Computational Science for many-body problems

- This class is from 15:10 to 16:40 (90 min.)
- The recordings of the previous lectures have been uploaded on ITC-LMS.
- Lecture slides are also available on ITC-LMS and github: https://github.com/compsci-alliance/many-body-problems
    - Sample codes of MD simulation were uploaded.

分子動力学法とその応用

Molecular Dynamics Simulation and Its Application

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Today

Classical

Quantum

1st: Many-body problems in physics and why they are hard to solve

2nd: Classical statistical models and numerical simulation

3rd: Classical Monte Carlo method

4th: Applications of classical Monte Carlo method

5th: Molecular dynamics simulation and its applications

6th: Extended ensemble method for Monte Carlo methods

7th: Quantum lattice models and numerical simulation

8th: Quantum Monte Carlo methods

9th: Applications of quantum Monte Carlo methods

10th: Linear algebra of large and sparse matrices for quantum many-body problems

11th: Krylov subspace methods and their applications to quantum many-body problems

12th: Large sparse matrices, and quantum statistical mechanics

13th: Parallelization for many-body problems

Contents

- Remaining topics for MCMC
  - ~~Application and analysis in the case of critical phenomena~~
    - ~~Simulation on Ising model~~
    - Finite size scaling
- Basics of MD simulation
  - Newton equation, purpose of MD simulation
  - Examples of numerical integrations
- NVE ensemble: standard MD simulation
  - Symplectic integral
- Control temperature and pressures (quick review)
  - Velocity scaling and Nosé-Hoover method
  - Andersen method for pressure

Application and analysis in the case of critical phenomena

Data analysis: Finite size scaling (outline)

Near the critical point (transition temperature):

The singular part of the free energy density satisfies finite size scaling

$$f_s(t,h,L) = L^{-d} f_s(tL^{y_t}, hL^{y_h})$$

$$t = T - T_c$$

y_t, y_h :scaling exponent $\Longleftrightarrow$ $y_t = 1/\nu, \quad y_h = (d+\gamma/\nu)/2$

By taking derivatives, we see

$$\chi = \frac{\partial M}{\partial h} = \frac{\partial^2 f}{\partial h^2} = L^{2y_h - d} g(tL^{y_t}, 0)$$ (we set $h=0$)

Physical quantity obeys common scaling function independent of L.

$\Rightarrow$ At the critical point, $\chi \sim L^{-x_\chi} \quad (x_\chi \equiv d - 2y_h)$

Note: $\chi = L^d \langle M^2 \rangle / T$

$\Rightarrow$
$$\boxed{\begin{aligned} x_{M^2} &= 2(d-y_h) \\ &= \eta + d - 2 \\ &= 2x_M \end{aligned}}$$

x: scaling dimension

If $x=0$, it has no size dependence at the critical point.

Data analysis: Finite size scaling (outline)

Similarly, the energy and the specific heat obey:

$$E = \frac{\partial f}{\partial T} = L^{y_t - d} g_E(tL^{y_t}) = L^{1/\nu - d} g_E(tL^{1/\nu})$$

$$C = \frac{\partial^2 f}{\partial T^2} = L^{2y_t - d} g_C(tL^{y_t}) = L^{2/\nu - d} g_C(tL^{1/\nu}) = (L^{\alpha/\nu} g_C(tL^{1/\nu}))$$

Note: scaling relations $\nu d = 2 - \alpha, 2 - \eta = \frac{\gamma}{\nu}, \cdots$

Scaling form of general quantities are $\boxed{O = L^{-x_o} g_o(tL^{1/\nu})}$

When we plot O as $(x = tL^{1/\nu}, y = OL^{x_o})$

All data are on a single curve corresponding to $y = g_o(x)$.

By using this property, we can estimate critical exponents and critical temperature.

Examples: Magnetization

(Squared) Magnetization: $\langle M^2 \rangle$

$$M = \frac{1}{N}\sum_i S_i$$

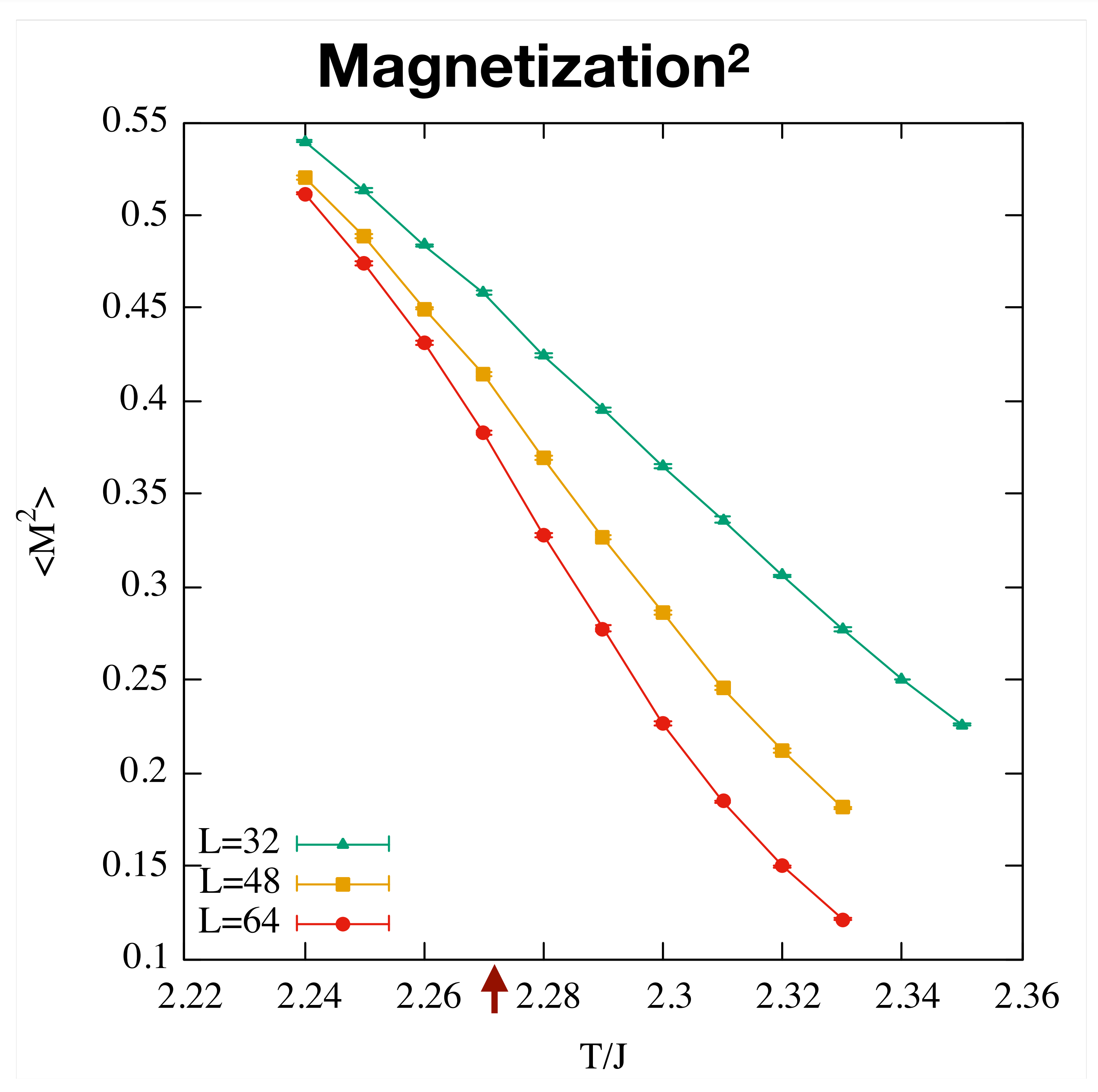
(Q. We cannot use <*M*>. Why?)

In the thermodynamic limit

$$\langle M^2 \rangle \begin{cases} = 0 & (T \geq T_c) \\ \neq 0 & (T < T_c) \end{cases}$$

So, in principle, we can estimate T_c by extrapolating the data.

Can we estimate T_c more easily?



$$T_c/J \simeq 2.269$$

Examples: Binder ratio

Binder ratio

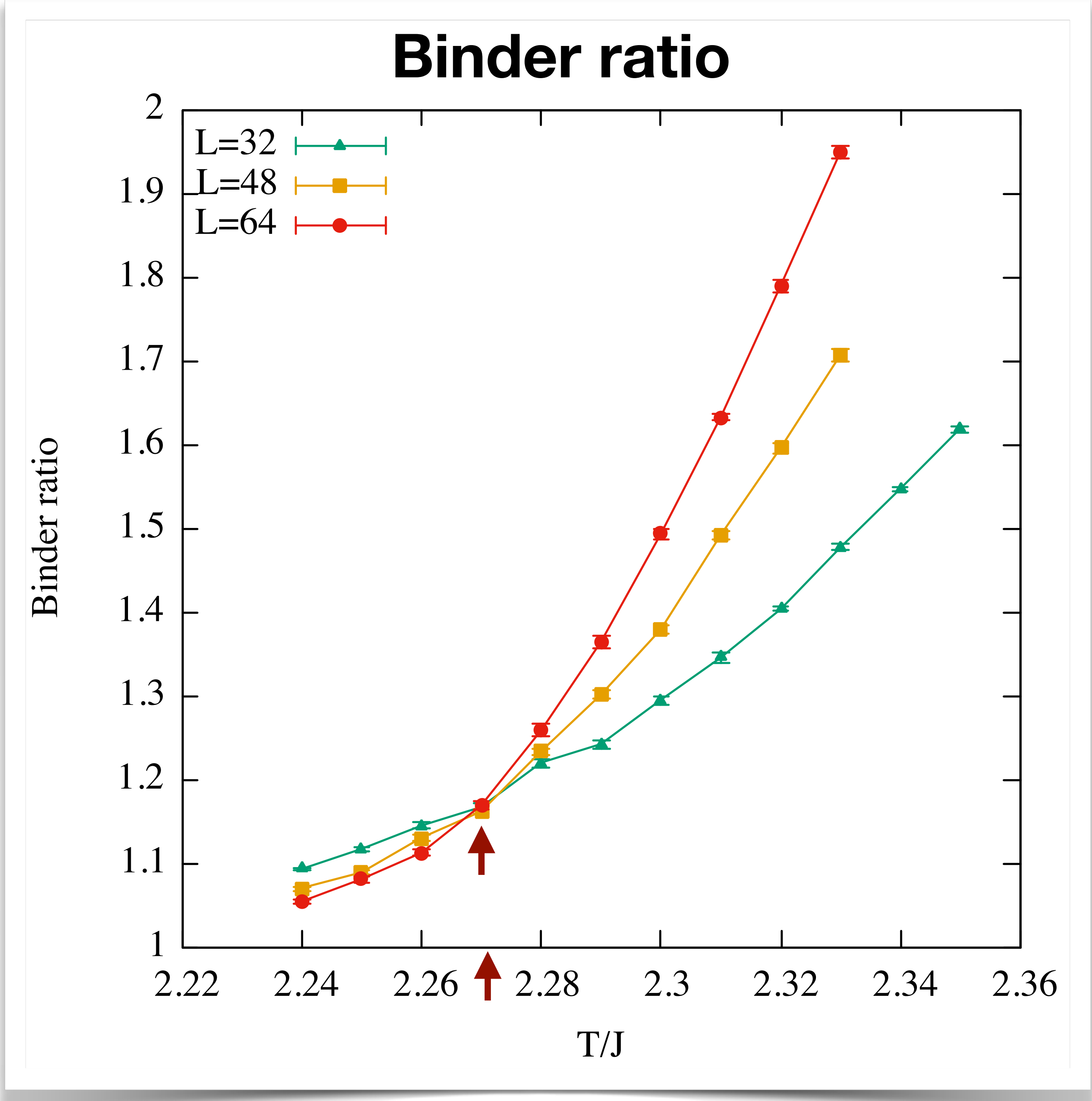
$$b = \frac{\langle M^4 \rangle}{\langle M^2 \rangle^2}$$

$$b = 3 \quad (T \to \infty)$$

$$b = 1 \quad (T \to 0)$$

The scaling dimension of b is exactly zero.

At T_c, the size dependence disappears in leading order!



$$T_c/J \simeq 2.269$$

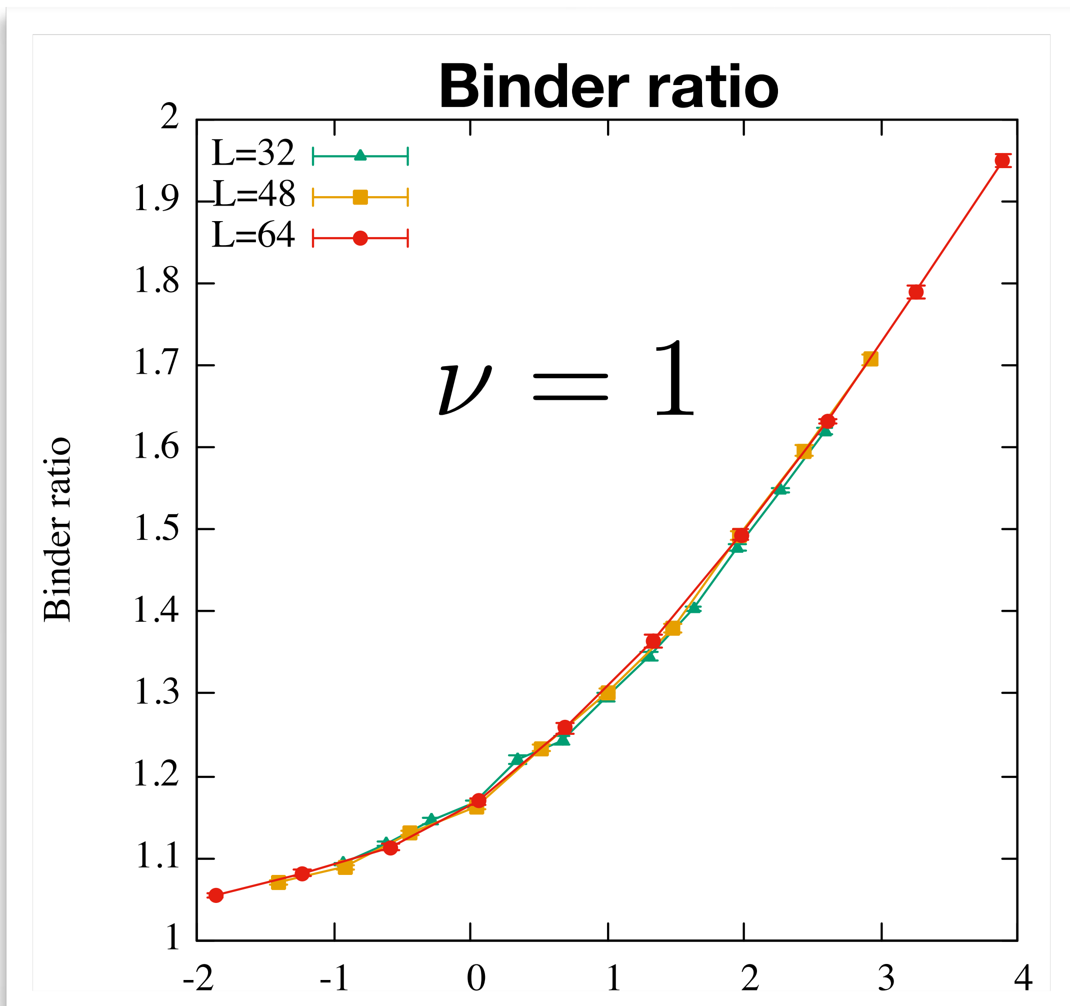
Finite size scaling: Binder ratio

Binder ratio $b = \frac{\langle M^4 \rangle}{\langle M^2 \rangle^2}$

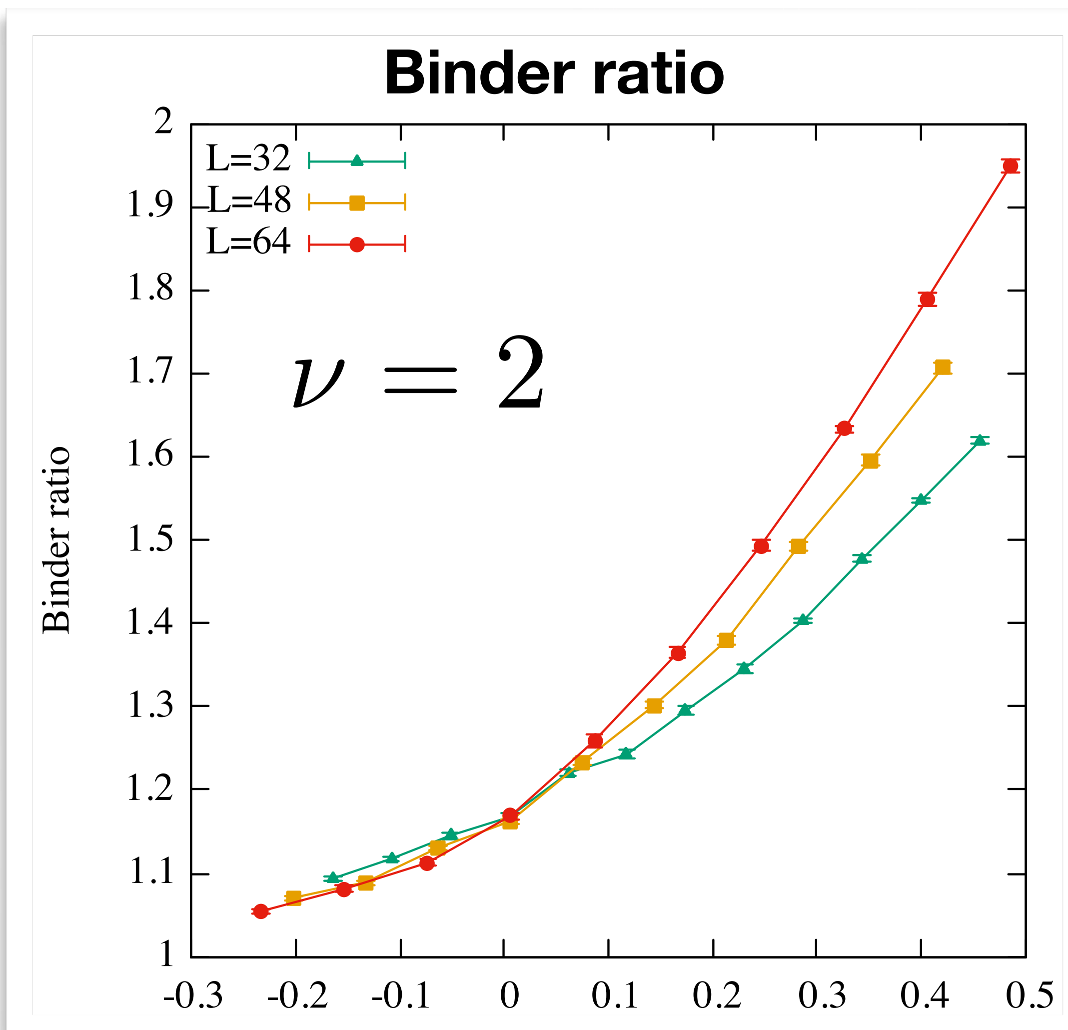
Finite size scaling around Tc

$$b = f((T - T_c)L^{1/\nu})$$

We can determine critical exponent! $\nu = 1$



$(T - T_c)L^{1/\nu}$



$(T - T_c)L^{1/\nu}$

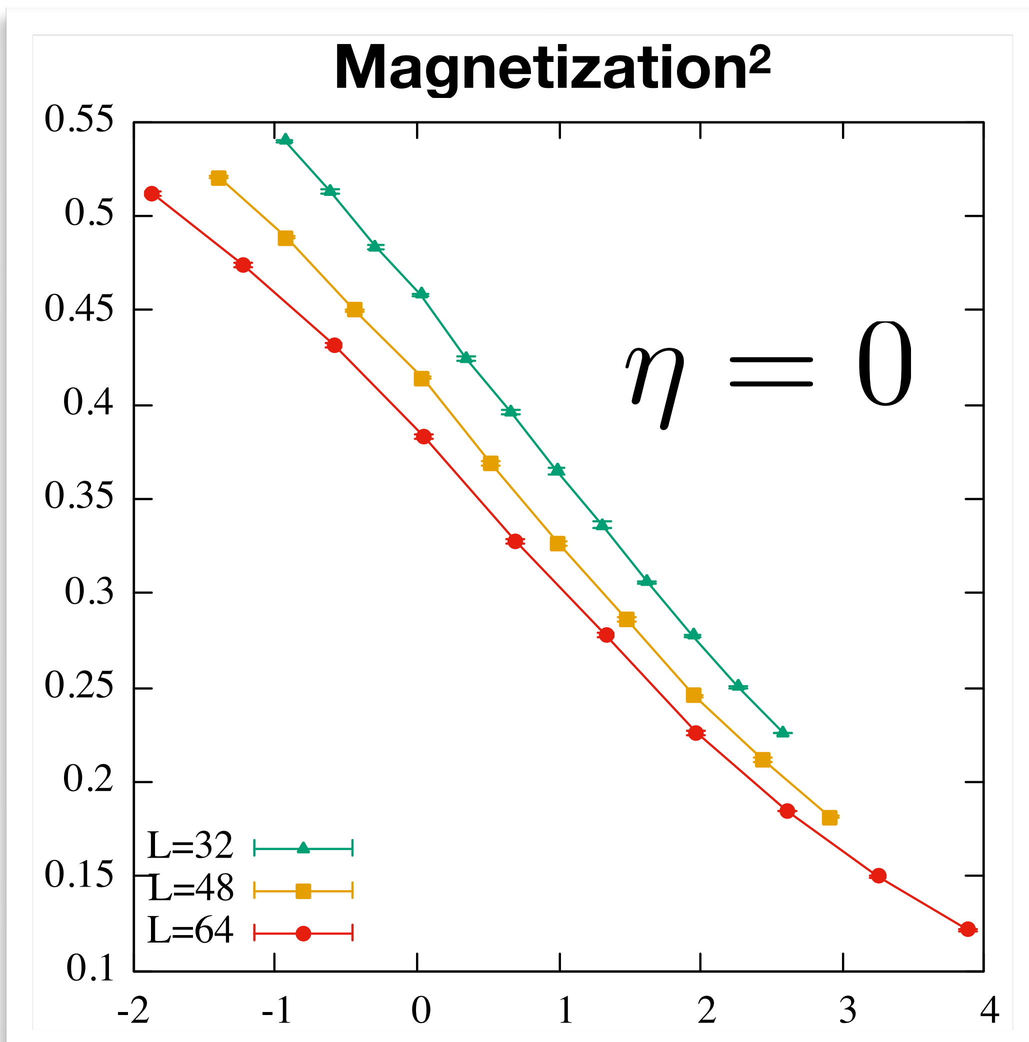
Finite size scaling: Magnetization

(Squared) Magnetization: $\langle M^2 \rangle$

Finite size scaling around Tc
$$\langle M^2 \rangle = L^{-\eta} g((T - T_c)L^{1/\nu})$$

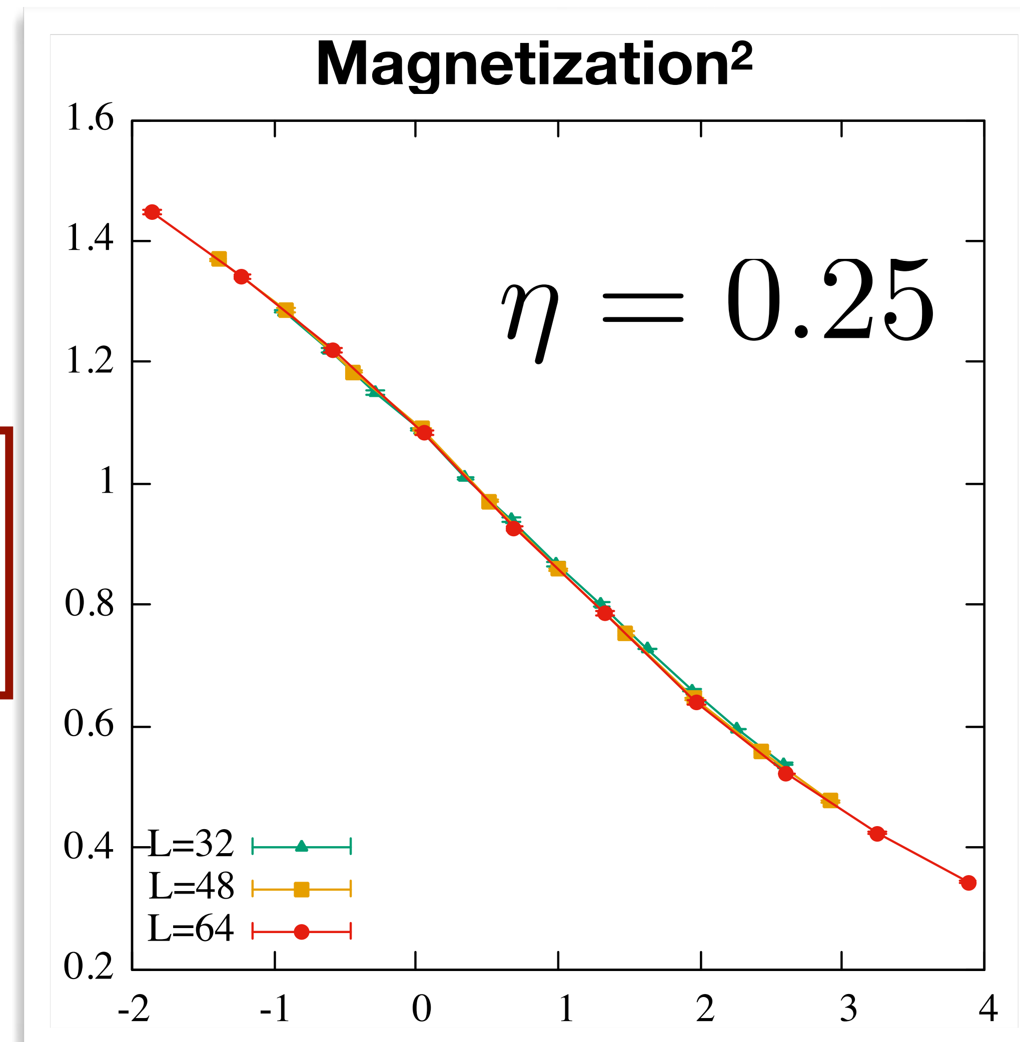
By fixing $\nu = 1$ and varying η,
we can also determine another critical exponent.

$\langle M^2 \rangle L^{\eta}$



$(T - T_c)L^{1/\nu}$

$\langle M^2 \rangle L^{\eta}$



$(T - T_c)L^{1/\nu}$

Exercises (not a report)

Exercise1: autocorrelation of MCMC

See correlation time or autocorrelation function of
Ising model calculated by Monte Carlo simulation.

- Around Tc, how does the correlation time behave by varying the temperature?
- At Tc, how about the size (L) dependence?
- Does the correlation time depend on the algorithms?

Exercise2: finite size scaling

Try the finite size scaling of, eg. binder ratio, in the case of Ising model.

- Calculate physical quantities for various system size (L).
- Plot them without scaling, and see they are actually different.
- Try finite size scaling by assuming values of critical exponents.
  - Even if you know the exact value, it is worth trying several different values.

Please enjoy exercised by sample codes!

References: textbook for MCMC in the physics

- "A guide to Monte Carlo simulation in statistical physics"
  D. P. Landau and K. Binder,
  Cambridge university press, (2014) (4th edition).
- “Computational Physics”, J. Thijssen, Cambridge University Press.
  （「計算物理学」J.M.ティッセン著、松田和典他訳、シュプリンガー・フェアラーク東京.）
- "統計科学のフロンティア12 計算統計II
  マルコフ連鎖モンテカルロ 法とその周辺"
  伊庭幸人ほか、岩波書店.
  (Unfortunately, I have not read it yet.)

Contents

- Basics of MD simulation
  - Newton equation, purpose of MD simulation
  - Examples of numerical integrations
- NVE ensemble: standard MD simulation
  - Symplectic integral
- Control temperature and pressures (quick review)
  - Velocity scaling and Nosé-Hoover method
  - Andersen method for pressure

Basics of MD simulation

Newton equation, purpose of MD simulation

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.

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

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 newtonian equation numerically.

Standard flow of MD simulation

1. Determine 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 $T(\{\boldsymbol{r}_i(t), \boldsymbol{v}_i(t)\})$, $P(\{\boldsymbol{r}_i(t), \boldsymbol{v}_i(t)\})$, $\cdots$
   - Constant temperature, Constant pressure, …
6. Analyze trajectories

Periodic boundary condition (will be skipped)

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

Short-range interaction

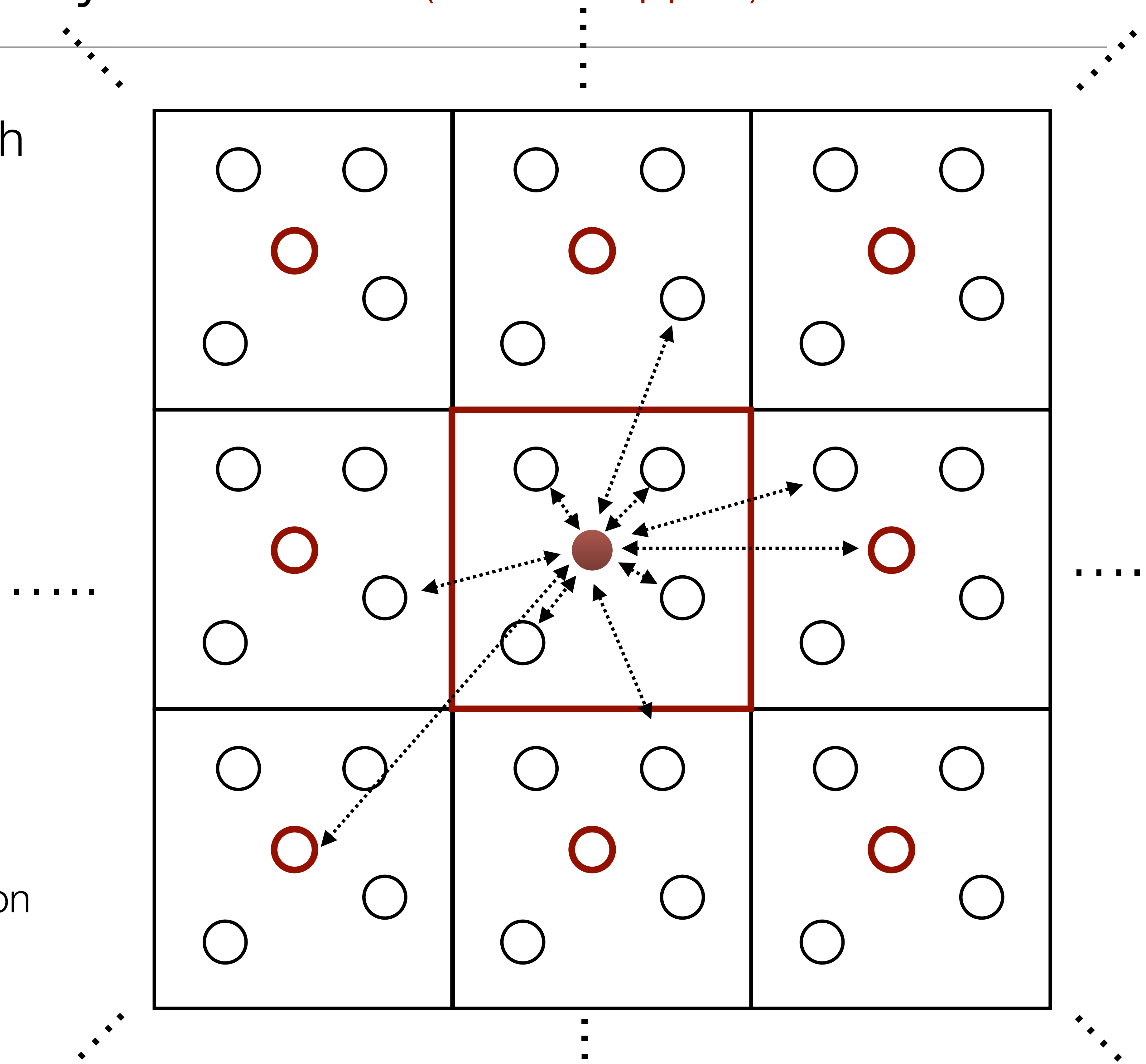
e.g. LJ potential

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 Newtonian dynamics give us the 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.

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

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

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

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

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

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

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 or 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 Green-Kubo formula:

$$\gamma = V\beta \int_0^\infty \langle J(0)J(t)\rangle dt$$

- It can be obtained by MD simulation applying the external field.
  - Usually the non-equilibrium calculation gives us smaller error.

Examples of numerical integrations

Numerical integration: Basics

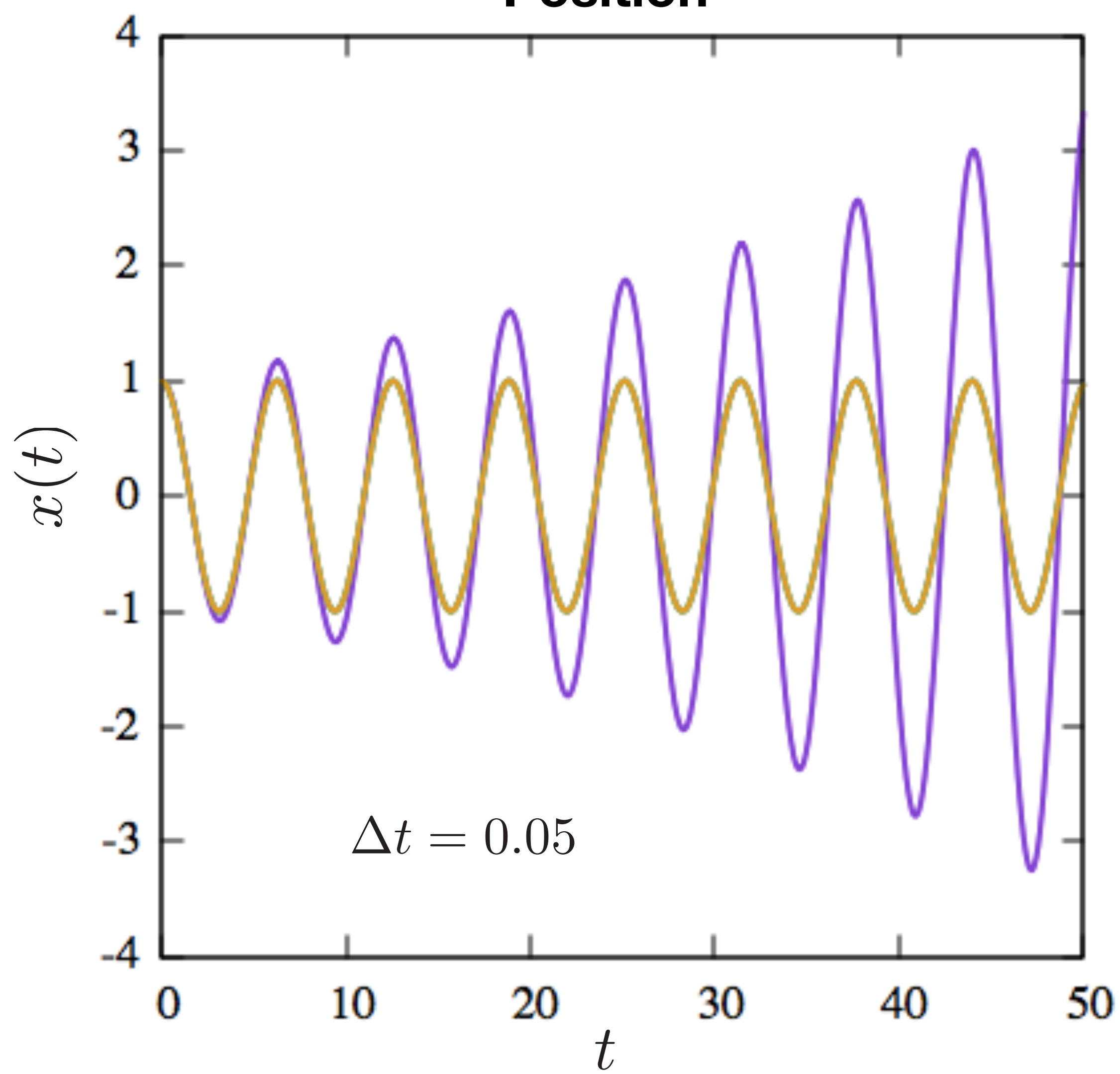
Example: 1d harmonic oscillator

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

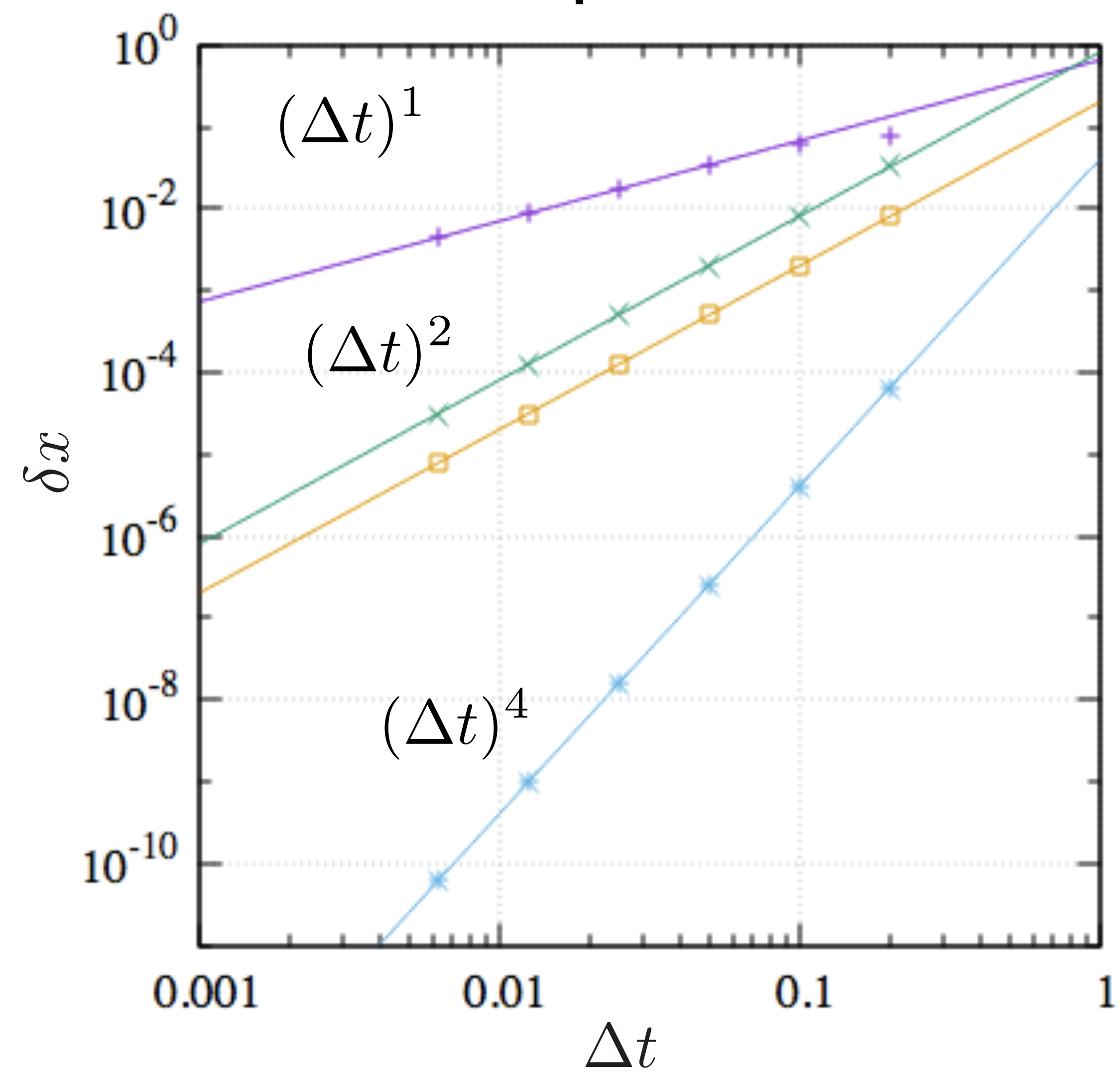
Several explicit methods

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 the cpu cost

e.g.

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

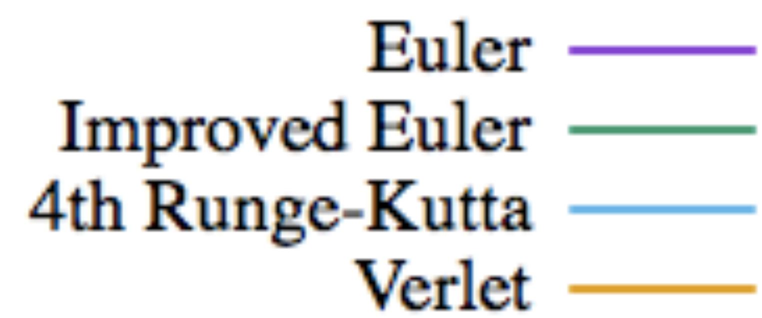
	order of error	#of force calculation	initial condition
Euler	Δt	1	$r(0)$, $v(0)$
Improved Euler	$(\Delta t)^2$	2	$r(0)$, $v(0)$
4th Runge-Kutta	$(\Delta t)^4$	4	$r(0)$, $v(0)$
Verlet	$(\Delta t)^2$	1	$r(0)$, $r(\Delta t)$ (velocity Verlet: $r(0)$, $v(0)$)
Predictor-Corrector	$(\Delta t)^5$	2 (or 1)	$r(0)$,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

Numerical integration: instability (energy drift)

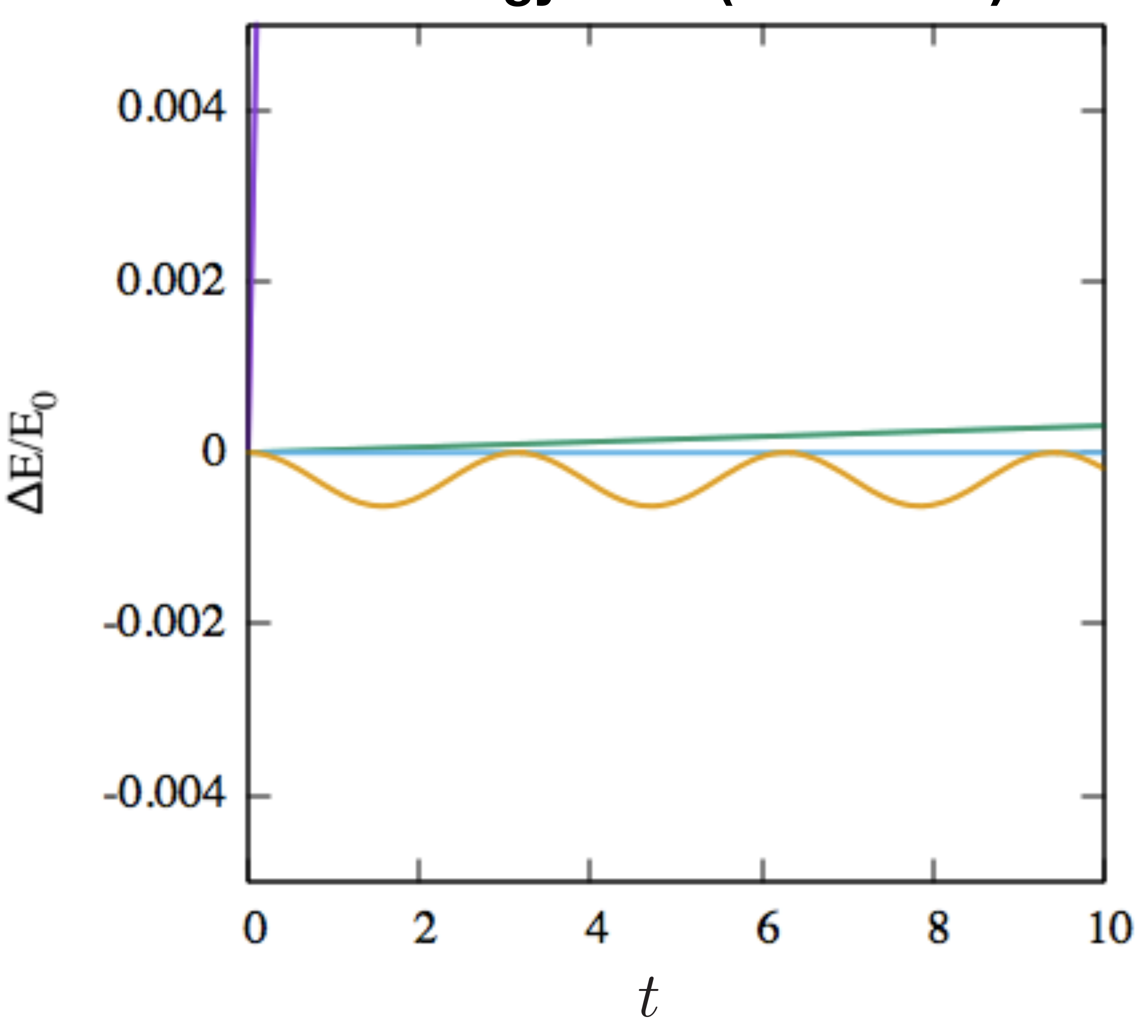
Example: 1d harmonic oscillator

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

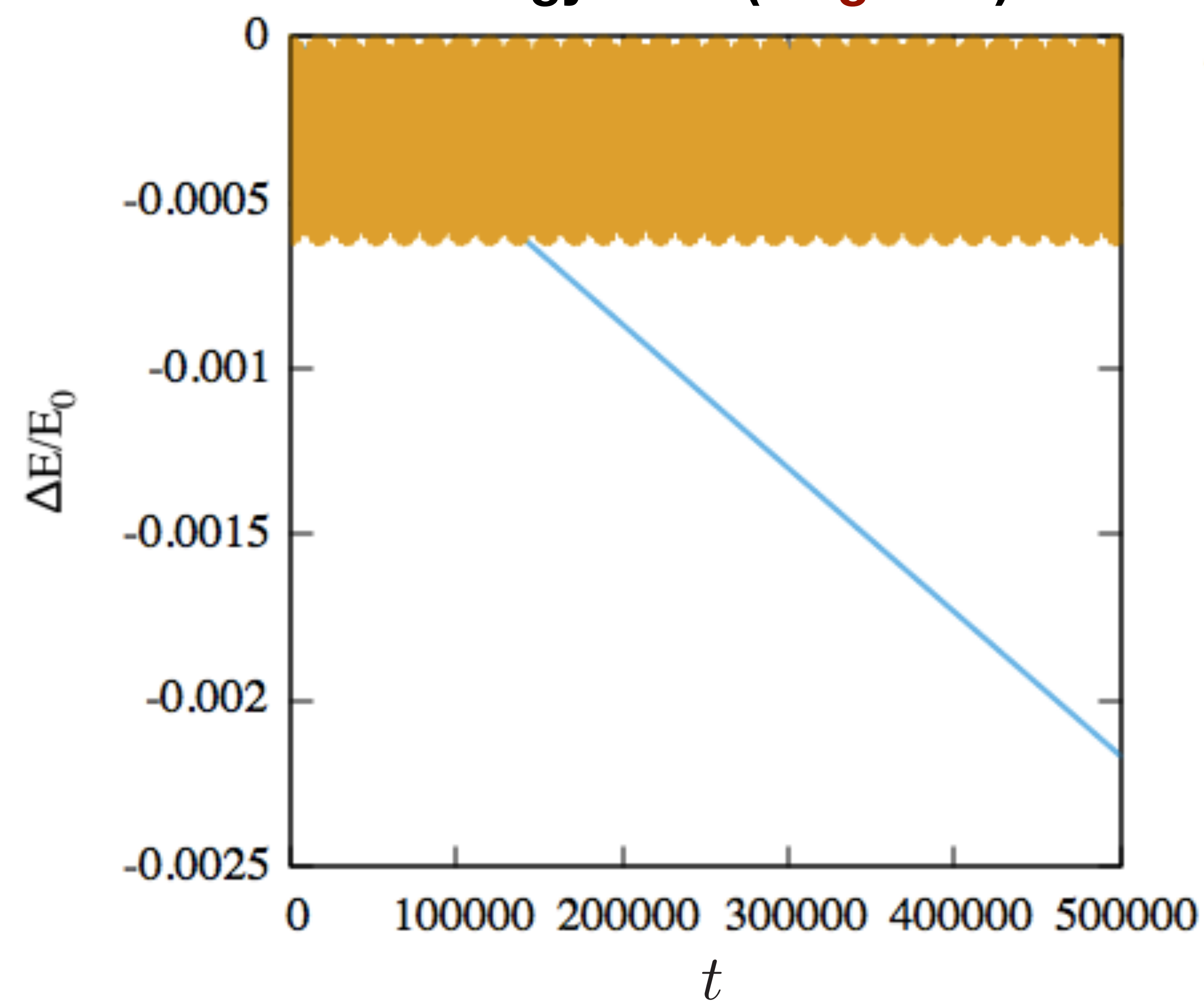
Verlet shows a very small energy drift.



Energy error (short time)



Energy error (long 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

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

Verlet method:

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

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

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

Hamiltonian mechanics

Hamiltonian mechanics

$$\mathcal{H}(\{q_i\},\{p_i\}) \Rightarrow \quad \frac{dq_i}{dt} = \frac{\partial \mathcal{H}}{\partial p_i}, \quad \frac{dp_i}{dt} = -\frac{\partial \mathcal{H}}{\partial q_i}$$

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

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

Poisson bracket:

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

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

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

Unitary operator

Liouville's theorem

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

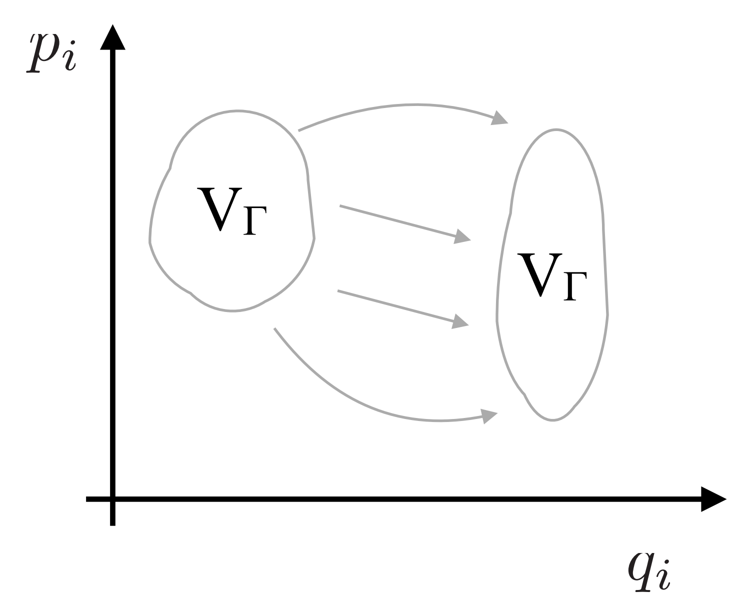
Liouville equation

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

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

Liouville's theorem:

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



Canonical transformation（正準変換）

Hamiltonian dynamics: $$\frac{dq_i}{dt} = \frac{\partial \mathcal{H}}{\partial p_i}\ ,\quad \frac{dp_i}{dt} = -\frac{\partial \mathcal{H}}{\partial q_i}$$

For $2n$-dim. vector representation:

$$\boldsymbol{\Gamma} = \begin{pmatrix} \boldsymbol{q} \\ \boldsymbol{p} \end{pmatrix}\ , \boldsymbol{q} = \begin{pmatrix} q_1 \\ q_2 \\ \vdots \\ q_n \end{pmatrix}, \boldsymbol{p} = \begin{pmatrix} p_1 \\ p_2 \\ \vdots \\ p_n \end{pmatrix}$$

Time evolution of $\boldsymbol{\Gamma}$:

$$\frac{d\boldsymbol{\Gamma}}{dt} = J\frac{\partial \mathcal{H}}{\partial \boldsymbol{\Gamma}}$$

$J = \begin{pmatrix} 0 & \mathbf{1} \\ -\mathbf{1} & 0 \end{pmatrix}$:$2n\times 2n$ matrix

($n=3N$ in 3d system)

$\mathbf{1}$:$n\times n$ identity matrix

Symplectic condition

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

Jacobian matrix S $\quad S_{ij} = \dfrac{\partial \Gamma_i'}{\partial \Gamma_j}$, $S = \begin{pmatrix} \dfrac{\partial \boldsymbol{q}'}{\partial \boldsymbol{q}} & \dfrac{\partial \boldsymbol{q}'}{\partial \boldsymbol{p}} \\ \dfrac{\partial \boldsymbol{p}'}{\partial \boldsymbol{q}} & \dfrac{\partial \boldsymbol{p}'}{\partial \boldsymbol{p}} \end{pmatrix}$

Time evolution of $\mathbf{\Gamma}'$:

$$\frac{d\mathbf{\Gamma}'}{dt} = S\frac{d\mathbf{\Gamma}}{dt} = SJ\frac{\partial \mathcal{H}}{\partial \mathbf{\Gamma}}$$

$$= SJS^T\frac{\partial \mathcal{H}}{\partial \mathbf{\Gamma}'} = J\frac{\partial \mathcal{H}}{\partial \mathbf{\Gamma}'}$$

From the relation $\dfrac{d\Gamma_i'}{dt} = \sum_j \dfrac{\partial \Gamma_i'}{\partial \Gamma_j}\dfrac{d\Gamma_j}{dt}$

$$\frac{\partial}{\partial \Gamma_i} = \sum_j \frac{\partial \Gamma_j'}{\partial \Gamma_i}\frac{\partial}{\partial \Gamma_j'} = \sum_j (S^T)_{ij}\frac{\partial}{\partial \Gamma_j'}$$

Definition of the canonical transformation

Canonical transformation satisfies the symplectic condition: $\boxed{SJS^T = J}$

(This condition is actually the necessary and sufficient condition for canonical transformation.)

Infinitesimal time evolution

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

$$\boxed{\begin{aligned} \boldsymbol{q}' &= \boldsymbol{q}(t+\Delta t) = \boldsymbol{q}(t) + \Delta t \frac{\partial \mathcal{H}}{\partial \boldsymbol{p}(t)} \\ \boldsymbol{p}' &= \boldsymbol{p}(t+\Delta t) = \boldsymbol{p}(t) - \Delta t \frac{\partial \mathcal{H}}{\partial \boldsymbol{q}(t)} \end{aligned}}$$

This is a canonical transformation, when Δt is infinitesimal.

→ Exact Hamiltonian dynamics satisfies the symplectic condition.

↔ For a finite Δt (Euler method), it breaks the symplectic condition, and it does not conserve the energy. (Main reason for the energy drift.)

If we can construct discrete approximations satisfying, at least, the symplectic condition, we may obtain more stable methods.

Symplectic integrator

Symplectic integrator:

Discrete approximation of a Hamiltonian dynamics satisfying the symplectic condition.

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

If the Hamiltonian can be decomposed, for example

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

$\Rightarrow$ There is a systematic derivation of symplectic integrators.

Good point:

Because the approximated dynamics corresponds to **another Hamiltonian dynamics** (with a slightly different Hamiltonian), the energy does not drift so much along this dynamics.

c.f. (Review) H. Yoshida, Celestial Mech Dyn Astr 56, 27 (1993).

Decomposition of exponential operator

Symplectic integrator:

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

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

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

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

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

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

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

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

Euler like equation
(but this is more stable!)

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

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

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

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

Exactly equal to
(Velocity) Verlet method

Control temperature

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:

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

Rescale velocities every time step as

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

Results of the velocity scaling

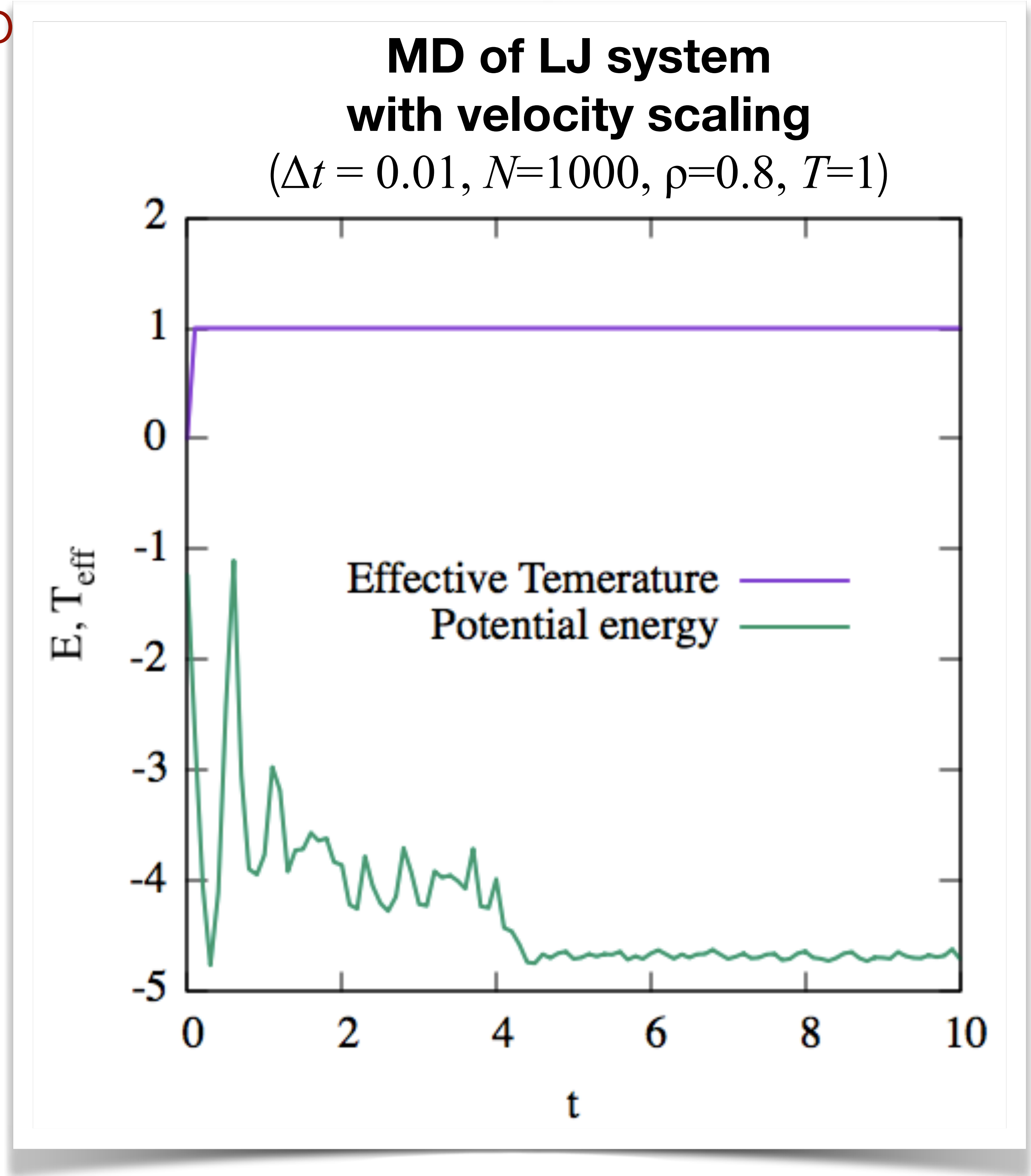
Total kinetic energy is artificially fixed to

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

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.



Temperature control: Langevin dynamics

Langevin dynamics

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

Random force

(Gaussian white noise)

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

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

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"

$$\mathcal{H}_N = \underbrace{\sum_i \frac{(\boldsymbol{p}_i')^2}{2m_i s^2} + V(\{\boldsymbol{q}_i\})}_{\text{Original Hamiltonian with scaled momentum}} + \underbrace{\frac{P_s^2}{2Q} + gk_B T \ln s}_{\text{Heat-bath}}$$

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
(along t')

$$\frac{d\boldsymbol{p}_i'}{dt'} = -\frac{\partial V}{\partial \boldsymbol{q}_i} = \boldsymbol{F}_i(\{\boldsymbol{q}_i\}) \qquad \frac{dP_s}{dt'} = \frac{1}{s}\left(\sum_i \frac{(\boldsymbol{p}_i')^2}{m_i s^2} - gk_B T\right)$$

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

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).)

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

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

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

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

$g = 3N$ (# 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")

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

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

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

s^{3N} comes from $\boldsymbol{p}_i' = s\boldsymbol{p}_i$

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

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

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

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

$$(f(x_0)=0)$$

Canonical ensemble if $g = 3N+1$

Nosé-Hoover dynamics becomes NVT ensemble 2

Time average on ***t*** :

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

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

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

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

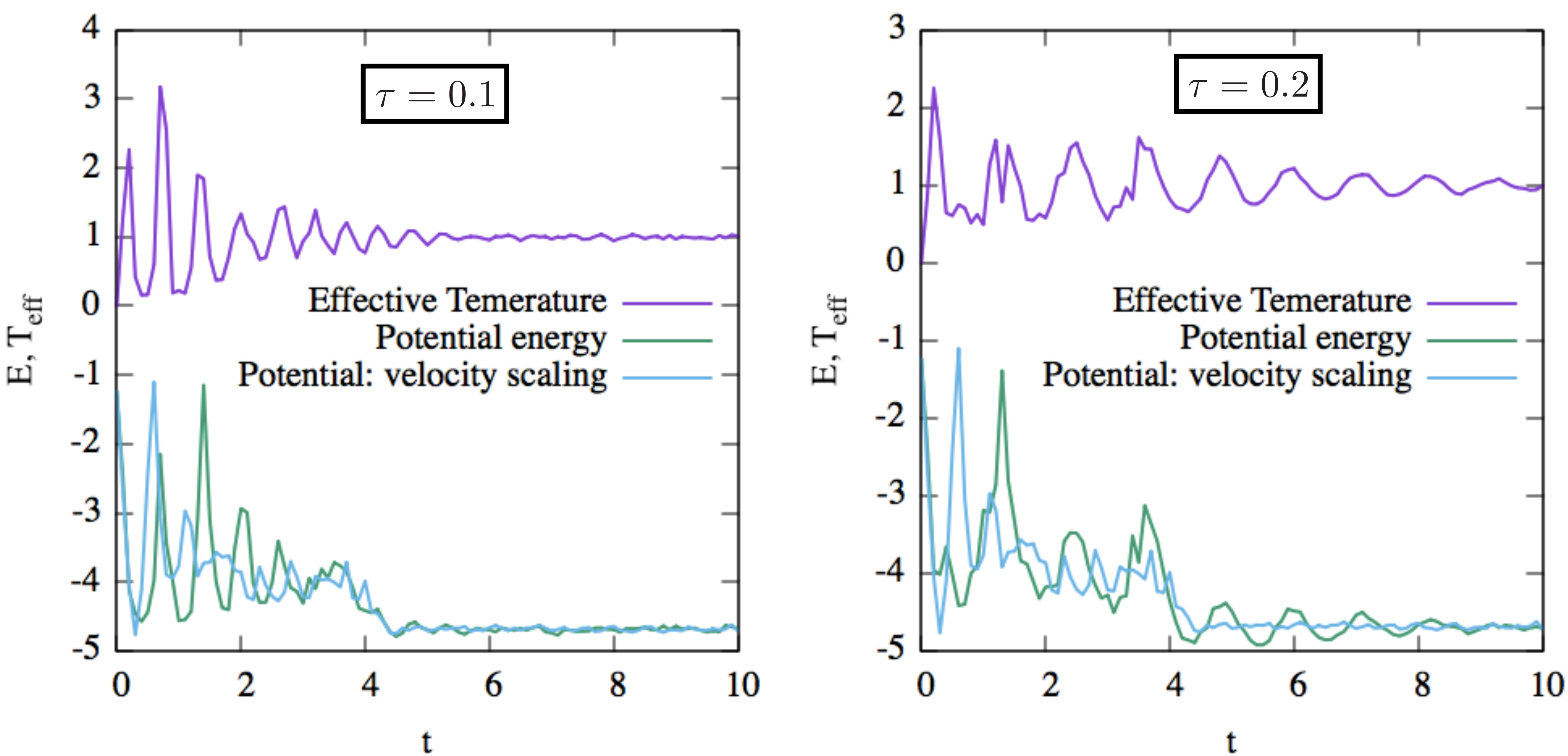
Canonical ensemble if $g = 3N$

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

(Δt = 0.01, N=1000, ρ=0.8, T=1)



Control pressure (will be skipped)

Pressure control: Andersen method

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

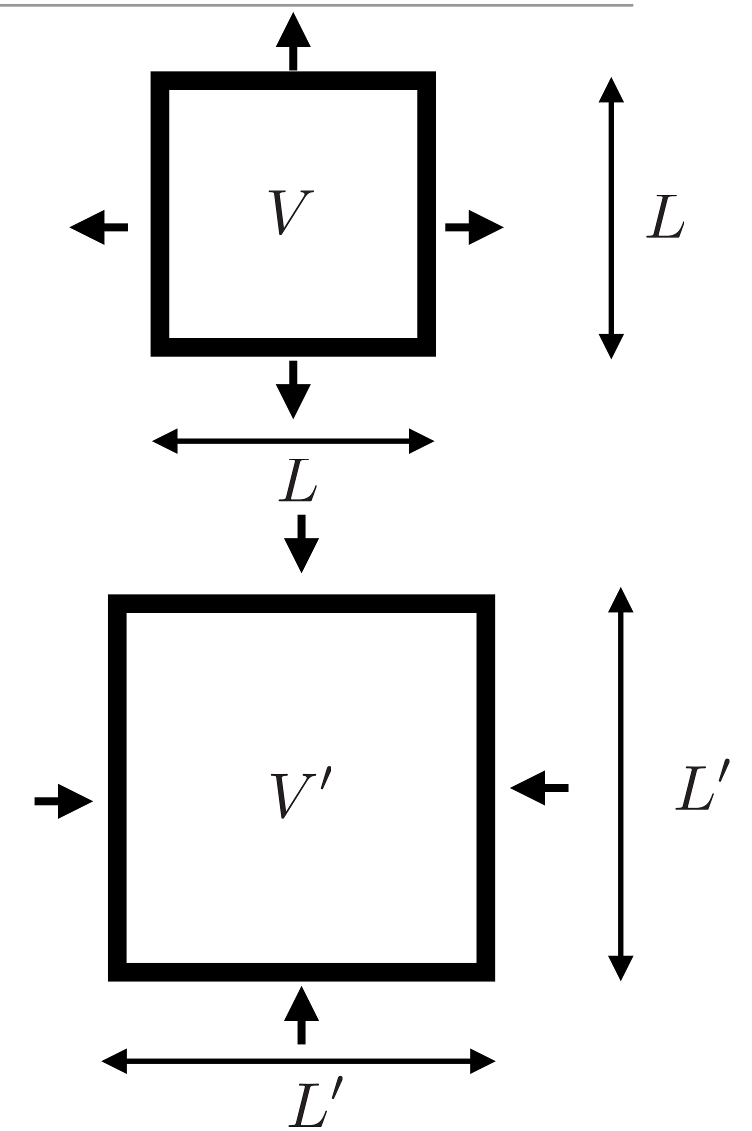
Extended Hamiltonian System with a "piston"

$$\mathcal{H}_A = \underbrace{\sum_i \frac{\tilde{\boldsymbol{p}}_i^2}{2m_i V^{\frac{2}{3}}} + V_p(\{V^{\frac{1}{3}}\tilde{\boldsymbol{q}}_i\})}_{\text{Original Hamiltonian with scaled coordinate and momentum}} + \underbrace{\frac{P_V^2}{2M} + PV}_{\text{Piston}}$$

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

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

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

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.

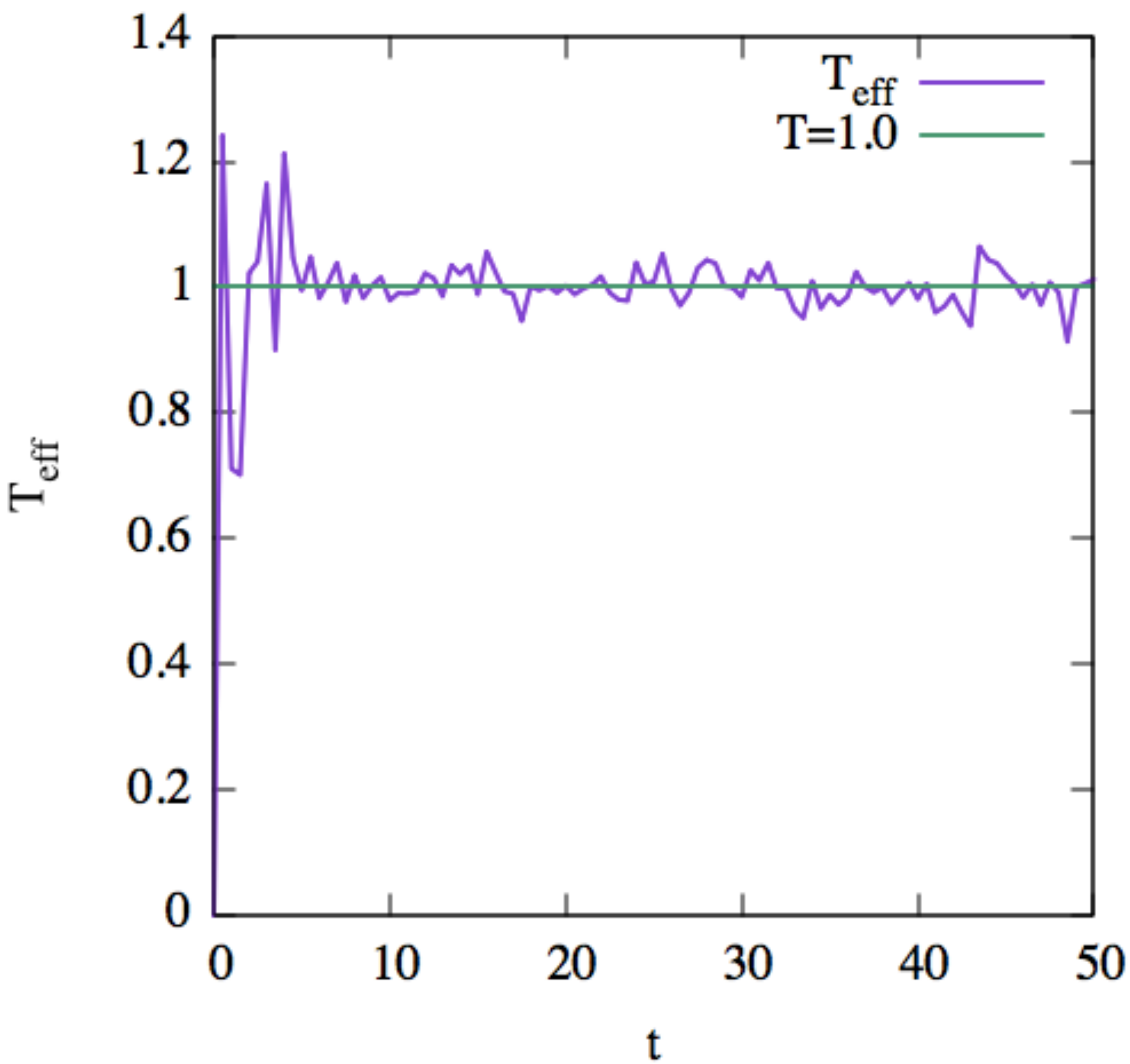
H = Enthalpy

NPT ensemble

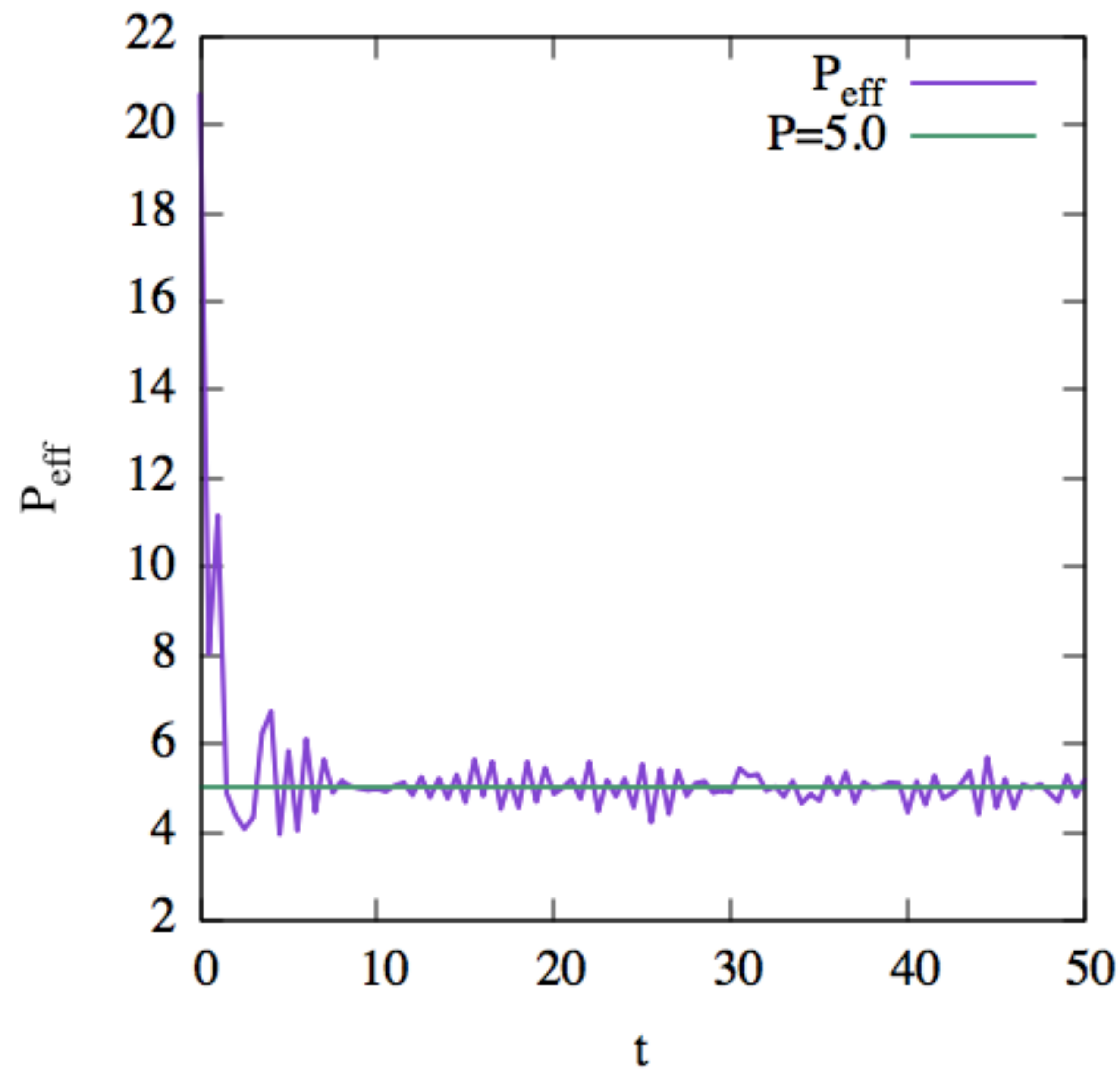
MD of LJ system
(Δt = 0.005, N=1000, T=1, P=5)

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

Temperature



Pressure



Exercise: MD simulation of LJ particles(not a report)

Let's try MD simulation of LJ particles with NVE, NVT, and NPT ensembles.

- In NVE simulation (e.g. by Verlet method), see the conservation of the total energy.
- By using, velocity scaling or Nose-Hoover thermostat, try to control temperature.
- By combining temperature control and pressure control try to simulate NPT ensemble.

To perform these exercise, you may use,

- Your own code
- LAMMPS
  - http://lammps.sandia.gov
- MDACP (for NVE simulation.)
  - http://mdacp.sourceforge.net/index.html
- My sample codes for jupyter notebook.
  - To run the sample code you need
    - numpy, and numba (numba is used for speed up)

References (books)

- “Computational Physics”, J. Thijssen, Cambridge University Press.
  （「計算物理学」J.M.ティッセン著、松田和典他訳、シュプリンガー・フェアラーク東京.
- 「分子シミュレーション」上田顯著、裳華房.

Next (5/24)

Classical

Quantum

1st: Many-body problems in physics and why they are hard to solve

2nd: Classical statistical models and numerical simulation

3rd: Classical Monte Carlo method

4th: Applications of classical Monte Carlo method

5th: Molecular dynamics simulation and its applications

6th: Extended ensemble method for Monte Carlo methods

7th: Quantum lattice models and numerical simulation

8th: Quantum Monte Carlo methods

9th: Applications of quantum Monte Carlo methods

10th: Linear algebra of large and sparse matrices for quantum many-body problems

11th: Krylov subspace methods and their applications to quantum many-body problems

12th: Large sparse matrices, and quantum statistical mechanics

13th: Parallelization for many-body problems