分子動力学法とその応用

Molecular Dynamics and Its Application

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Contents

- Basics of MD simulation
  - Newton equation, purpose of MD simulation
  - Examples of discrete equations and their stabilities
- NVE ensemble: standard MD simulation
  - Symplectic integral
- Control temperature and pressures
  - Velocity scaling, Nosé-Hoover method, …
  - Andersen method

Target: Newtonian mechanics

N-particle system:

$$m_i \frac{d^2 \boldsymbol{r}_i}{dt^2} = \boldsymbol{F}_i(\{\boldsymbol{r}_i\}) \qquad i = 1, 2, \cdots, N$$

e.g.

$$\boldsymbol{F}_i(\{\boldsymbol{r}_i\}) \equiv \sum_{j \neq i} F(|\boldsymbol{r}_i - \boldsymbol{r}_j|)\hat{\boldsymbol{r}}_{ij}$$

Unit vector

$$\hat{\boldsymbol{r}}_{ij} = \frac{\boldsymbol{r}_j - \boldsymbol{r}_i}{|\boldsymbol{r}_j - \boldsymbol{r}_i|}$$

Molecular Dynamics (MD) simulation:

Solve the newton equation numerically

Standard flow of MD simulation

1. Determined the model
   - Potential energies, Constraints (*e.g.* polymers)
   - Periodic boundary, Open boundary, …
2. Prepare initial conditions $\{\boldsymbol{r}_i(t=0), \boldsymbol{v}_i(t=0)\}$
3. Calculate forces acting to all particles $\{\boldsymbol{F}_i(\{\boldsymbol{r}_i(t)\})\}$
4. Change positions and velocities by a discrete method $\{\boldsymbol{r}_i(t+\Delta t), \boldsymbol{v}_i(t+\Delta t)\}$
5. Calculate physical quantities and control them if we need $T(\{\boldsymbol{r}_i(t), \boldsymbol{v}_i(t)\})$, $P(\{\boldsymbol{r}_i(t), \boldsymbol{v}_i(t)\})$, …
   - Constant temperature, Constant pressure, …
6. Analyze trajectories

Periodic boundary condition

A particle interacts with all other particles in “image cells”.

Short-range interaction

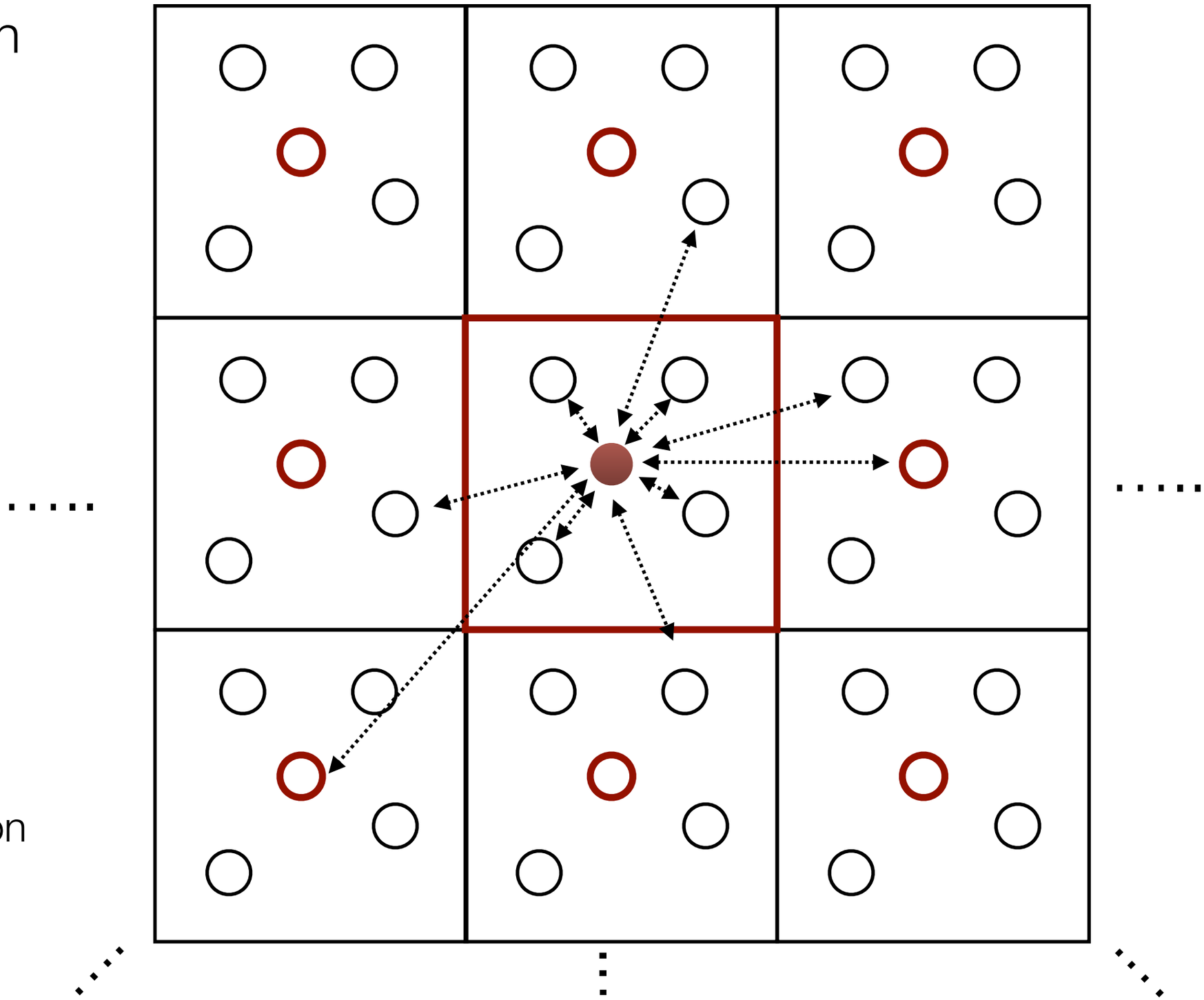
e.g. LJ potential

→ Introduce cut-off

Long-range interaction

e.g. Coulomb potential

→
- Ewald sum
- Multipole expansion



Purpose of MD simulation: Equilibrium properties

By MD simulation, we can calculate equilibrium properties.

Usual newton dynamics give us a NVE ensemble.

$$\langle \hat{O} \rangle_{NVE} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau dt \hat{O}(\Gamma(t))$$

By using temperature or pressure controls, we can also obtain other ensemble averages.

$$\langle \hat{O} \rangle_{NVT} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau dt \hat{O}(\Gamma_{NVT}(t))$$

$$\langle \hat{O} \rangle_{NPT} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau dt \hat{O}(\Gamma_{NPT}(t))$$

Modified dynamics!

Note: For large N limit, difference among ensembles is negligible.

We can use any ensembles for simulation.

Purpose of MD simulation: Equilibrium dynamics

By MD simulation, we can also calculate equilibrium dynamics

$$\langle \hat{A}\hat{B}(\Delta t)\rangle_{NVE} = \lim_{\tau\to\infty}\frac{1}{\tau}\int_0^\tau dt \hat{A}(\Gamma(t))\hat{B}(\Gamma(t+\Delta t))$$

$$\langle \hat{A}\hat{B}(\Delta t)\rangle_{NPT} = \lim_{\tau\to\infty}\frac{1}{\tau}\int_0^\tau dt \hat{A}(\Gamma_{NPT}(t))\hat{B}(\Gamma_{NPT}(t+\Delta t))$$

$$\langle \hat{A}\hat{B}(\Delta t)\rangle_{NVT} = \lim_{\tau\to\infty}\frac{1}{\tau}\int_0^\tau dt \hat{A}(\Gamma_{NVT}(t))\hat{B}(\Gamma_{NVT}(t+\Delta t))$$

Modified dynamics!

Note:

In this case, as far as I know, there is no proof that the modified dynamics for different ensembles give us same results in large N limit.

Probably, it is better to use NVE ensemble, after proper initialization using NPT of NVT dynamics.

Purpose of MD simulation: Non-Equilibrium

We can also calculate non-equilibrium properties using MD

- applying external fields
- observing relaxation from initial conditions

e.g. linear response coefficients

- We can calculation the coefficient from equilibrium simulation by using Kubo formula
- It can be obtained by MD simulation applying the external field
  - Usually the non-equilibrium calculation gives us smaller error

Numerical integration: Basics

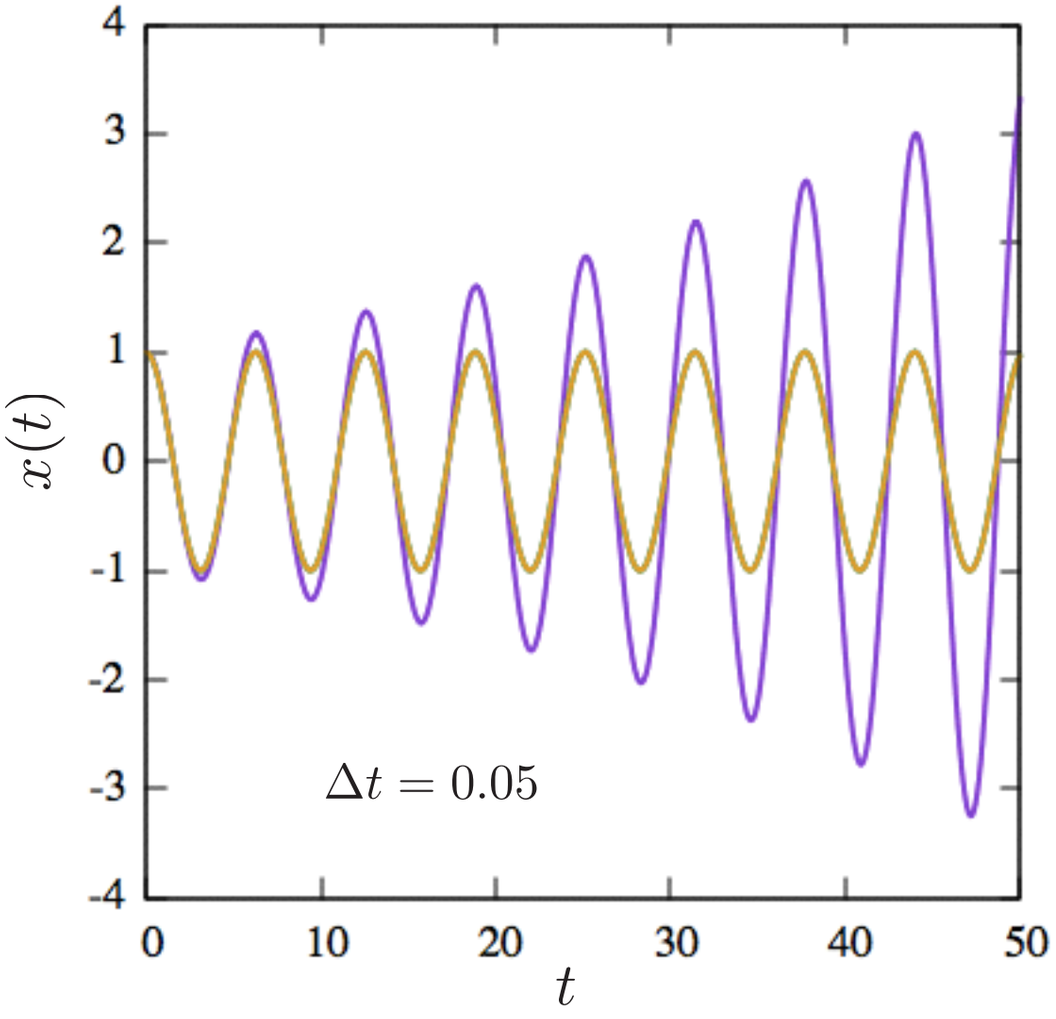
Example: 1d harmonic oscillator

$$\mathcal{H}(x) = \frac{1}{2}x^2 + \frac{1}{2}v^2 \quad \Rightarrow \quad \frac{dv}{dt} = -x, \quad \frac{dx}{dt} = v$$

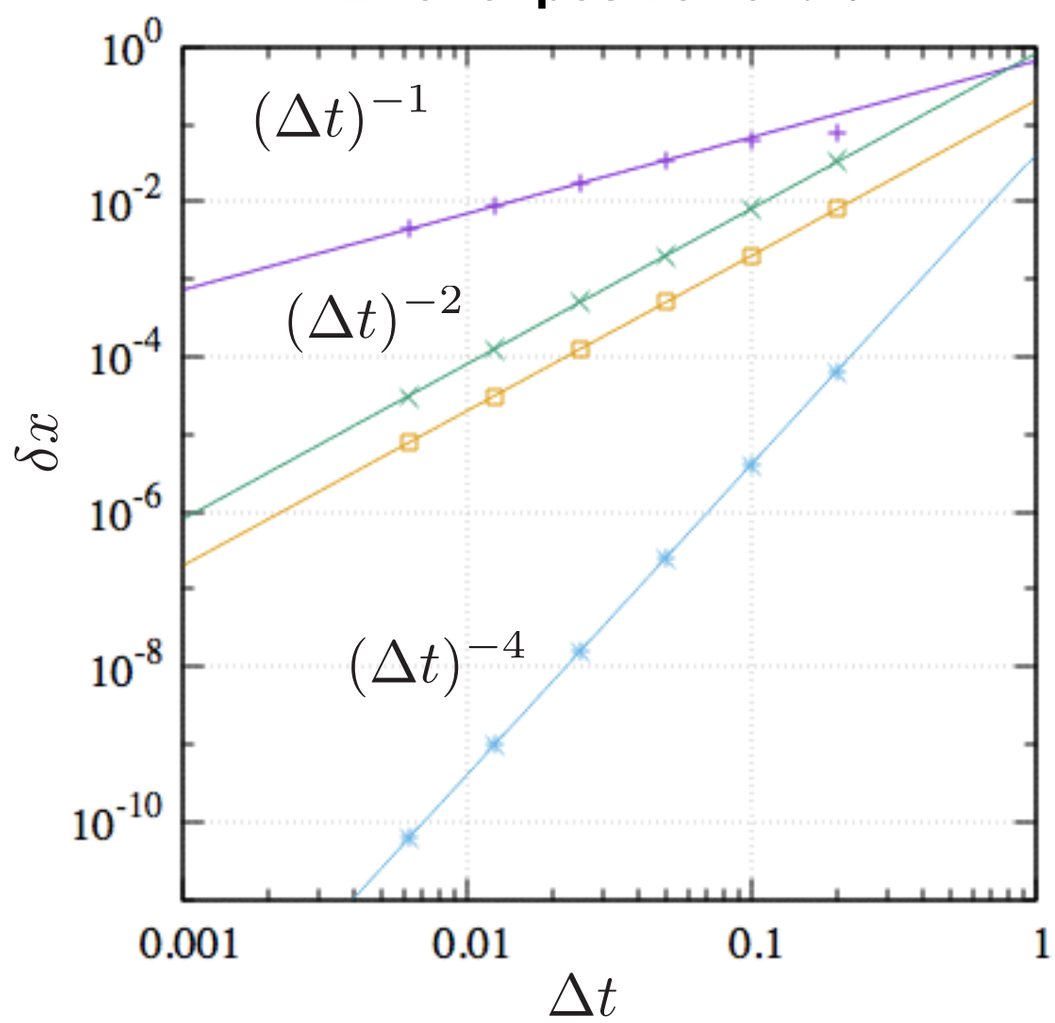
Several explicit methods

Euler
Improved Euler
4th Runge-Kutta
Verlet

Position



Error of position at t=5



Numerical integration: accuracy and cost

Important points for molecular dynamics simulation

- Error
- Stability
- Number of force calculations

Main part of cpu cost

e.g.

$$\boldsymbol{F}_i(\{\boldsymbol{r}_i\}) \equiv \sum_{j \neq i} F(|\boldsymbol{r}_i - \boldsymbol{r}_j|)\hat{\boldsymbol{r}}_{ij}$$

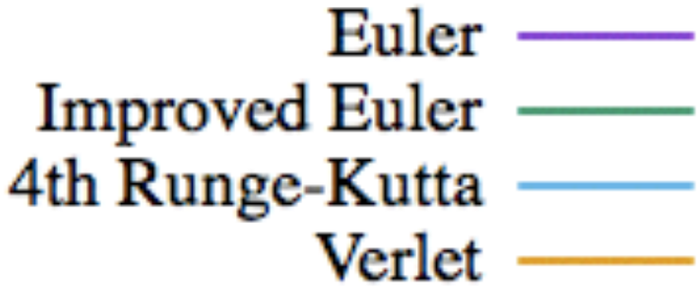
	order of error	#of force calculation	initial condition
Euler	Δt	1	$r(0)$, $v(0)$
Improved Euler	$(\Delta t)^2$	2	$r(0)$, $v(0)$
4th Runge-Kutta	$(\Delta t)^4$	4	$r(0)$, $v(0)$
Verlet	$(\Delta t)^2$	1	$r(0)$, $r(\Delta t)$ (velocity Verlet:$r(0)$, $v(0)$)
Predictor-Corrector	$(\Delta t)^5$	2 (or 1)	$r(0)$, $r'(0)$, $r''(0)$, $r'''(0)$, $r''''(0)$, $r'''''(0)$

Numerical integration: instability (energy drift)

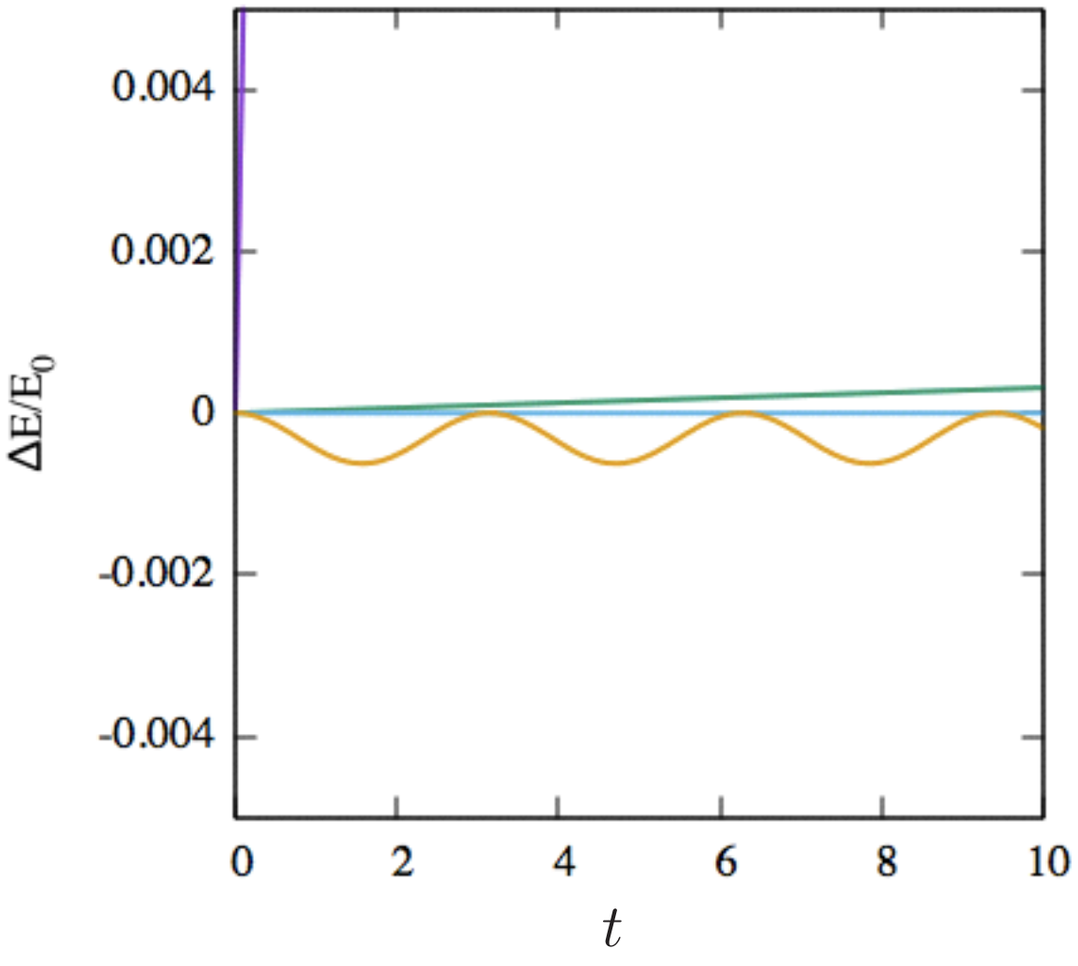
Example: 1d harmonic oscillator

Usual methods shows a drift of energy!
(Predictor-Corrector also shows large energy drift)

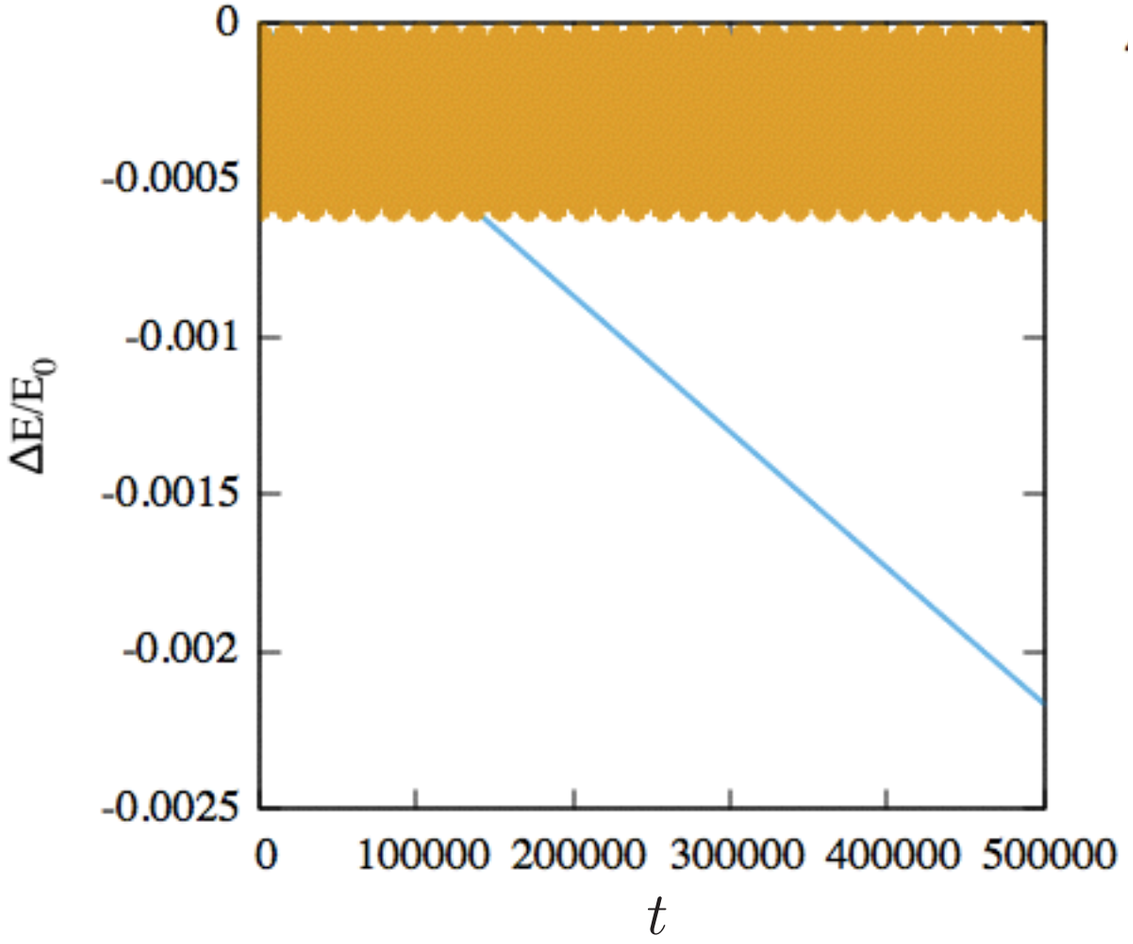
Verlet shows a very small energy drift



Energy error (short time)



Energy error (short time)



Better methods for molecular dynamics simulation

Verlet method:

- Error
  - $(\Delta t)^2 \rightarrow$not bad
- Stability
  - It seems to so stable!
- Number of force calculations
  - Only 1 force calculation for 1 step

Verlet method:

$$\boldsymbol{r}_i(t+\Delta t) = 2\boldsymbol{r}_i(t) - \boldsymbol{r}_i(t-\Delta t) + \frac{(\Delta t)^2}{m_i}\boldsymbol{F}_i(\{\boldsymbol{r}_i(t)\})$$

$$\boldsymbol{v}_i(t) = \frac{\boldsymbol{r}_i(t+\Delta t) - \boldsymbol{r}_i(t-\Delta t)}{2\Delta t}$$

$$m_i \frac{d^2\boldsymbol{r}_i}{dt^2} = \boldsymbol{F}_i(\{\boldsymbol{r}_i\})$$

Velocity Verlet method:

$$\boldsymbol{r}_i(t+\Delta t) = \boldsymbol{r}_i(t) + \Delta t\boldsymbol{v}_i(t) + \frac{(\Delta t)^2}{2m_i}\boldsymbol{F}_i(\{\boldsymbol{r}_i(t)\})$$

$$\boldsymbol{v}_i(t+\Delta t) = \boldsymbol{v}_i(t) + \Delta t\frac{\boldsymbol{F}_i(\{\boldsymbol{r}_i(t)\}) + \boldsymbol{F}_i(\{\boldsymbol{r}_i(t+\Delta t)\})}{2m_i}$$

Leap-frog method:

$$\boldsymbol{r}_i(t+\Delta t) = \boldsymbol{r}_i(t) + \boldsymbol{v}_i\left(t+\frac{\Delta t}{2}\right)\Delta t$$

$$\boldsymbol{v}_i\left(t+\frac{\Delta t}{2}\right) = \boldsymbol{v}_i\left(t-\frac{\Delta t}{2}\right) + \Delta t\frac{\boldsymbol{F}_i(\{\boldsymbol{r}_i(t)\})}{m_i}$$

These methods are basically equivalent.
They are based on the second-order symplectic integration scheme.

NVE ensemble: symplectic integrator

Hamilton mechanics

Hamilton mechanics

$$\mathcal{H}(\{q_i\},\{p_i\}) \Rightarrow \begin{aligned} \frac{dq_i}{dt} &= \frac{\partial \mathcal{H}}{\partial p_i} \\ \frac{dp_i}{dt} &= -\frac{\partial \mathcal{H}}{\partial q_i} \end{aligned}$$

Any quantities: $A(t) = A[\{q_i(t)\},\{p_i(t)\}]$

$$\frac{dA}{dt} = \{A, \mathcal{H}\}$$

Poisson bracket:

$$\{u, v\} = \sum_i \left(\frac{\partial u}{\partial q_i}\frac{\partial v}{\partial p_i} - \frac{\partial u}{\partial p_i}\frac{\partial u}{\partial p_i} \right)$$

Liouville operator: $i\mathcal{L} = \{\quad, \mathcal{H}\}$

$$\frac{dA}{dt} = i\mathcal{L}A \Rightarrow A(t) = e^{it\mathcal{L}}A(0)$$

Unitary operator

Liouville's theorem

Distribution function: $\rho(\{q_i\}, \{p_i\}; t)$

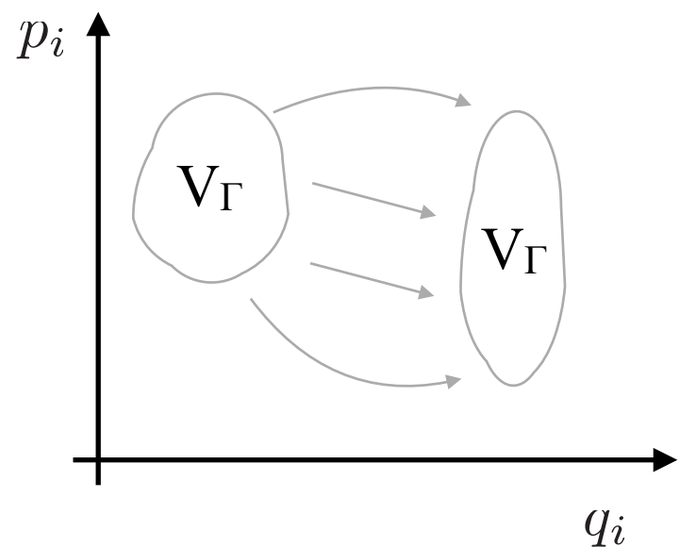
Liouville equation

$$\frac{\partial \rho}{\partial t} = \{\mathcal{H}, \rho\} = -i\mathcal{L}\rho$$

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_i \left(\frac{\partial \rho}{\partial q_i}\frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\frac{\partial \mathcal{H}}{\partial q_i} \right) = \frac{\partial \rho}{\partial t} + i\mathcal{L}\rho = 0$$

Liouville's theorem

Along Hamilton mechanics,
the volume in phase space is conserved.



Symplectic condition

$$\boldsymbol{\Gamma} = (\{q_i\}, \{p_i\}) = (\boldsymbol{q}, \boldsymbol{p})$$

Canonical transform: $\boldsymbol{\Gamma} \to \boldsymbol{\Gamma}' = (\boldsymbol{q}'(\boldsymbol{q}, \boldsymbol{p}), \boldsymbol{p}'(\boldsymbol{q}, \boldsymbol{p}))$

Canonical transform satisfy the symplectic condition:

$$SJS^T = J$$

$$S_{ij} = \frac{\partial \Gamma_i'}{\partial \Gamma_j} \quad , \quad J = \begin{pmatrix} \mathbf{1} & 0 \\ 0 & -\mathbf{1} \end{pmatrix}$$

Hamiltonian dynamics can be seen as a canonical transform.

$$\Gamma(\boldsymbol{q}(t), \boldsymbol{p}(t)) \to \Gamma'(\boldsymbol{q}(t + \Delta t), \boldsymbol{p}(t + \Delta t))$$

Exact Hamiltonian dynamics satisfy the symplectic condition.

*The symplectic condition contains Liouville's theorem

Symplectic integrator

Symplectic integrator:

Discrete approximation of Hamilton dynamics
satisfying the symplectic condition

$$e^{it\mathcal{L}} \simeq \dots$$

→ Because the volume of phase space is conserved,
the energy does not drift along this dynamics
(if there is no numerical error)

If the Hamiltonian can be decomposed, for example

$$\mathcal{H} = K(\{p_i\}) + V(\{q_i\})$$
$$i\mathcal{L} = i\mathcal{L}_K + i\mathcal{L}_V$$

→ There is a systematic derivation of
symplectic integrators

Decomposition of exponential operator

Symplectic integrator:

$$e^{it\mathcal{L}} = \prod_{k=1}^{n} \left[e^{ia_k t\mathcal{L}_K} e^{ib_k t\mathcal{L}_V} \right] + O(t^{n+1})$$

$$\sum_{k=1}^{n} a_k = \sum_{k=1}^{n} b_k = 1$$

$$\mathcal{H} = K(\{p_i\}) + V(\{q_i\})$$

$$i\mathcal{L} = i\mathcal{L}_K + i\mathcal{L}_V$$

Note: $e^{ia_k t\mathcal{L}_K}, e^{ia_k t\mathcal{L}_V}$ satisfy the symplectic condition

n=1 $e^{it\mathcal{L}} \simeq e^{it\mathcal{L}_K} e^{it\mathcal{L}_V}$

$$q(t+\Delta t) = q(t) + p(t)\delta t$$
$$p(t+\Delta t) = p(t) + F(q(t+\Delta))\delta t$$

Euler like equation
(but this is more stable!)

n=2 $e^{it\mathcal{L}} \simeq e^{i\frac{t}{2}\mathcal{L}_K} e^{it\mathcal{L}_V} e^{i\frac{t}{2}\mathcal{L}_K}$

$$p(t+\frac{\Delta t}{2}) = p(t) + F(q(t))\frac{\Delta t}{2}$$
$$q(t+\Delta t) = q(t) + p(t+\frac{\Delta t}{2})\Delta t$$
$$p(t+\Delta t) = p(t+\frac{\Delta t}{2}) + F(q(t+\Delta))\frac{\Delta t}{2}$$

Exactly equal to
(Velocity) Verlet method

Control temperature and pressure

Temperature control: velocity scaling

The most simplest method for temperature setting: **Velocity Scaling**

(L. V. Woodcock, Chem. Phys. Lett. **10** ,257 (1971).)

Total kinetic energy: $K = \sum_i \frac{\boldsymbol{p}_i^2}{2m_i}$

Under the canonical (NVT) ensemble

$$\langle K \rangle = \frac{3}{2} N k_B T$$ (Equipartition of energy in 3d)

➡ Define effective temperature of a snapshot:

$$T_{\text{eff}} \equiv \frac{2K}{3Nk_B}$$

Rescale velocities every time step as

$$\boldsymbol{p}_i' = \boldsymbol{p}_i \sqrt{\frac{T}{T_{\text{eff}}}} \quad \Rightarrow \quad K' = \frac{3}{2} N k_B T$$

Results of the velocity scaling

Total kinetic energy is artificially fixed to

$$K = \frac{3}{2} N k_B T$$

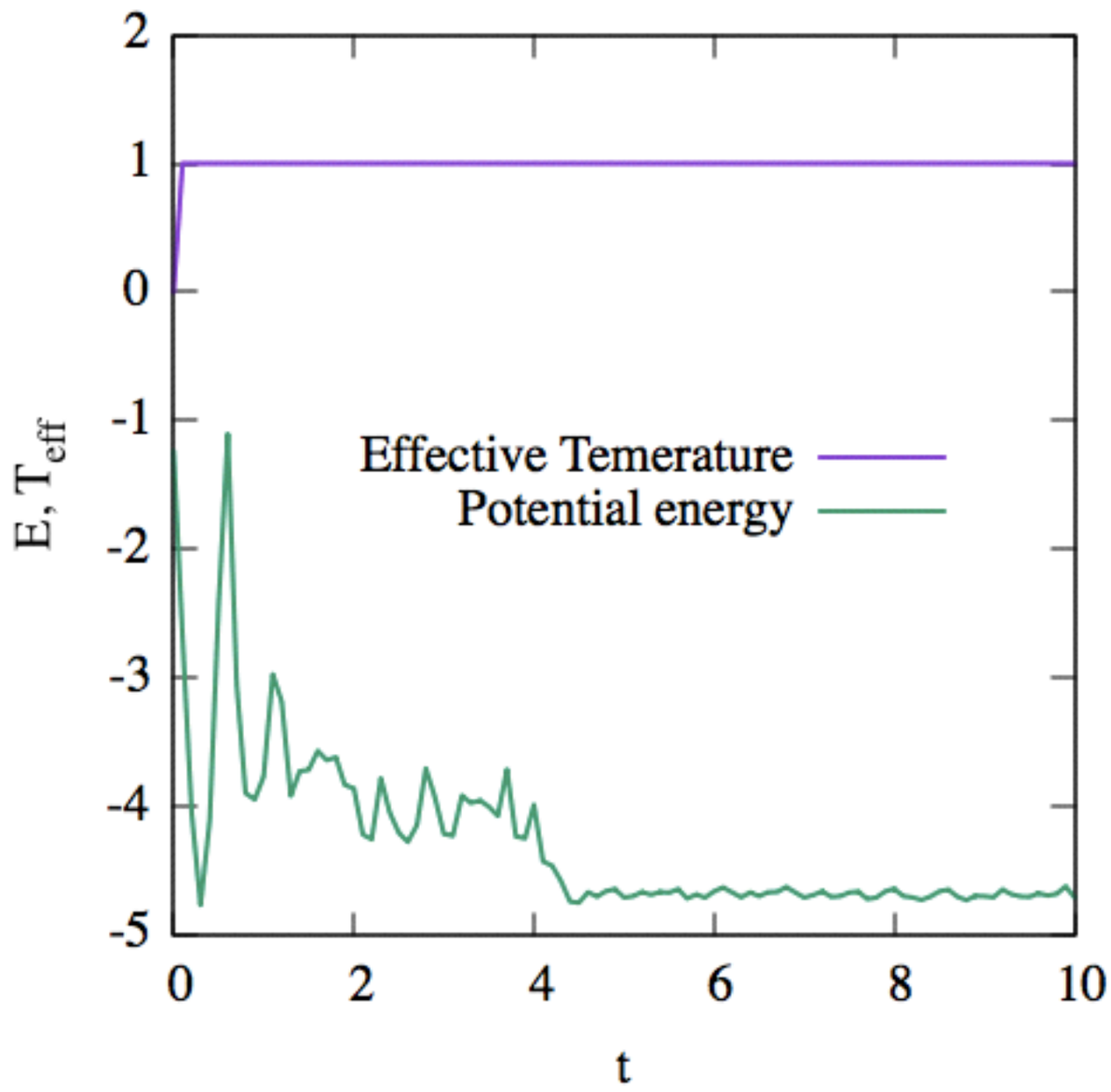
Under velocity scaling dynamics,
the trajectories do not
necessarily obey
the canonical ensemble.

However,

- We can use it for an initialization for NVE ensemble
- Position fluctuation could be effectively similar to that of NVT ensemble

MD of LJ system with velocity scaling

($\Delta t = 0.01$, N=1000, ρ=0.8, T=1)



Temperature control: Langevin dynamics

Langevin dynamics

$$\frac{d\boldsymbol{p}_i}{dt} = \boldsymbol{F}_i(\{\boldsymbol{q}_i\}) \underline{- \gamma \boldsymbol{p}_i} + \underline{\boldsymbol{R}_i}$$

Dissipation

Random force

(Gaussian white noise)

$$\langle \boldsymbol{R}_i(t) \rangle = \boldsymbol{0}$$

$$\langle \boldsymbol{R}_i(0) \boldsymbol{R}_j(t) \rangle = 2D_i \delta_{ij} \delta(t)$$

Long-time average of Langevin dynamics becomes
the canonical ensemble with temperature T,
if random forces satisfy the relation

$$D_i = \frac{k_B T}{m_i \gamma}$$

Einstein relation

Fluctuation-dissipation theorem

Temperature control: Nosé thermostad

Nose thermostad S. Nosé, Mol. Phys., **52**, 255 (1984). S. Nosé, J. Chem. Phys., **81**, 511 (1984).

Extended Hamiltonian System with a "heat bath"

$$\mathcal{H}_N = \sum_i \frac{(\boldsymbol{p}_i')^2}{2m_i s^2} + V(\{\boldsymbol{q}_i\}) + \frac{P_s^2}{2Q} + gk_BT\ln s$$

Original Hamiltonian with scaled momentum

$$\mathcal{H}\left(\left\{\frac{\boldsymbol{p}_i'}{s}\right\}, \{\boldsymbol{q}_i\}\right)$$

Heat-bath

s: scale factor for time

$$t' = st$$
$$\boldsymbol{p}_i' = s\boldsymbol{p}_i$$

Canonical equation

$$\frac{d\boldsymbol{p}_i'}{dt'} = -\frac{\partial V}{\partial \boldsymbol{q}_i} = \boldsymbol{F}_i(\{\boldsymbol{q}_i\}) \qquad \frac{dP_s}{dt'} = \frac{1}{s}\left(\sum_i \frac{(\boldsymbol{p}_i')^2}{m_i s^2} - gk_BT\right)$$

$$\frac{d\boldsymbol{q}_i}{dt'} = \frac{\boldsymbol{p}_i'}{m_i s^2} \qquad \frac{ds}{dt'} = \frac{P_s}{Q}$$

Temperature control: Nosé-Hoover method

Nosé-Hoover dynamics

Real-time dynamics with $\zeta = \dfrac{ds}{dt'}$ (W. G. Hoover, Phys. Rev. A, **31**, 1695 (1985).)

$$\boldsymbol{p}_i = \frac{\boldsymbol{p}_i'}{s} \qquad t = \frac{t'}{s}$$

$$\frac{d\boldsymbol{q}_i}{dt} = \frac{\boldsymbol{p}_i}{m_i}$$

$$\frac{d\boldsymbol{p}_i}{dt} = \boldsymbol{F}_i(\{\boldsymbol{q}_i\}) - \zeta \boldsymbol{p}_i$$

$$\frac{d\zeta}{dt} = \frac{gk_B}{Q}\left[\frac{1}{gk_B}\sum_i \frac{\boldsymbol{p}_i^2}{2m_i} - T\right] = \frac{1}{\tau^2}\left[T_{\mathrm{eff}} - T\right]$$

$g = 3N$ (# of DOF)

$\tau^2 = \dfrac{Q}{gk_B}$ (characteristic time scale)

New degree of freedom represents viscosity: ζ

➡ It changes the sign depending on the difference between the effective temperature and the aimed temperature.

(It also accelerates the velocity if $T_{\mathrm{eff}} < T$)

* This dynamics is not symplectic. ➡ Symplectic version: Nosé-Poincare method

S. D. Bond, *et.al.* J. Comp. Phys. **151**, 114 (1999)

Nosé-Hoover dynamics becomes NVT ensemble

Short proof:

(Based on Hisashi Okumura's review paper,
"分子動力学シミュレーションにおける温度・圧力制御")

$$\mathcal{H}_N = \mathcal{H}\left(\left\{\frac{\boldsymbol{p}'_i}{s}\right\}, \{\boldsymbol{q}_i\}\right) + \frac{P_s^2}{2Q} + gk_BT\ln s$$

MD on (q, p',t') dynamics yields NVE ensemble of H_N

$$\lim_{\tau'\to\infty}\frac{1}{\tau'}\int_0^{\tau'} dt' O(\{\frac{\boldsymbol{p}'_i}{s}\},\{\boldsymbol{q}_i\}) = \frac{\int d\boldsymbol{p}'_i d\boldsymbol{q}_i dP_s ds O(\{\frac{\boldsymbol{p}'_i}{s}\},\{\boldsymbol{q}_i\})\delta(E-\mathcal{H}_N)}{\int d\boldsymbol{p}'_i d\boldsymbol{q}_i dP_s ds \delta(E-\mathcal{H}_N)}$$

$$= \frac{\int d\boldsymbol{p}_i d\boldsymbol{q}_i dP_s ds s^{3N} O(\{\boldsymbol{p}_i\},\{\boldsymbol{q}_i\})\delta(E-\mathcal{H}-\frac{P^2}{2Q}-gk_BT\ln s)}{\int d\boldsymbol{p}_i d\boldsymbol{q}_i dP_s ds s^{3N}\delta(E-\mathcal{H}-\frac{P^2}{2Q}-gk_BT\ln s)}$$

from $$\int ds s^{3N}\delta(E-\mathcal{H}-\frac{P^2}{2Q}-gk_BT\ln s) = \frac{1}{gk_BT}e^{-\frac{3N+1}{gk_BT}(\mathcal{H}+\frac{P^2}{2Q}-E)}$$

$$= \frac{\int d\boldsymbol{p}_i d\boldsymbol{q}_i O(\{\boldsymbol{p}_i\},\{\boldsymbol{q}_i\}) e^{-\frac{3N+1}{gk_BT}\mathcal{H}}}{\int d\boldsymbol{p}_i d\boldsymbol{q}_i e^{-\frac{3N+1}{gk_BT}\mathcal{H}}}$$

$$\delta(f(x)) = \frac{\delta(x-x_0)}{|f'(x_0)|} \qquad (f(x_0)=0)$$

Canonical ensemble if $g = 3N+1$

Nosé-Hoover dynamics becomes NVT ensemble 2

Time average on t

$$\lim_{\tau\to\infty}\frac{1}{\tau}\int_0^{\tau} dtO(\{\boldsymbol{p}_i\},\{\boldsymbol{q}_i\}) = \lim_{\tau\to\infty}\frac{\tau'}{\tau}\frac{1}{\tau'}\int_0^{\tau'} dt'\frac{O(\{\boldsymbol{p}_i\},\{\boldsymbol{q}_i\})}{s}$$

from $\boxed{\tau = \int_0^{\tau'}\frac{1}{s}dt'}$

$$= \frac{\lim_{\tau'\to\infty}\frac{1}{\tau'}\int_0^{\tau'} dt'\frac{O(\{\boldsymbol{p}_i\},\{\boldsymbol{q}_i\})}{s}}{\lim_{\tau'\to\infty}\frac{1}{\tau'}\int_0^{\tau'} dt'\frac{1}{s}}$$

$$= \frac{\int d\boldsymbol{p}_i d\boldsymbol{q}_i O(\{\boldsymbol{p}_i\},\{\boldsymbol{q}_i\})e^{-\frac{3N}{gk_BT}\mathcal{H}}}{\int d\boldsymbol{p}_i d\boldsymbol{q}_i e^{-\frac{3N}{gk_BT}\mathcal{H}}}$$

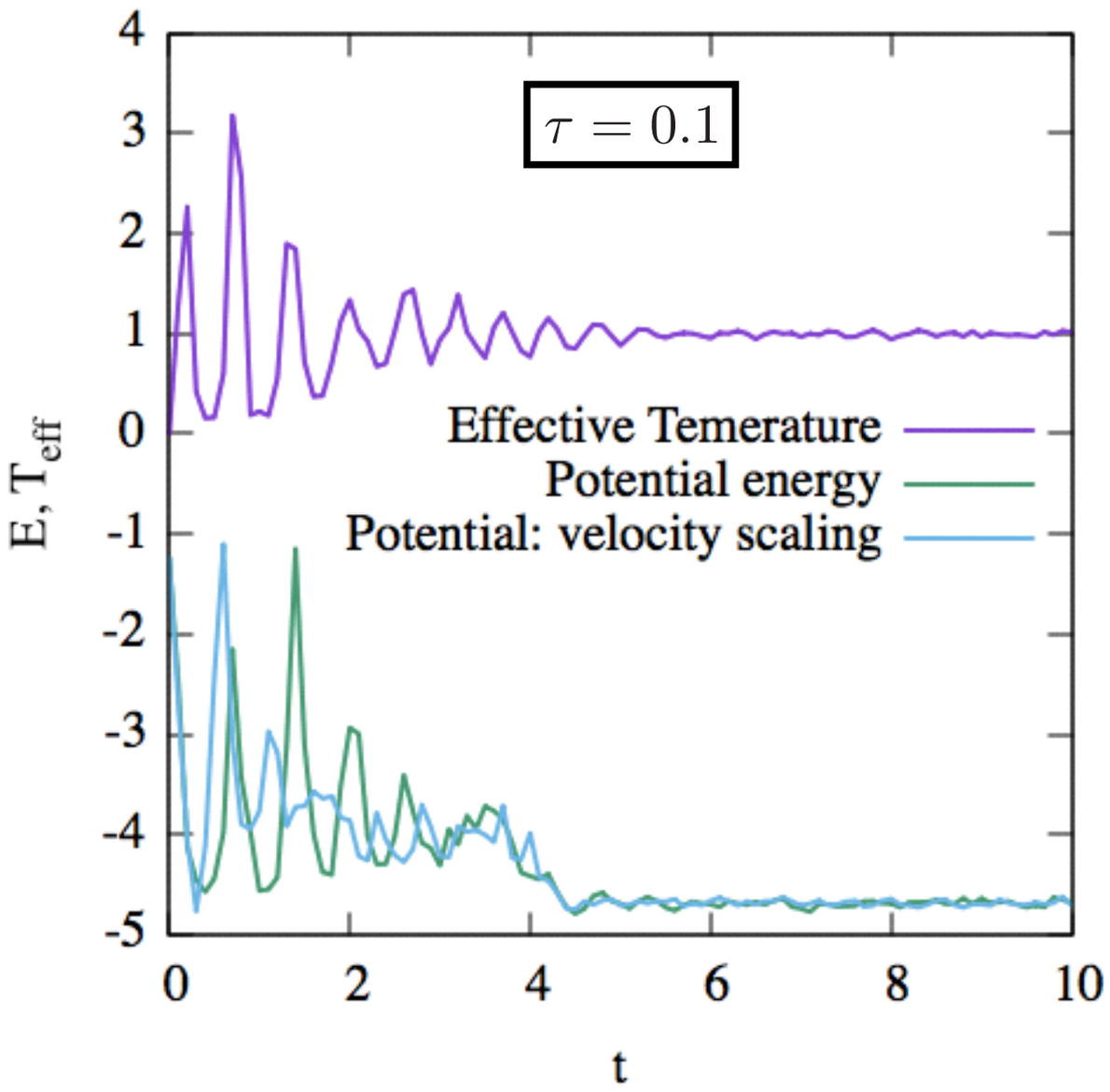
Canonical ensemble if $g = 3N$

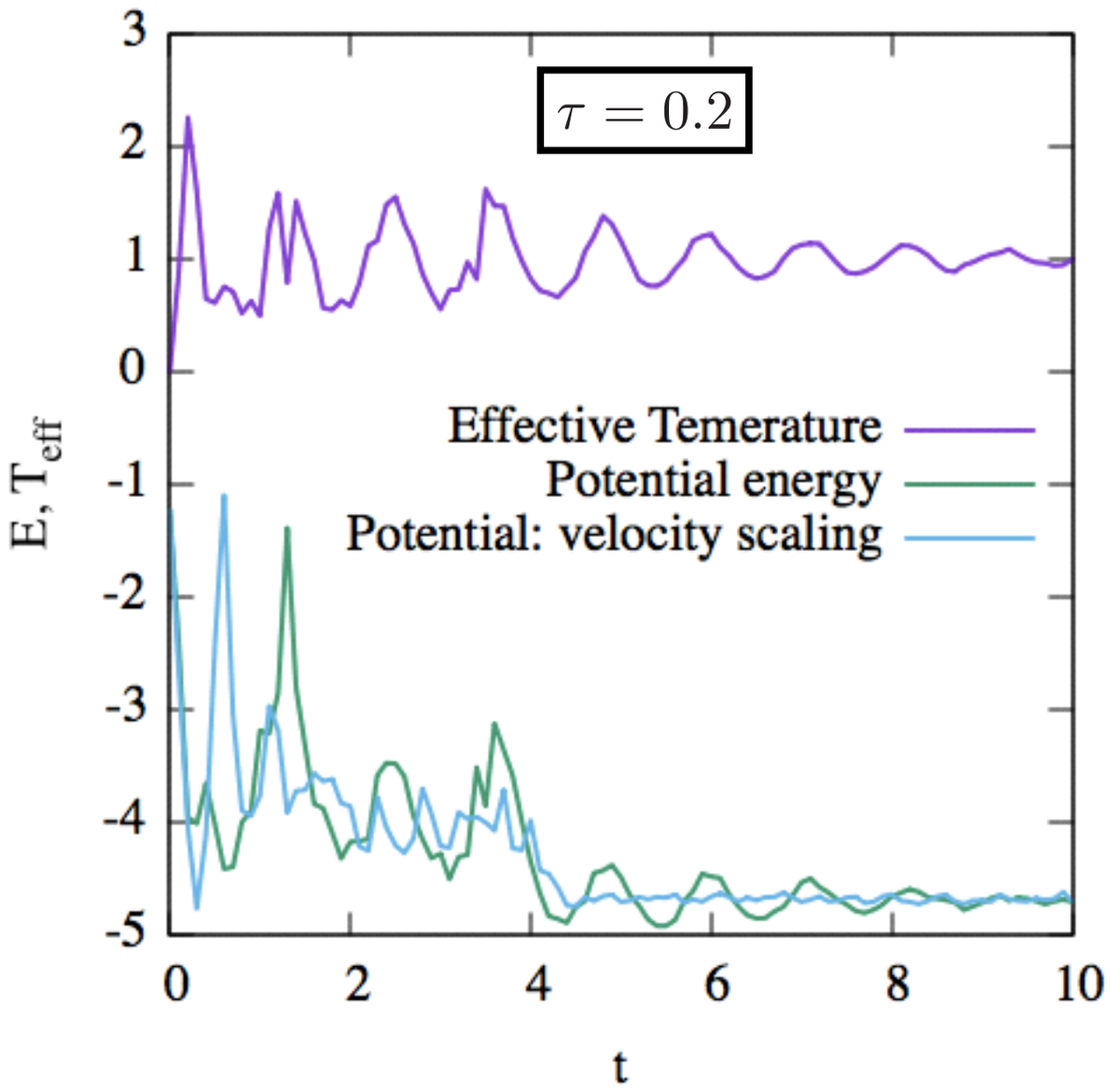
Results of the Nose-Hoover dynamics

- Temperature behaves like damped oscillation.
  - Period is related to τ (or Q)
- Potential energy converges almost same value with that of velocity scaling.

MD of LJ system

($\Delta t = 0.01$, N=1000, ρ=0.8, T=1)





Pressure control: Andersen method

H. C. Andersen, J. Chem. Phys. **72** (1980) 2384.

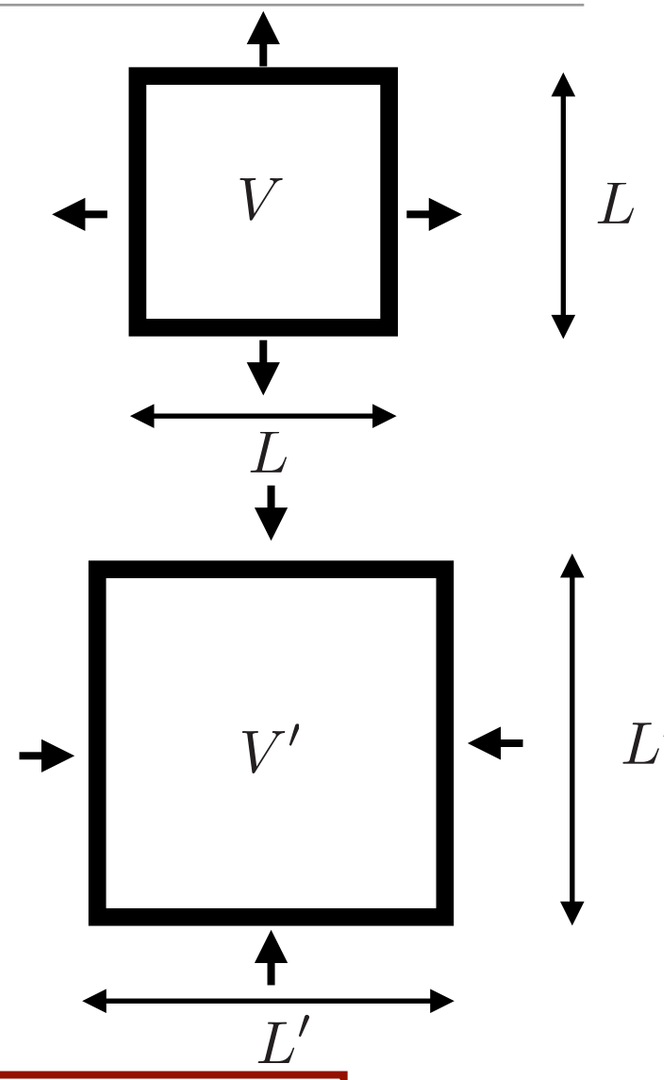
Extended Hamiltonian System with a "piston"

$$\mathcal{H}_A = \sum_i \frac{\tilde{\boldsymbol{p}}_i^2}{2m_i V^{\frac{2}{3}}} + V(\{V^{\frac{1}{3}}\tilde{\boldsymbol{q}}_i\}) + \frac{P_V}{2M} + PV$$

Original Hamiltonian with scaled coordinate and momentum

Piston

$$\tilde{\boldsymbol{q}}_i = V^{-\frac{1}{3}}\boldsymbol{q}_i$$
$$\tilde{\boldsymbol{p}}_i = V^{\frac{1}{3}}\boldsymbol{p}_i$$



Canonical equation

$$\frac{d\tilde{\boldsymbol{q}}_i}{dt} = \frac{\tilde{\boldsymbol{p}}_i}{m_i V^{\frac{2}{3}}} \qquad \frac{dV}{dt} = \frac{P_V}{M}$$

$$\frac{d\tilde{\boldsymbol{p}}_i}{dt} = V^{\frac{1}{3}}\boldsymbol{F}_i(\{V^{\frac{1}{3}}\tilde{\boldsymbol{q}}_i\}) \qquad \frac{dP_V}{dt} = \frac{1}{3V}\sum_i \left[\frac{{\tilde{\boldsymbol{p}}_i}^2}{m_i V^{\frac{2}{3}}} + \boldsymbol{F}_i \cdot (V^{\frac{1}{3}}\tilde{\boldsymbol{q}}_i)\right] - P$$

Pressure control: Andersen method

H. C. Andersen, J. Chem. Phys. **72** (1980) 2384.

In original coordinates

$$\frac{d\boldsymbol{q}_i}{dt} = \frac{\boldsymbol{p}_i}{m_i} + \frac{\dot{V}}{3V}\boldsymbol{q}_i \qquad \frac{dV}{dt} = \frac{P_V}{M}$$

$$\frac{d\boldsymbol{p}_i}{dt} = \boldsymbol{F}_i - \frac{\dot{V}}{3V}\boldsymbol{p}_i \qquad \frac{dP_V}{dt} = \underline{\frac{1}{3V}\sum_i \left[\frac{\boldsymbol{p}_i^2}{m_i} + \boldsymbol{F}_i \cdot \boldsymbol{q}_i\right]} - P$$

P_{eff} :virial theorem

$$= P_{\mathrm{eff}} - P$$

New degree of freedom controls the pressure like a piston.

P_{v} changes the sign depending on the difference between the effective pressure and the aimed pressure

Andersen method gives us “approximate” NPH ensemble

H = Enthalpy

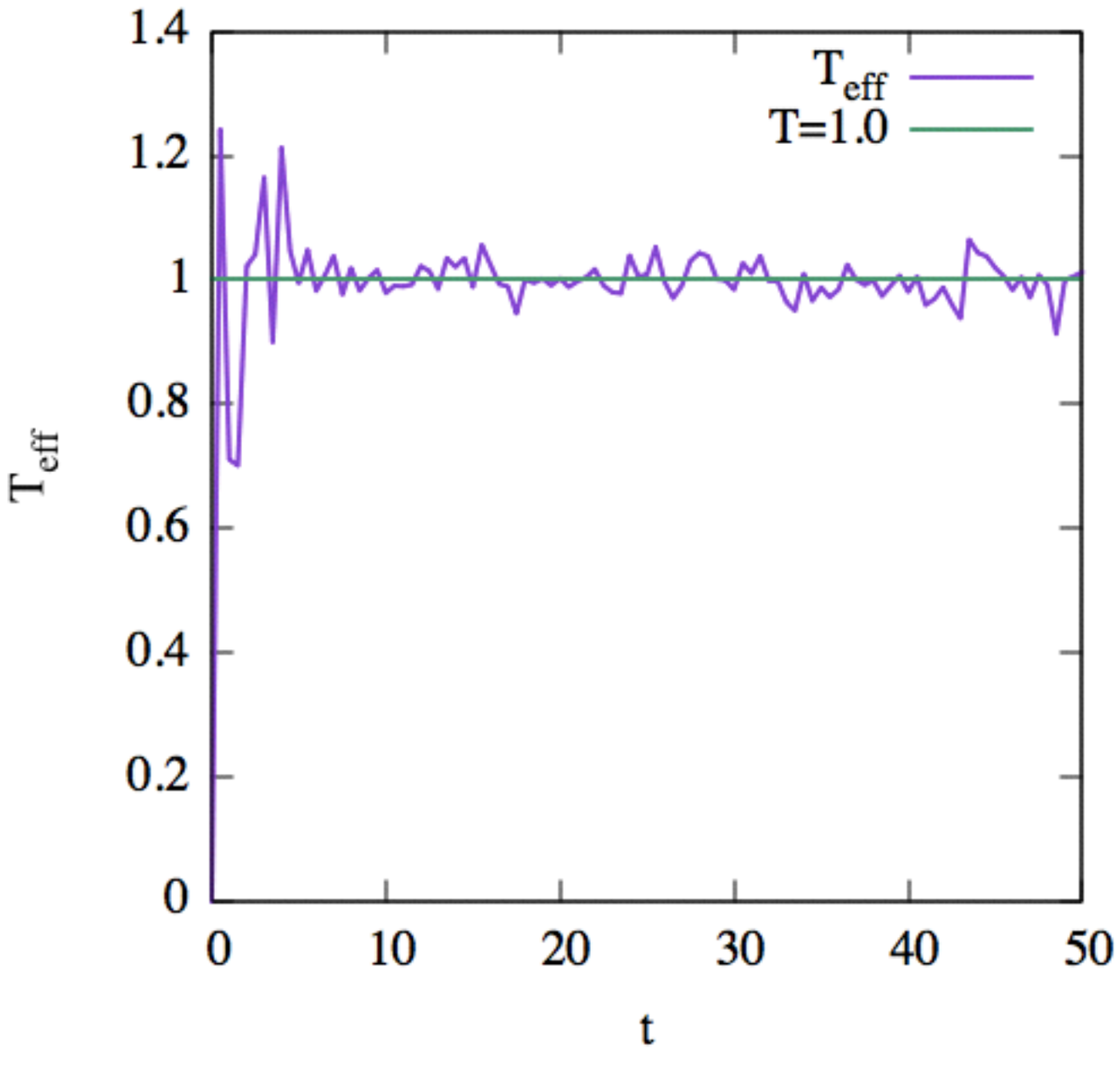
NPT ensemble

MD of LJ system

($\Delta t = 0.005$, N=1000, T=1, P=5)

By combining temperature and pressure controls,
we can obtain NPT ensemble. *e.g.* Nosé-Andersen method

Temperature



Pressure