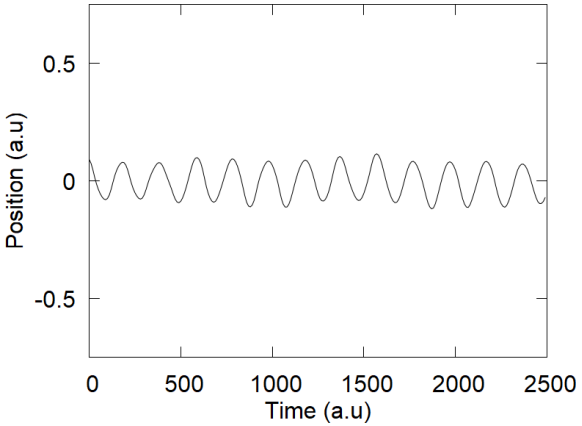
$\nu = 0.01$





$\nu = 0.05$





NVE limit

unstable

Observables 1: Initial velocities and Temperature

$$\rho(v_x)dv_x = \frac{dN_{v_x}}{N} = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{mv_x^2}{2k_B T}\right) dv_x$$

$$\rho(v)dv = \frac{dN_v}{N} = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv_x^2}{2k_B T}\right) dv$$

Average velocity (magnitude):

$$\langle v \rangle = \int_0^\infty v\rho(v)dv = \sqrt{\frac{8k_B T}{\pi m}}$$

Average squared velocity:

$$\langle v^2 \rangle = \int_0^\infty v^2\rho(v)dv = \frac{3k_B T}{m}$$

Kinetic energy:

$$K = \frac{1}{2}\sum_{i=1}^{N} m_i v_i^2$$

Average kinetic energy:

$$\langle K \rangle = \frac{3Nk_B T}{2}$$

Instantaneous temperature:

$$T = \frac{\sum_{i=1}^{N} m_i v_i^2}{3Nk_B}$$

Equipartition Principle: in classical limit, the average energy corresponding to any quadratic term in Hamiltonian is $\frac{1}{2}k_B T$

Observables 2: Pressure

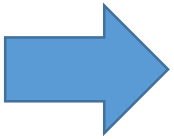
Virial theorem gives:

$$\langle K \rangle = -\frac{1}{2}\sum_{i=1}^{N}\langle q_i F_i \rangle$$

from which, one can find:

$$PV = Nk_BT - \frac{1}{3}\sum_{i=1}^{N}\left\langle q_i \frac{\partial U}{\partial q_i}\right\rangle$$

If the particles do not interact ($U = 0$):



$$PV = Nk_BT$$

the ideal gas law

Observables 3: Thermodynamics fluctuations

Within the canonic (NVT) ensemble

$$\langle \delta E^2 \rangle = k_B T^2 C_V$$

Heat capacity and phase transitions

$$\langle \delta K^2 \rangle = \frac{3}{2} N (k_B T)^2$$

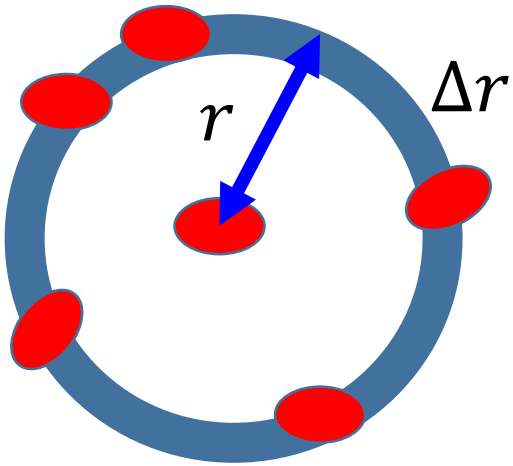
$$\langle \delta U^2 \rangle = k_B T^2 \left(C_V - \frac{3 N k_B}{2} \right)$$

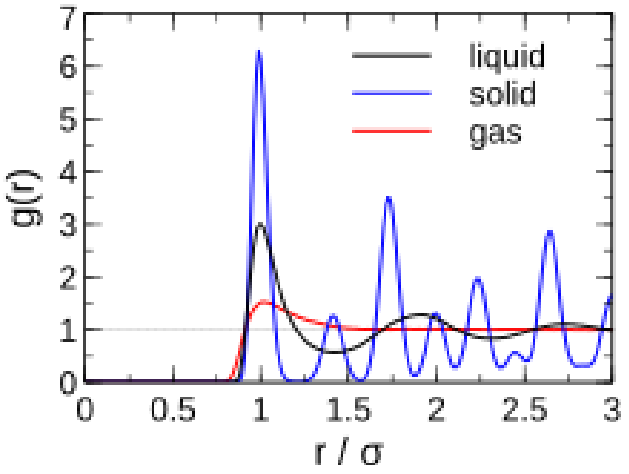
Observables 4: Radial distribution function (RDF)

- **RDF, $g(r)$:**
  The probability to find two atoms at a given distance r from each other in comparison to the probability of the same but in an uniformly distributed system of the same density

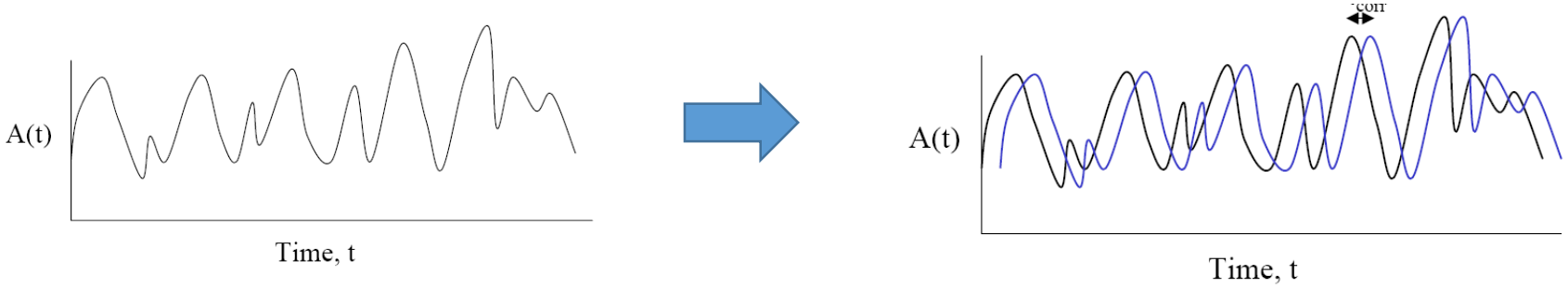
$$g(r) = \frac{\rho(r)}{\langle\rho\rangle} = \frac{VN(r)}{4\pi r^2 \Delta r N}$$

The average number of particles that are within the shell $[r, r + \Delta r]$ from any other particle

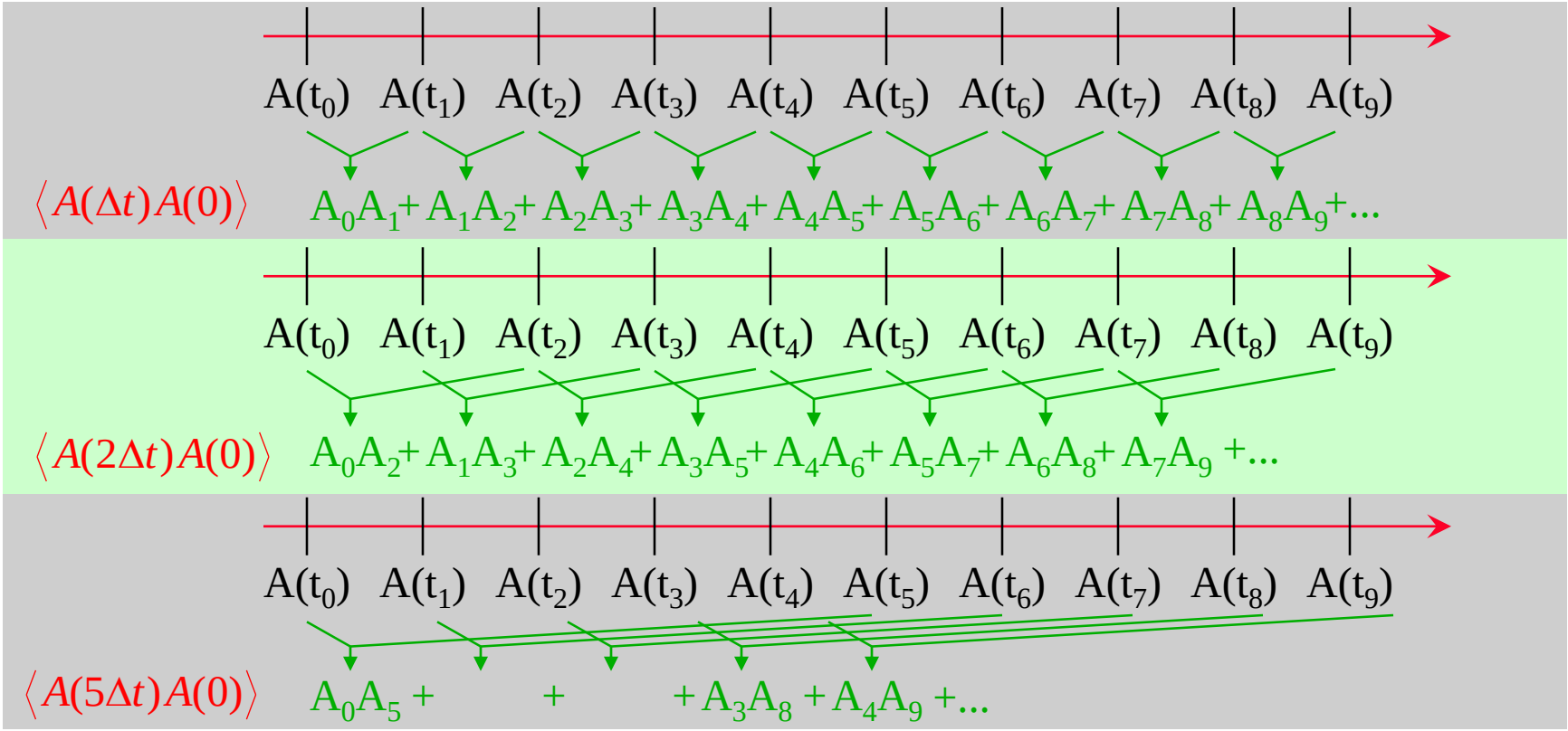




Observables 5: Time-correlation function



$$C_{AB}(\tau) = \langle A(t)B(t+\tau)\rangle_{ens}$$



Observables 5: Velocity autocorrelation function

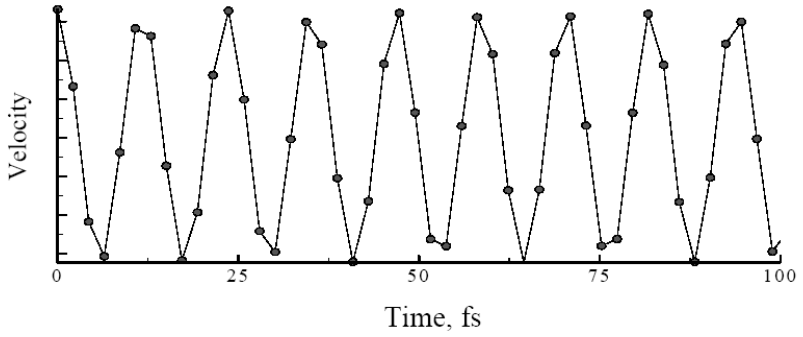
$$C_{vv}(\tau) = \langle v(t)v(t+\tau)\rangle_{ens} = \frac{1}{N}\sum_{i=1}^{N}\frac{1}{N_{in}}\sum_{t_0=1}^{N_{in}} v_i(t_0)v_i(t_0+\tau)$$

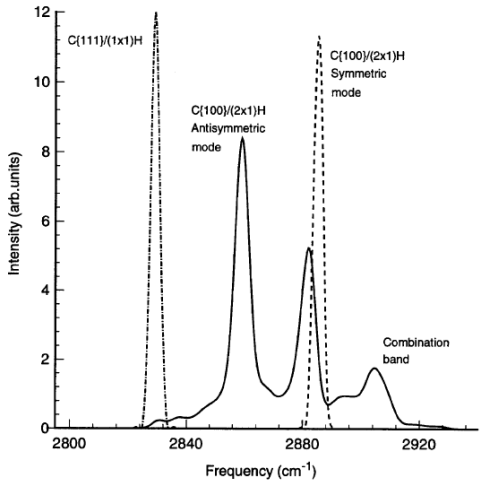
Averaging is done w.r.t. the number of **particles** and w.r.t. the **initial times**

Optical response theory:

Fourier transform of the ACF gives an IR spectrum

$$I_{vv}(\omega) = \int_{-\infty}^{\infty} \exp(-i\omega\tau)\, C_{vv}(\tau) d\tau$$





Observables 6: Transport properties

$$\langle |q(t) - q(0)|^2 \rangle = 6Dt$$

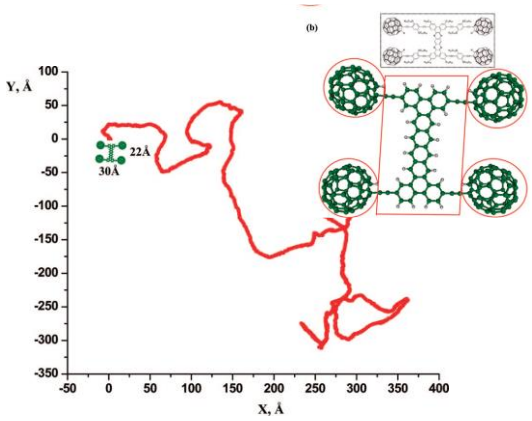
Einstein formula for diffusion coefficient in 3D

$$D = \int_0^\infty C_{vv}(\tau) d\tau$$

Green-Kubo formula

- **Good with PBC**
- **Careful if stochastic thermostat**

Activation energy for diffusion: $D \sim \exp(-\Delta E_a / k_B T)$



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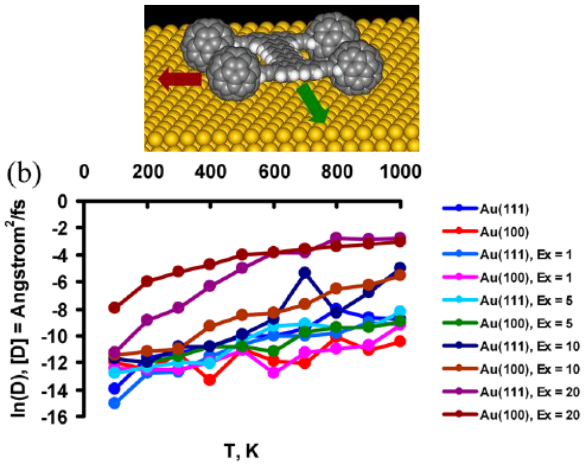
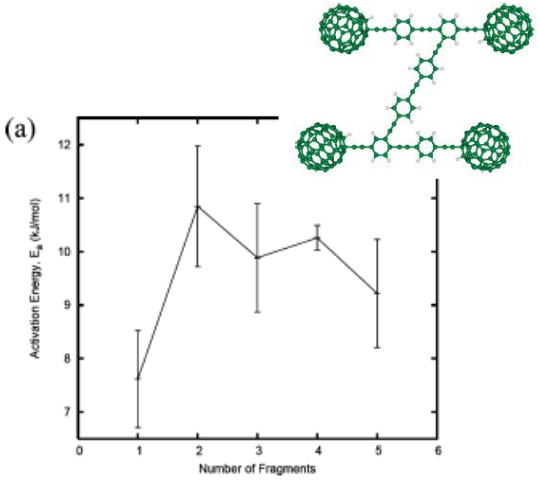
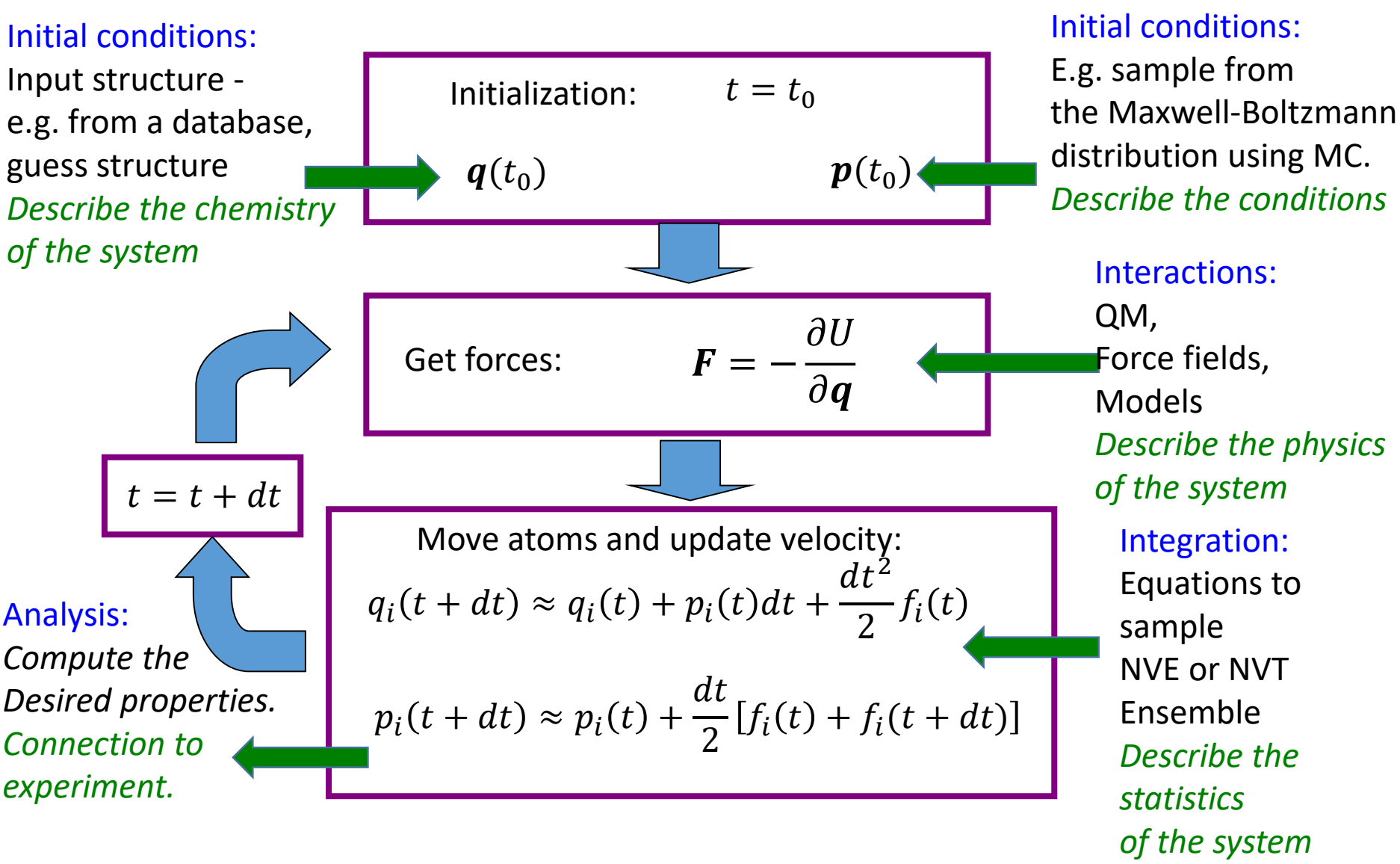


J. Phys. Chem. C **2012**, *116*, 22595–22601.

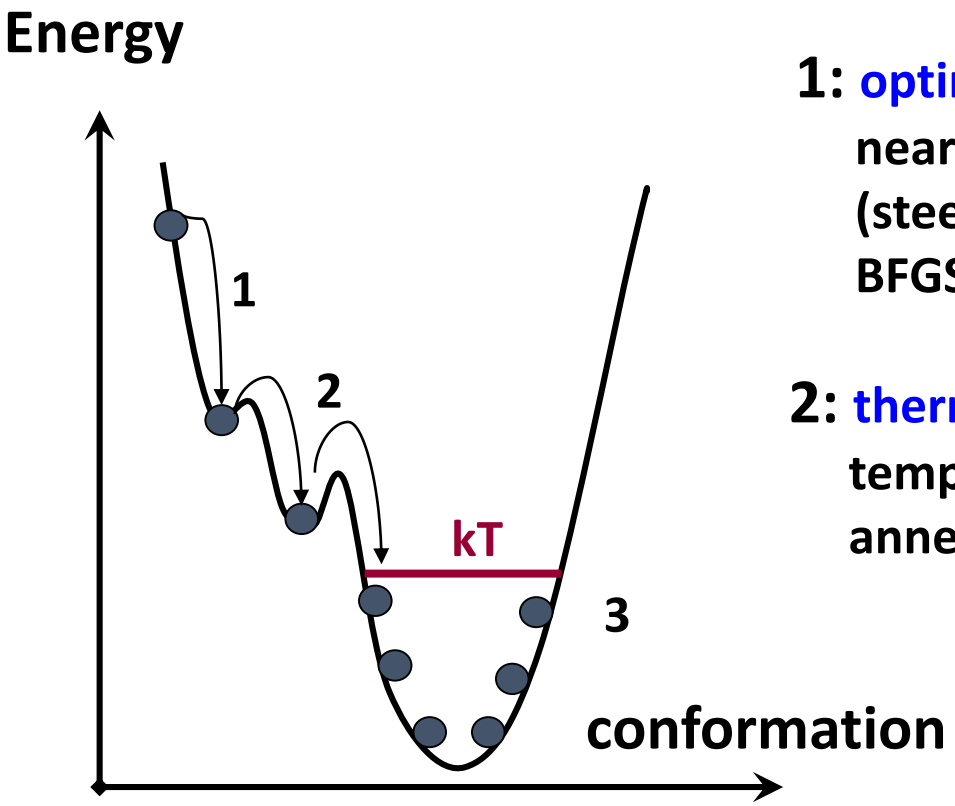


J. Chem. Theory Comput. **2010**, *6*, 2581–2590.

General MD algorithm

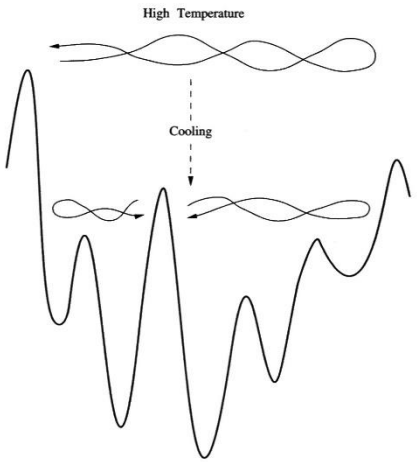


Preparation to MD simulations



1: optimize your structure to the nearby (local) energy minimum (steepest descent, Newton's method, BFGS, etc.)

2: thermalize your structure to target temperature (NVT ensemble MD, simulated annealing, etc.)



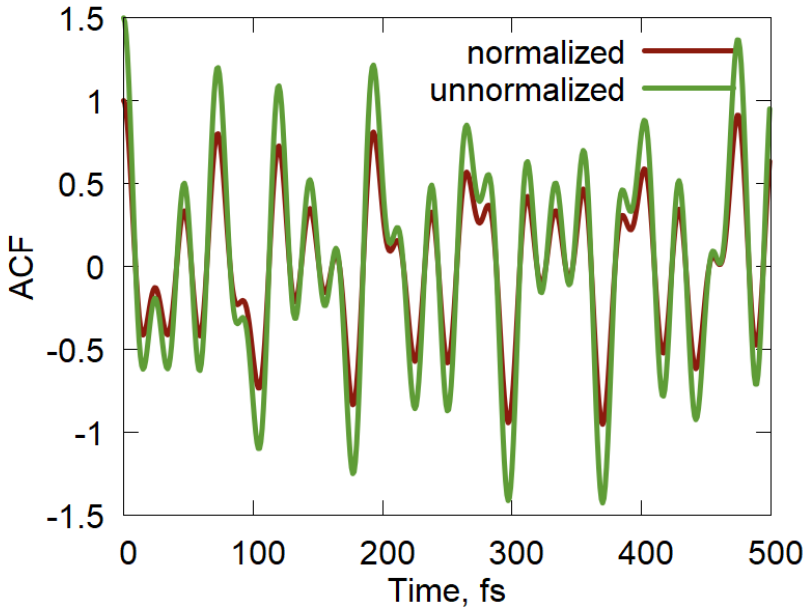
3: production run. Sample conformation from desired distribution using suitable MD or MC algorithm

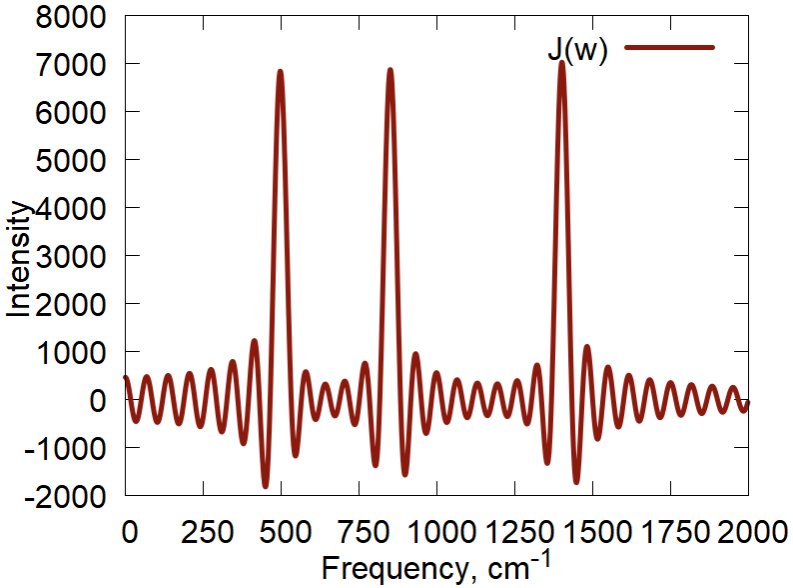
Exercises: ACF and Spectrum of a predefined data

In Tut2

$$r(t) = (\sin(\omega_1 t), \cos(\omega_2 t), \sin(\omega_3 t))$$

$$\omega_1 = 500\ cm^{-1}$$
$$\omega_2 = 1400\ cm^{-1}$$
$$\omega_3 = 850\ cm^{-1}$$



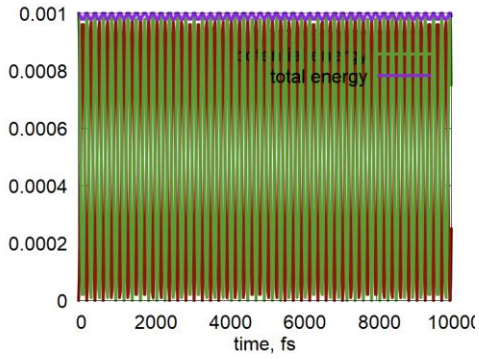


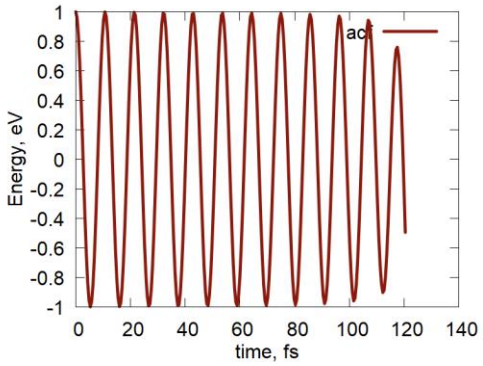
Exercises: ACF and Spectrum of 2-atomic system

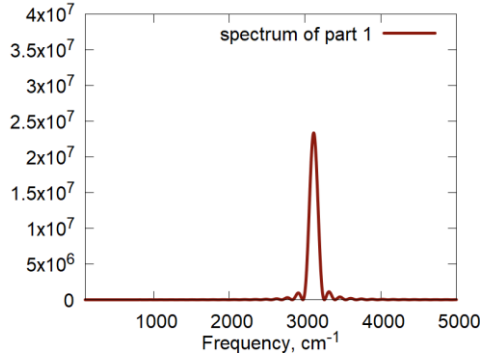
In Tut3, prefix = “test1”

Analytic calculation:
Frequency = 3103.79623215 cm^-1

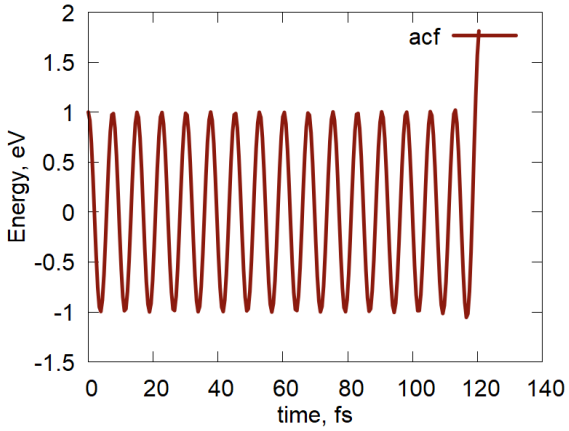
Normal modes give: 3103.79623 cm^-1

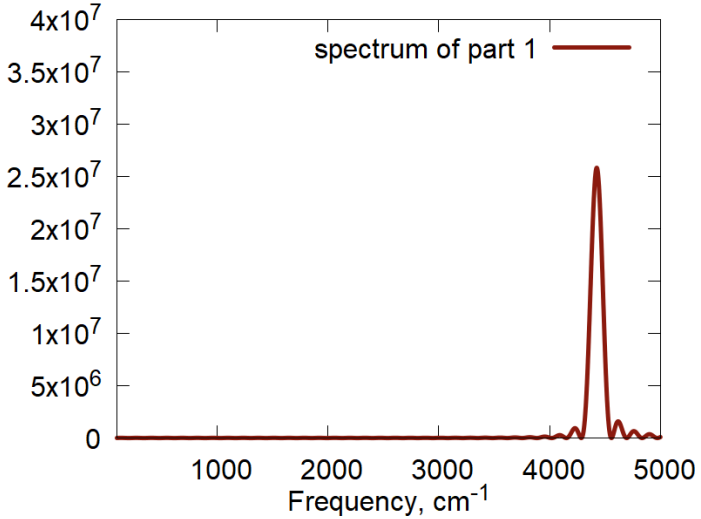






In Tut3, prefix = “test2”

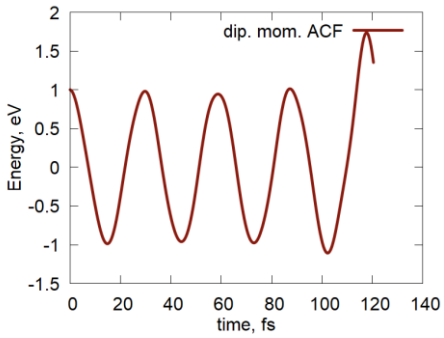


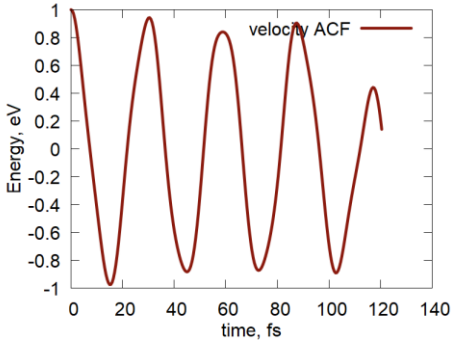


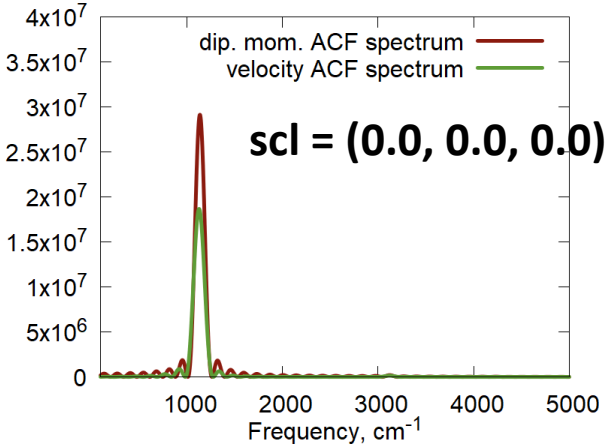
Normal modes give:
4389.43073

Exercises: ACF and Spectrum of a linear chain

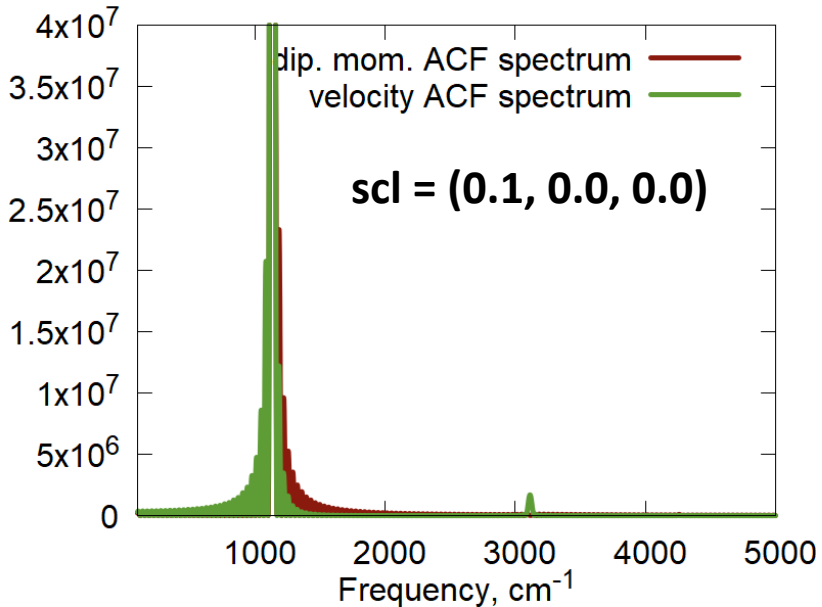
In Tut3, prefix = “test3”







In Tut3, prefix = “test4”,

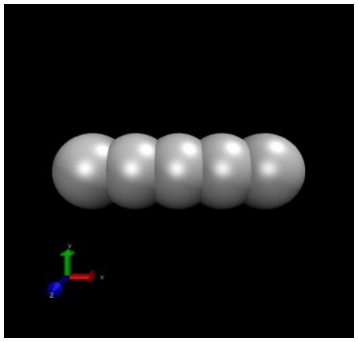


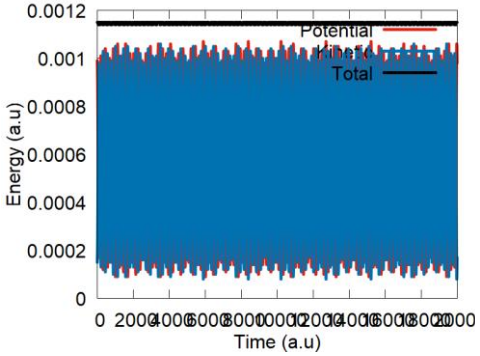
Normal modes give:

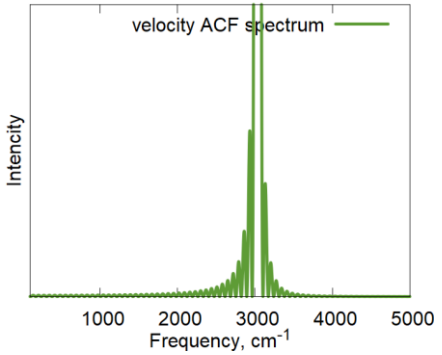
1136.06827 cm^-1
2194.71536 cm^-1
3103.79623 cm^-1
3801.35852 cm^-1
4239.86450 cm^-1

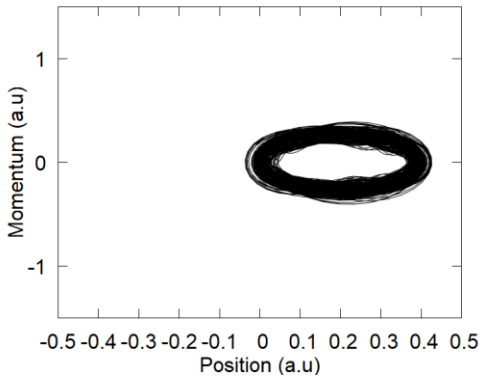
Exercises: Linear chain in NVE ensemble

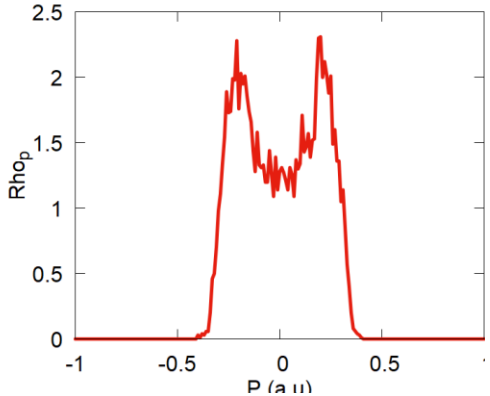
Tut4: NVE

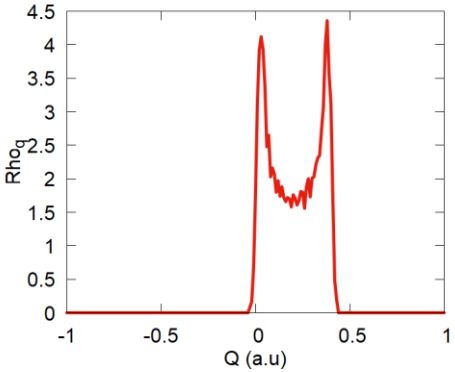


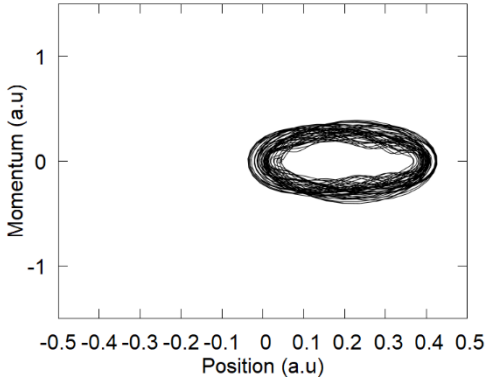


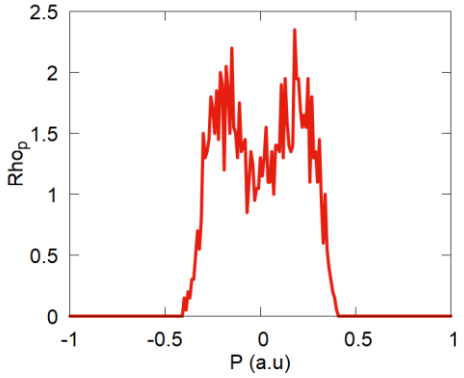


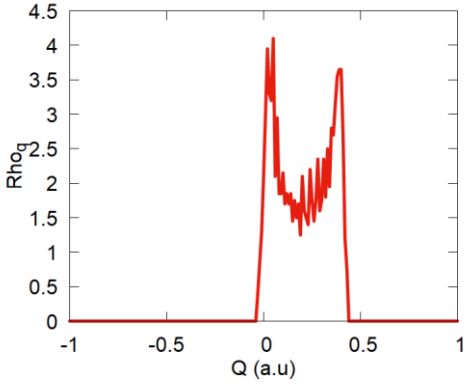






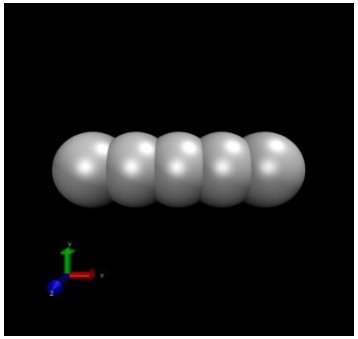


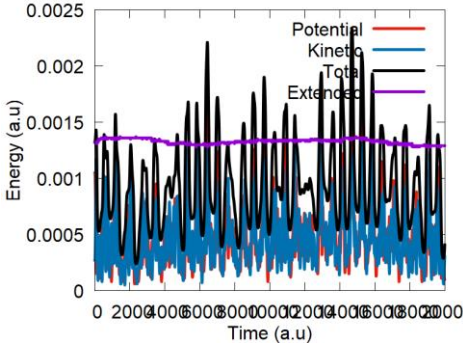


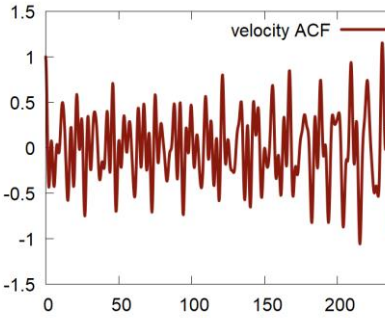


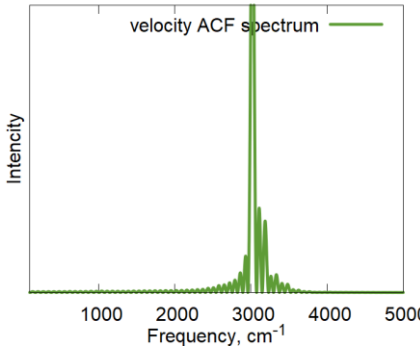
Exercises: Linear chain in NVT ensemble

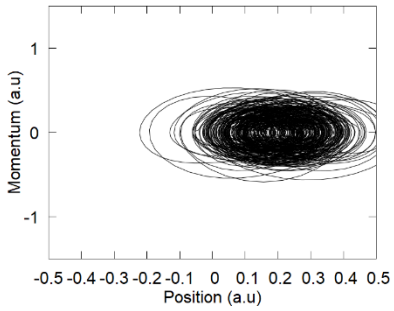
Tut4: NVT

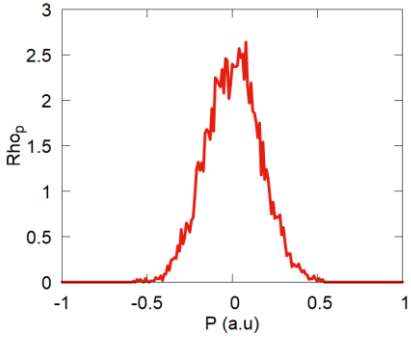


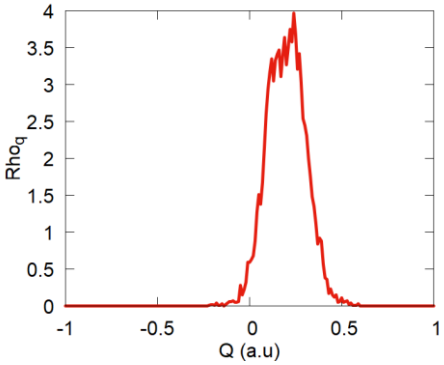


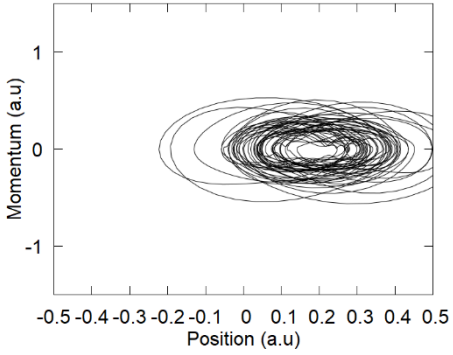


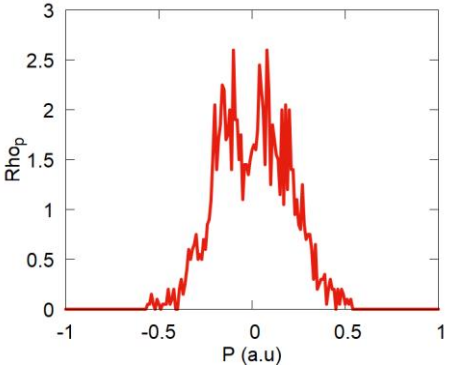


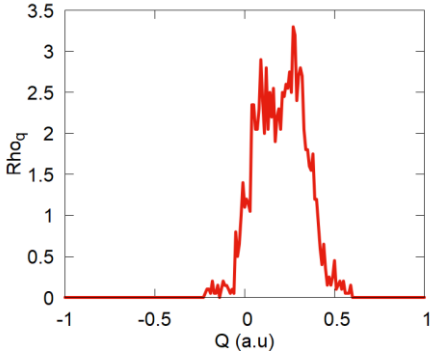






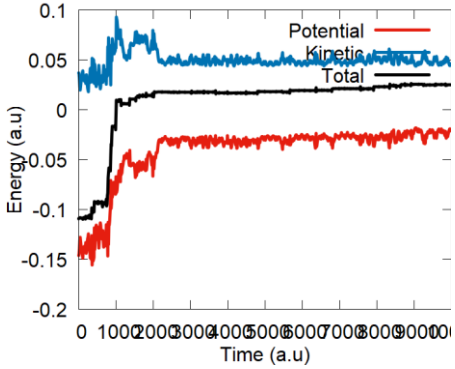


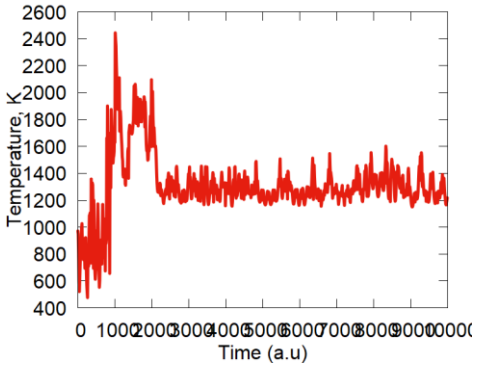


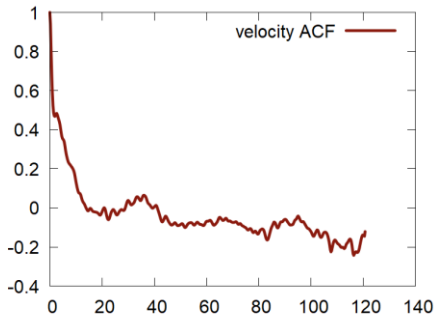


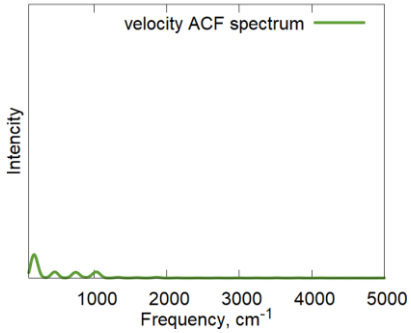
Exercises: Dynamics of LJ cluster

Tut5: NVE of LJ cluster, no thermalization – nve.py





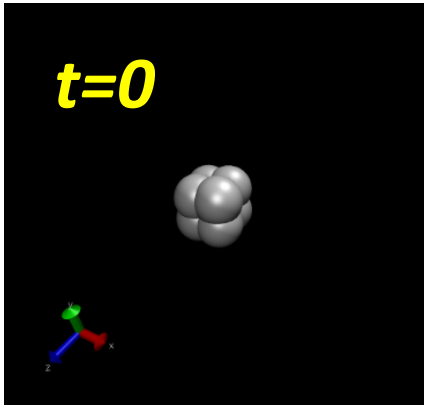


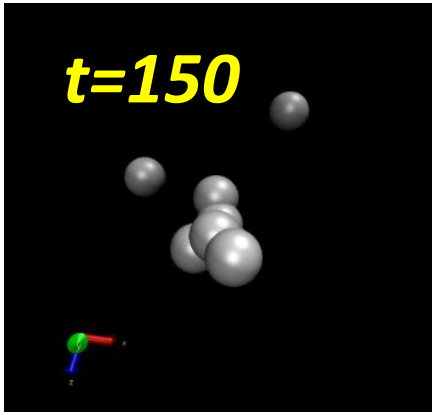


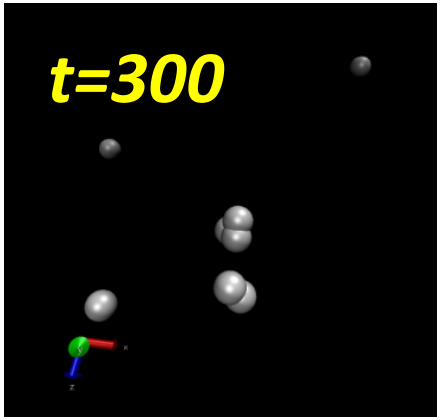
Energy is not conserved!
(phase transitions)

Temperature is high!

Low-frequency modes
are indicative of translational motion

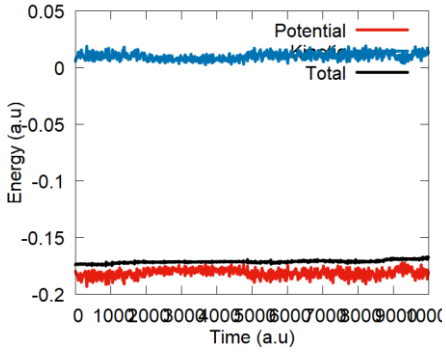


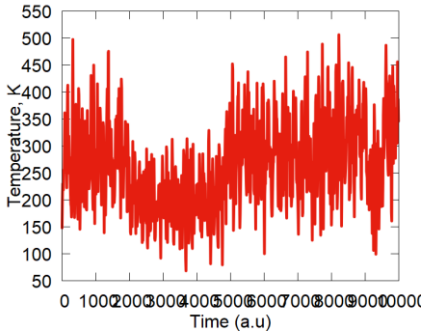


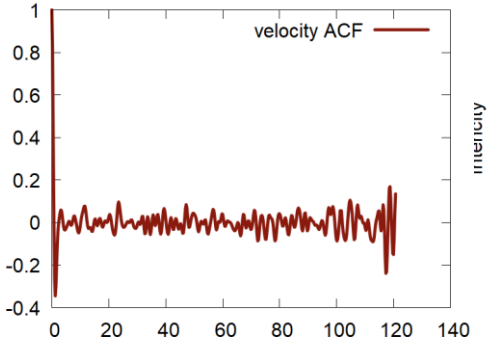


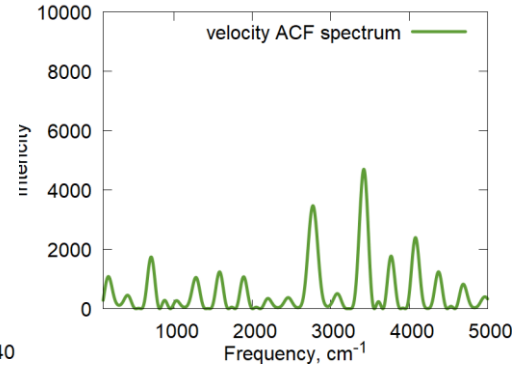
Exercises: Dynamics of LJ cluster

Tut5: NVE of LJ cluster, with thermalization (simulated annealing) – nve2.py





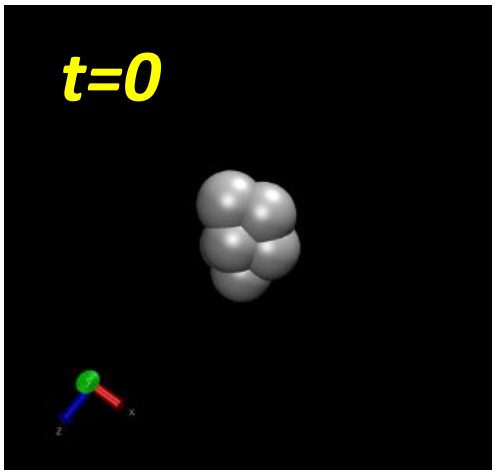


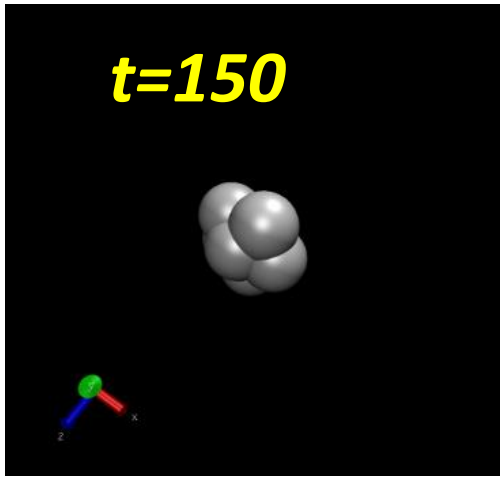


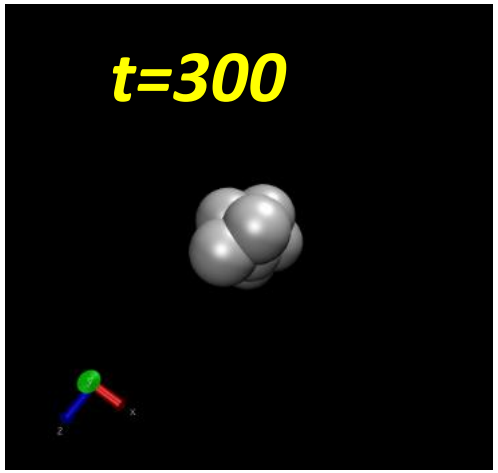
Energy is well conserved!

Temperature is reasonable

Higher-frequency modes are resolved

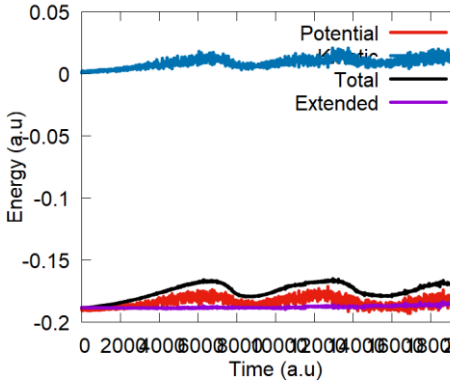


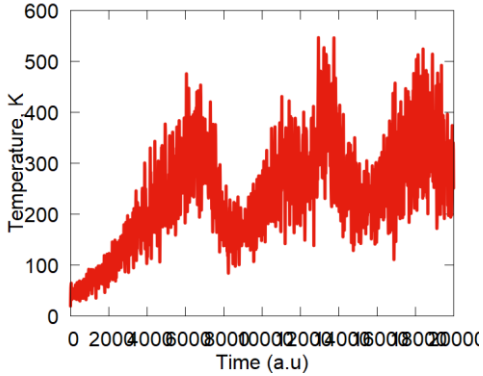


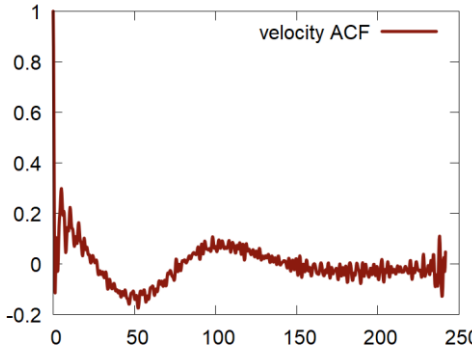


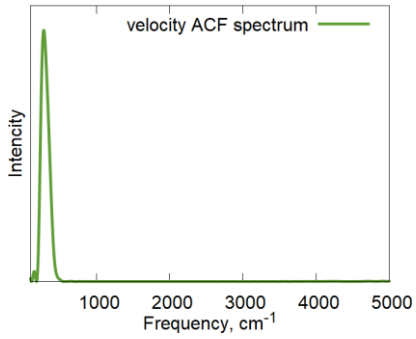
Exercises: Dynamics of LJ cluster

Tut5: NVT of LJ cluster after simulated annealing (nvt.py), slow bath

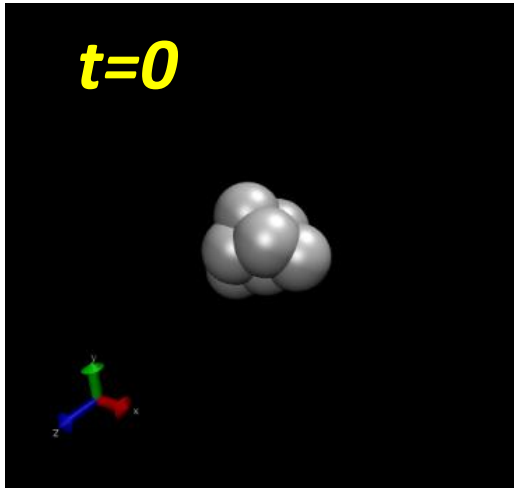


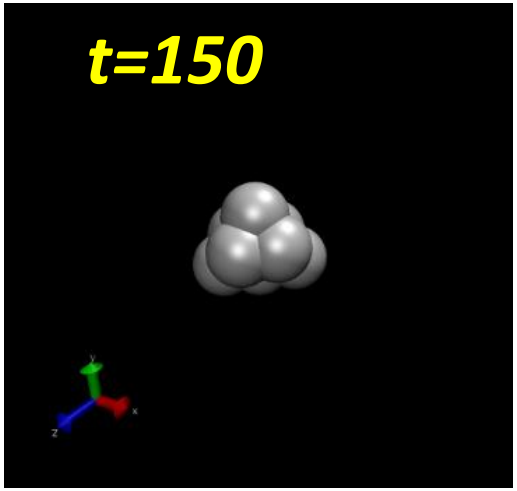


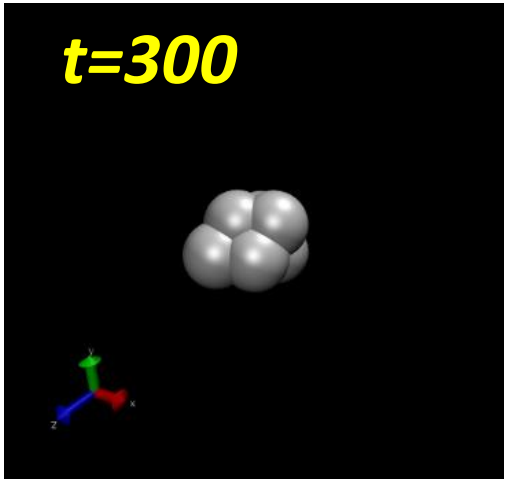




Beware: Bath modes!

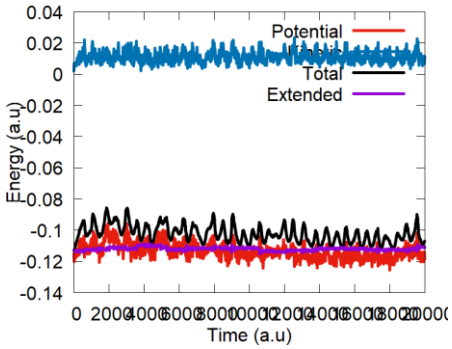


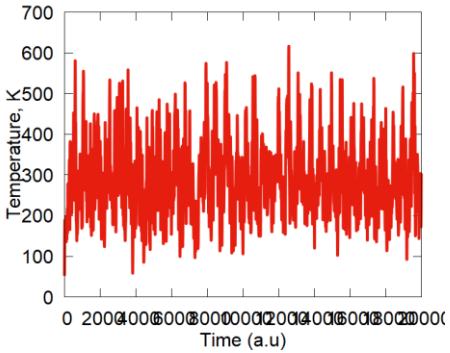


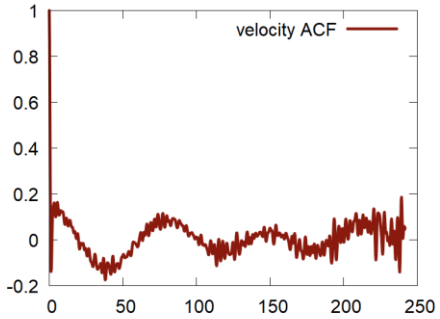


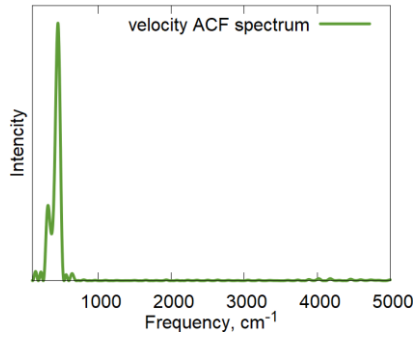
Exercises: Dynamics of LJ cluster

Tut5: NVT of LJ cluster after simulated annealing (nvt.py), fast bath

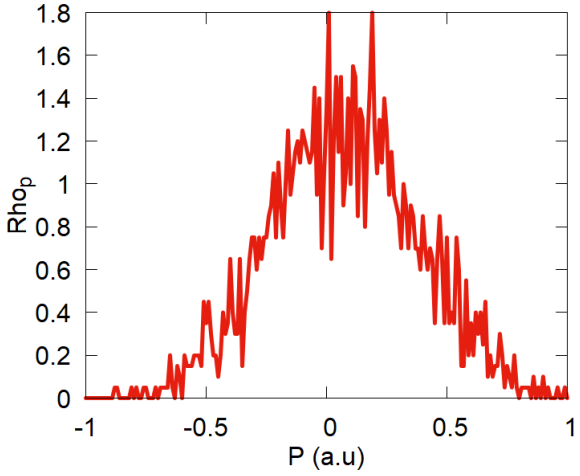


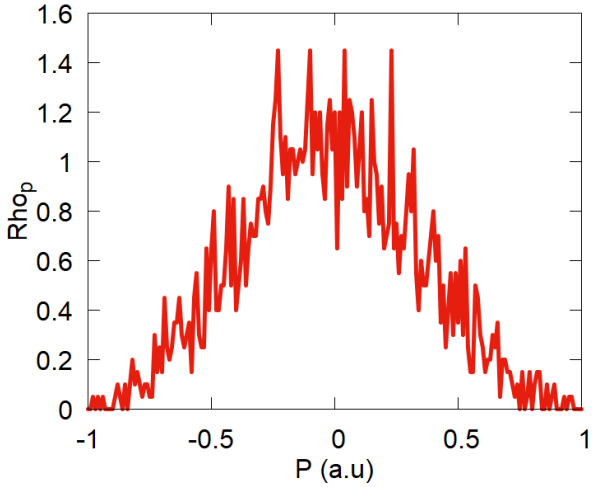






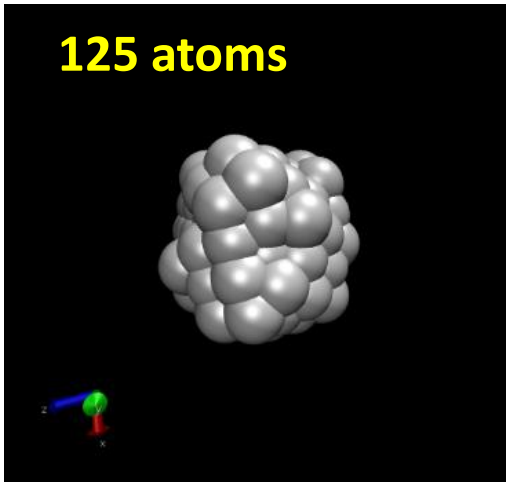
Beware: Bath modes!

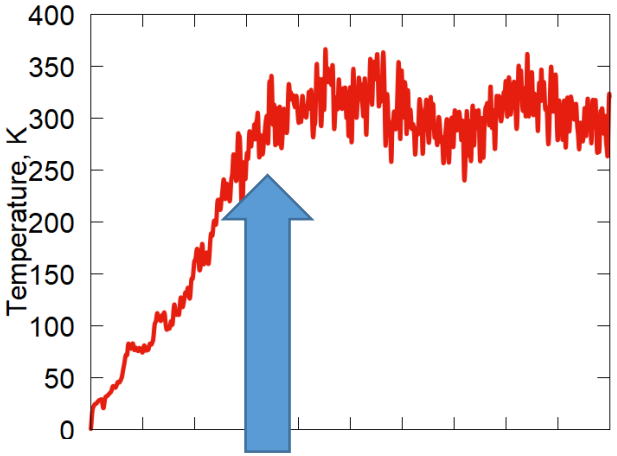


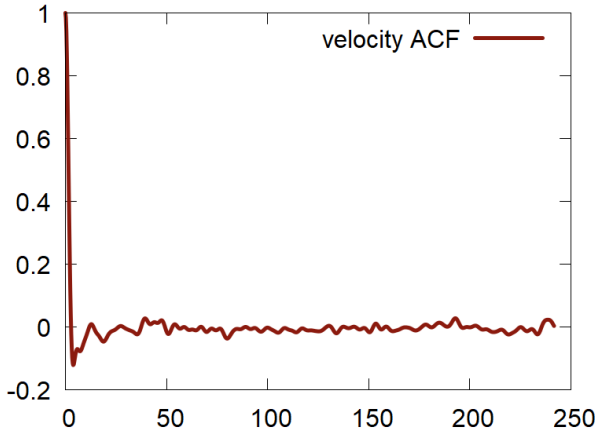


Exercises: Diffusion coefficient, larger cluster

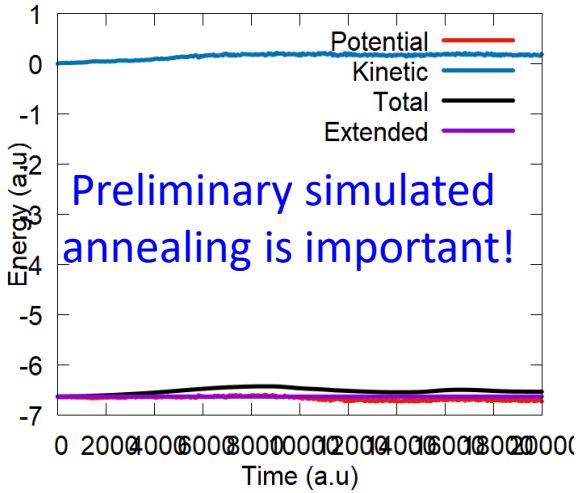
Tut6:

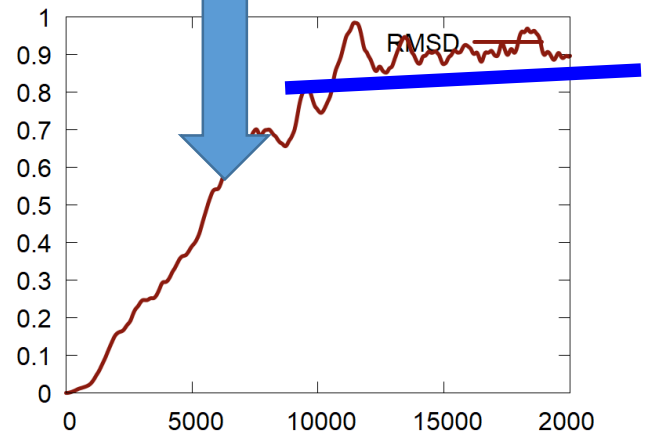


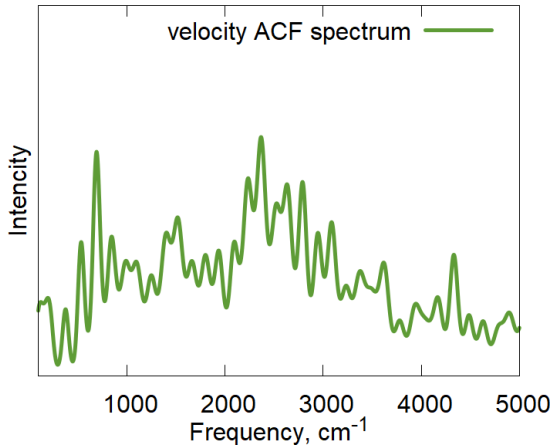




Equilibration period!!!



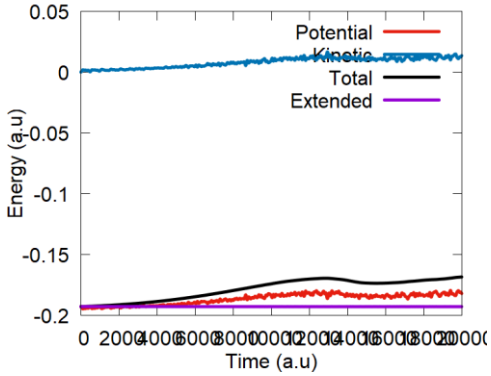


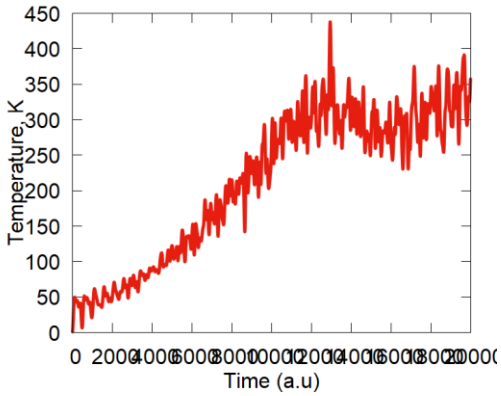


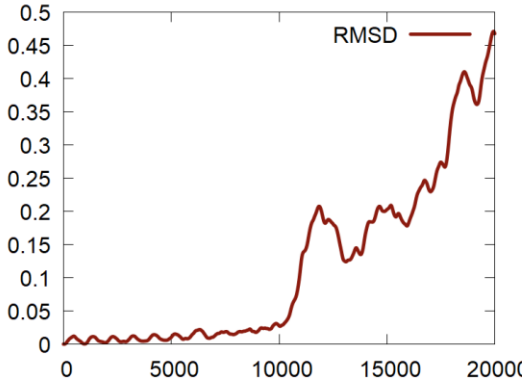
$$D = \frac{\langle |q(t) - q(0)|^2 \rangle}{6t}$$

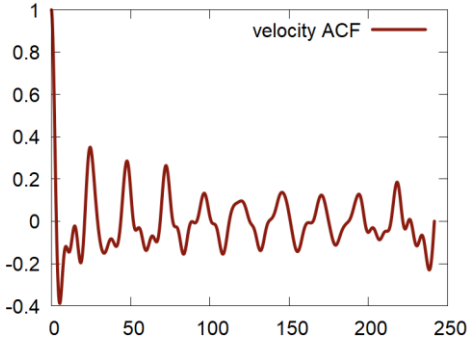
Exercises: Heat capacity

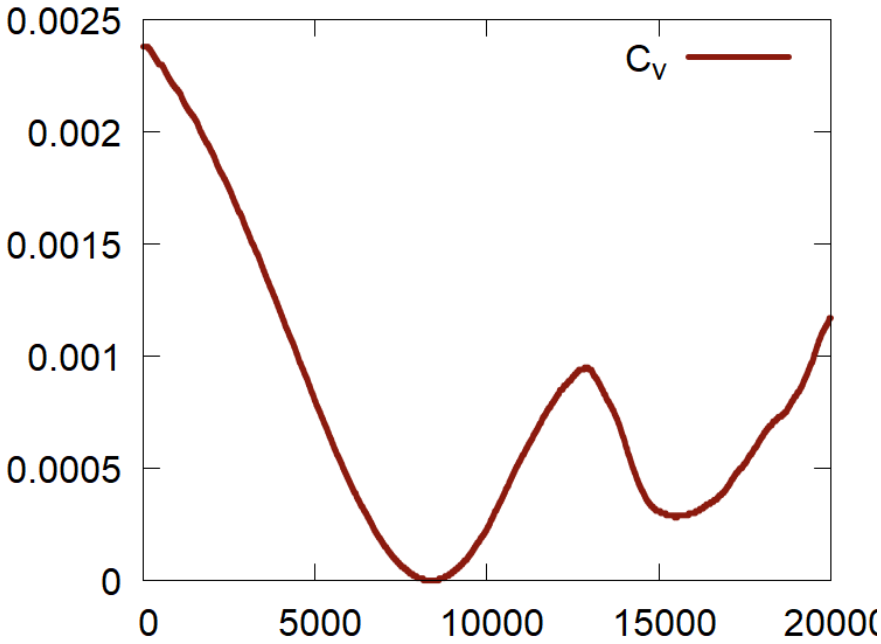
Tut7:

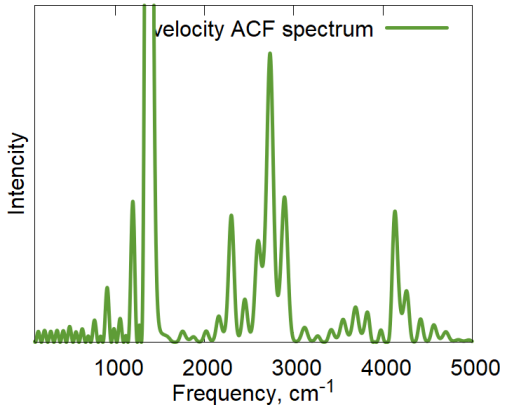












Summary of Tutorials

Tut1 – demonstration of MD for N_{traj} trajectories, each with 1 particle. NVE and NVT

Tut2 – demonstration of computing the ACF and its FT for a predefined sequence

Tut3 – computing ACF for a chain of particles connected by springs

Tut4 – going back to MD, for a chain of atoms.

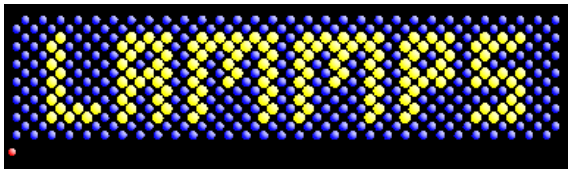
Tut5 – MD of a LJ cluster

Tut6 – MD of a larger LJ cluster, computing diffusion coefficients

Tut7 – MD of a LJ cluster, computing heat capacity

Overview of software

Material Simulations



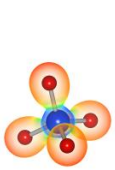
Biological Systems

Molecular Dynamics Simulations
HARMM

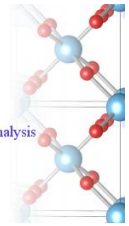
NAMD
Scalable Molecular Dynamics

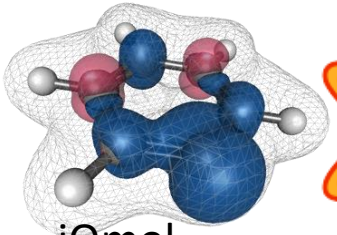
GROMACS
FAST. FLEXIBLE. FREE.

Visualization



VESTA
Visualization for Electronic and STructural Analysis





iQmol

Quantum Calculations