

拡張アンサンブル法によるモンテカルロ計算

Extended Ensemble method for Monte Carlo Methods

理学系研究科 物理学専攻 大久保 豪

Contents

- Basics of MD simulation
 - Newtonian 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

Examples of numerical integrations

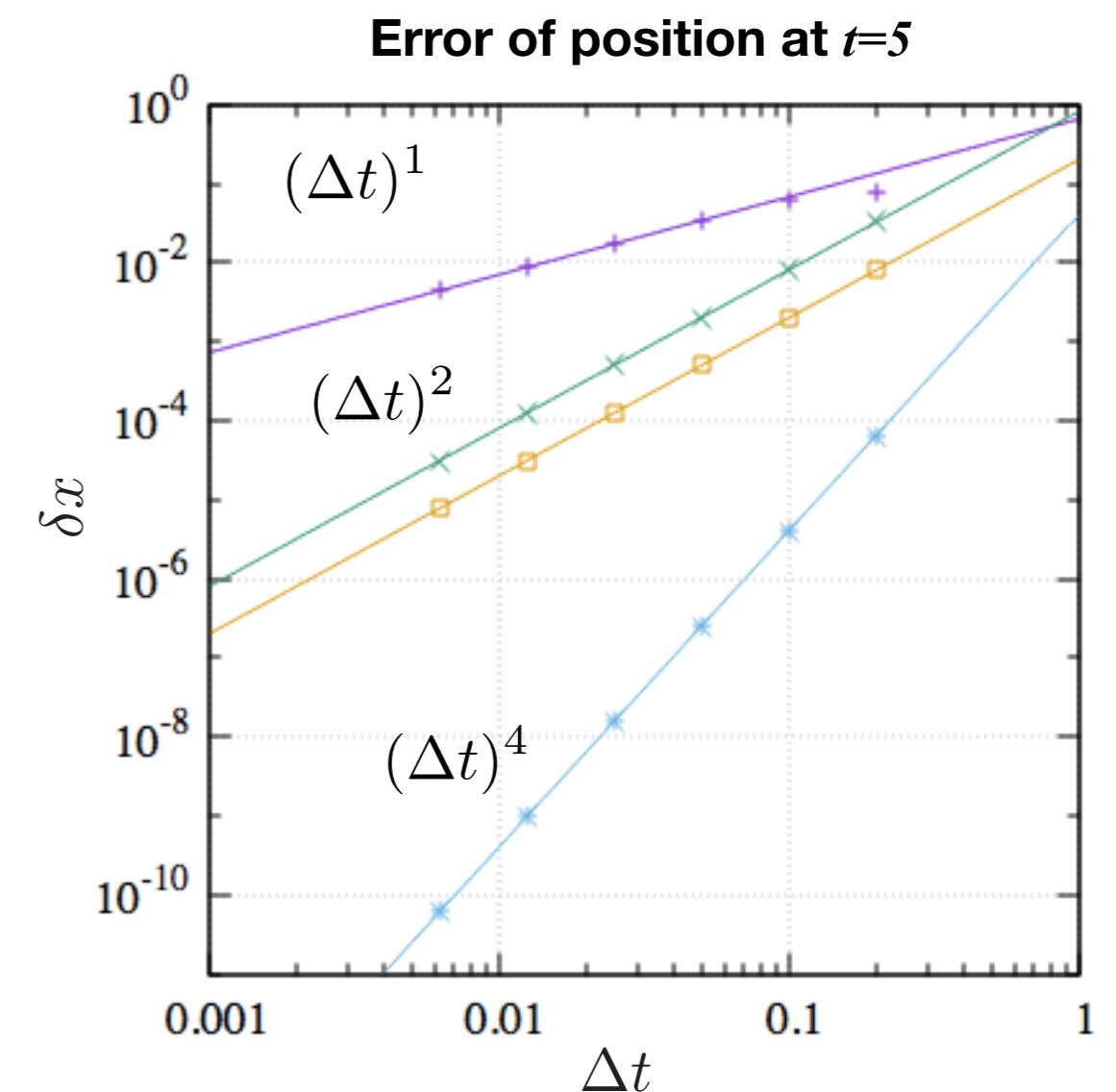
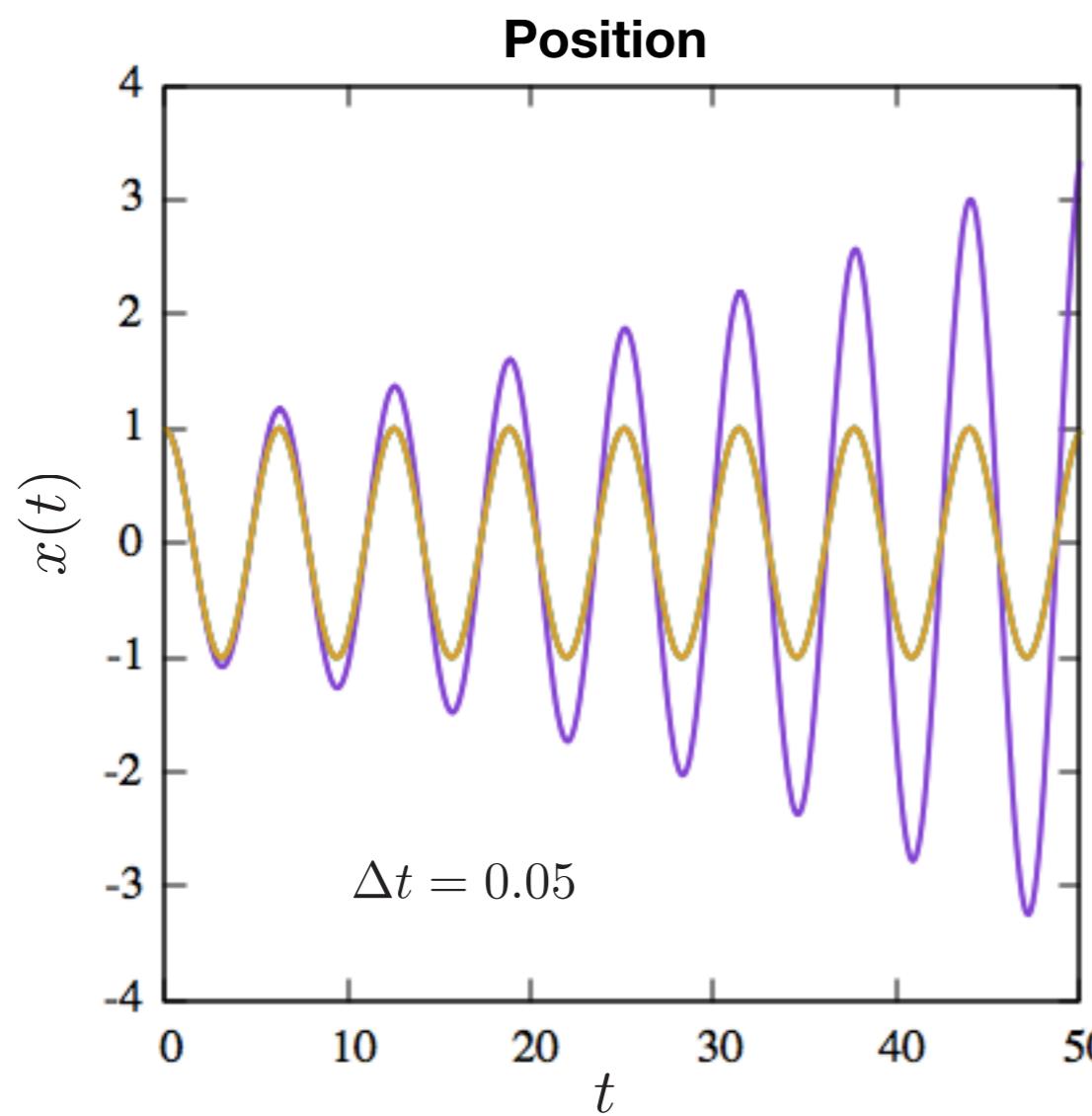
Numerical integration: Basics

Example: 1d harmonic oscillator

$$\mathcal{H}(x) = \frac{1}{2}x^2 + \frac{1}{2}v^2 \quad \rightarrow \quad \begin{aligned}\frac{dv}{dt} &= -x \\ \frac{dx}{dt} &= v\end{aligned}$$

Several explicit methods

Euler —————
Improved Euler —————
4th Runge-Kutta —————
Verlet —————



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.

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

	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)	$r(0), r'(0), r''(0), r'''(0), r''''(0)$

Numerical integration: instability (energy drift)

Example: 1d harmonic oscillator

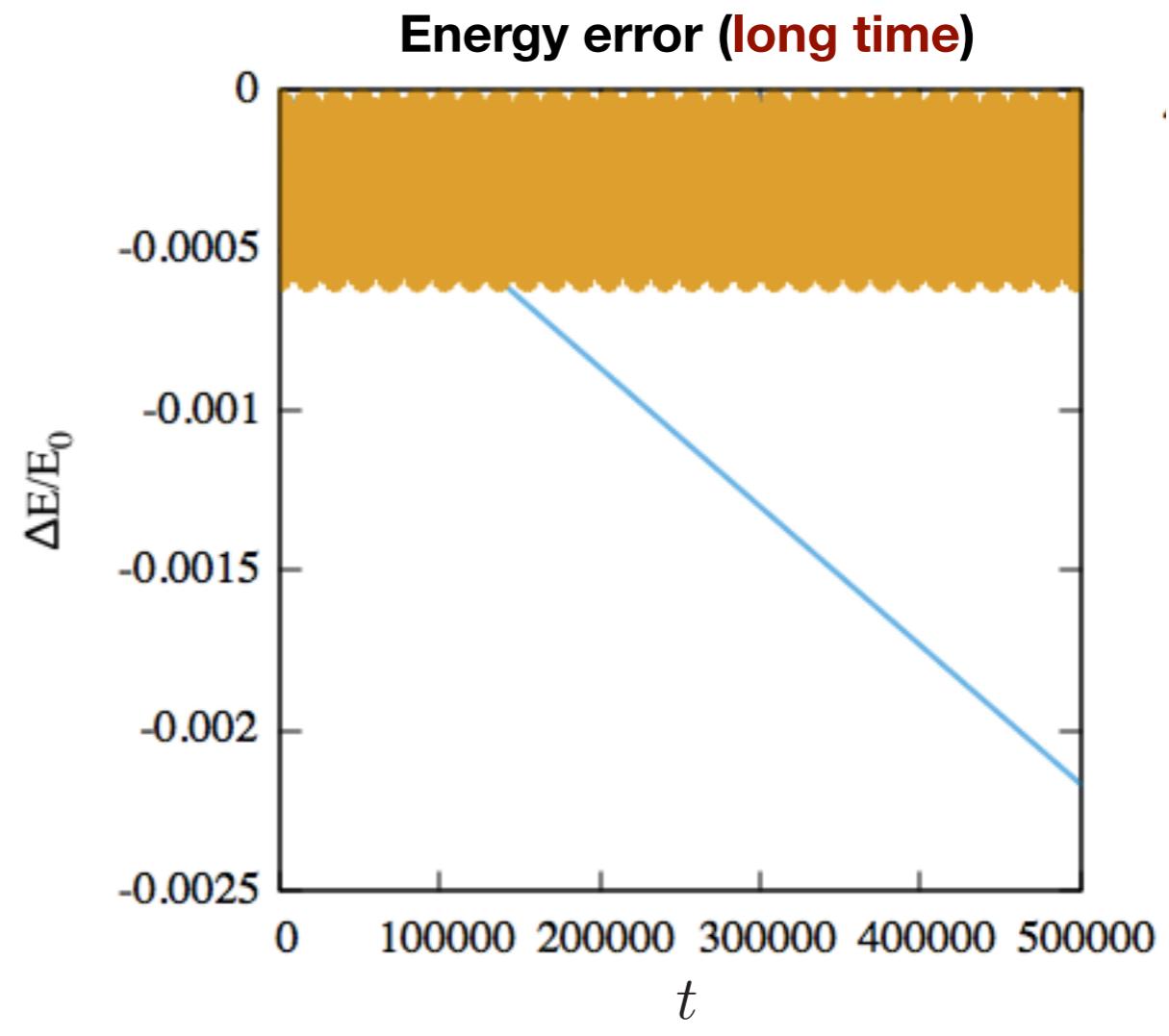
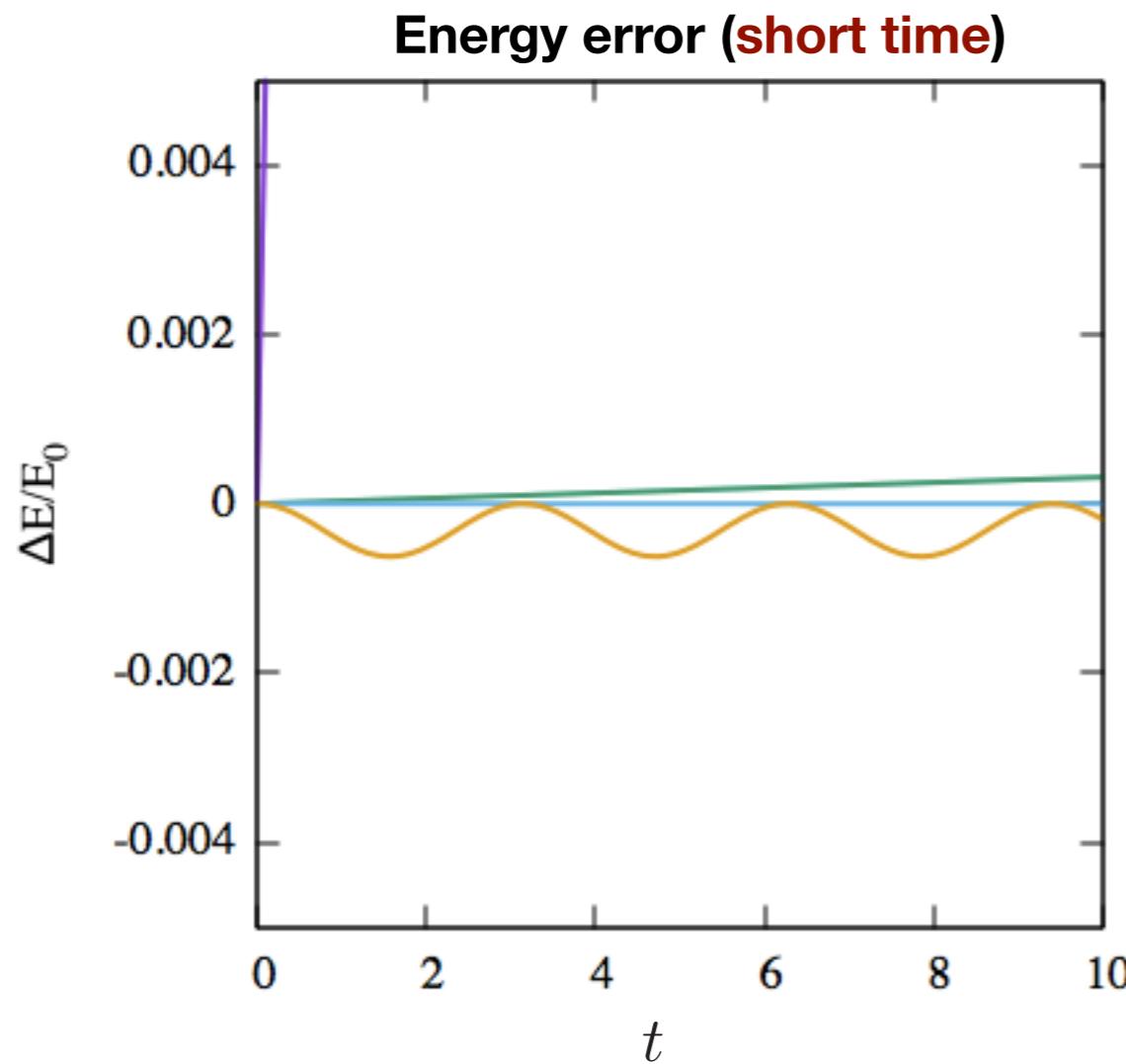
Usual methods shows a drift of energy!

(Predictor-Corrector also shows large energy drift)



Verlet shows a very small energy drift.

Euler
Improved Euler
4th Runge-Kutta
Verlet



Better methods for molecular dynamics simulation

Verlet method:

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

Verlet method:

$$\begin{aligned} \mathbf{r}_i(t + \Delta t) &= 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \Delta t) + \frac{(\Delta t)^2}{m_i} \mathbf{F}_i(\{\mathbf{r}_i(t)\}) \\ \mathbf{v}_i(t) &= \frac{\mathbf{r}_i(t + \Delta t) - \mathbf{r}_i(t - \Delta t)}{2\Delta t} \end{aligned}$$

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

Velocity Verlet method:

$$\begin{aligned} \mathbf{r}_i(t + \Delta t) &= \mathbf{r}_i(t) + \Delta t \mathbf{v}_i(t) + \frac{(\Delta t)^2}{2m_i} \mathbf{F}_i(\{\mathbf{r}_i(t)\}) \\ \mathbf{v}_i(t + \Delta t) &= \mathbf{v}_i(t) + \Delta t \frac{\mathbf{F}_i(\{\mathbf{r}_i(t)\}) + \mathbf{F}_i(\{\mathbf{r}_i(t + \Delta t)\})}{2m_i} \end{aligned}$$

Leap-frog method:

$$\begin{aligned} \mathbf{r}_i(t + \Delta t) &= \mathbf{r}_i(t) + \mathbf{v}_i \left(t + \frac{\Delta t}{2} \right) \Delta t \\ \mathbf{v}_i \left(t + \frac{\Delta t}{2} \right) &= \mathbf{v}_i \left(t - \frac{\Delta t}{2} \right) + \Delta t \frac{\mathbf{F}_i(\{\mathbf{r}_i(t)\})}{m_i} \end{aligned}$$

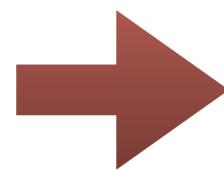
These methods are basically equivalent.
They are based on the second-order
symplectic integration scheme.

NVE ensemble: symplectic integrator

Hamilton mechanics

Hamilton mechanics

$$\mathcal{H}(\{q_i\}, \{p_i\})$$



$$\frac{dq_i}{dt} = \frac{\partial \mathcal{H}}{\partial p_i}$$
$$\frac{dp_i}{dt} = -\frac{\partial \mathcal{H}}{\partial q_i}$$

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

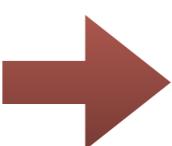
$$\frac{dA}{dt} = \{A, \mathcal{H}\}$$

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

$$\frac{dA}{dt} = i\mathcal{L}A$$



$$A(t) = e^{it\mathcal{L}}A(0)$$

Unitary operator

Liouville's theorem

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

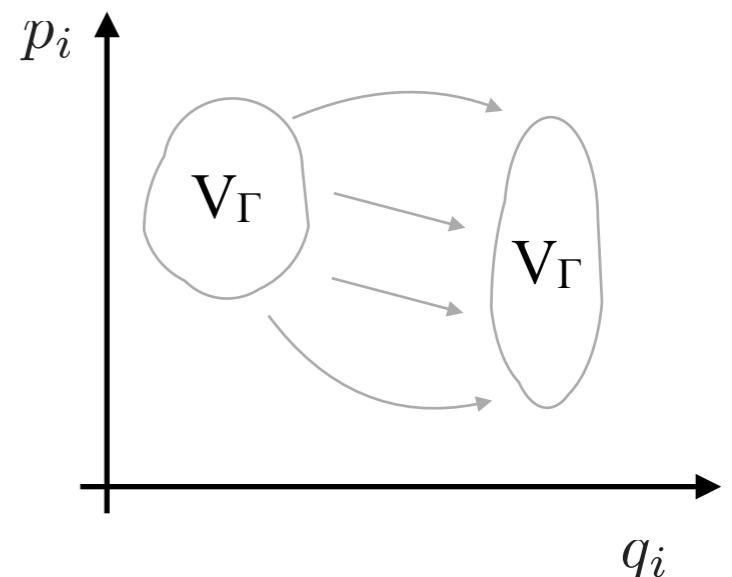
Liouville equation

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

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

Liouville's theorem:

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



Canonical transformation (正準変換)

Hamilton 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:

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

→ Time evolution of Γ :

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

$$J = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \quad : 2n \times 2n \text{ matrix} \\ (n=3N \text{ in 3d system})$$

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

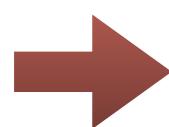
Symplectic condition

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

Jacobian matrix S

$$S_{ij} = \frac{\partial \Gamma'_i}{\partial \Gamma_j}, \quad S = \begin{pmatrix} \frac{\partial \mathbf{q}'}{\partial \mathbf{q}} & \frac{\partial \mathbf{q}'}{\partial \mathbf{p}} \\ \frac{\partial \mathbf{p}'}{\partial \mathbf{q}} & \frac{\partial \mathbf{p}'}{\partial \mathbf{p}} \end{pmatrix}$$

Time evolution of Γ' :



$$\begin{aligned} \frac{d\Gamma'}{dt} &= S \frac{d\Gamma}{dt} = SJ \frac{\partial \mathcal{H}}{\partial \Gamma} \\ &= SJS^T \frac{\partial \mathcal{H}}{\partial \Gamma'} = J \frac{\partial \mathcal{H}}{\partial \Gamma'} \end{aligned}$$

From the relation $\frac{d\Gamma'_i}{dt} = \sum_j \frac{\partial \Gamma'_i}{\partial \Gamma_j} \frac{d\Gamma_j}{dt}$

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

Definition of the canonical transformation

Canonical transformation satisfies the symplectic condition:

$$SJS^T = J$$

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

Infinitesimal time evolution

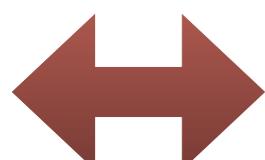
$$\Gamma(\mathbf{q}(t), \mathbf{p}(t)) \rightarrow \Gamma'(\mathbf{q}(t + \Delta t), \mathbf{p}(t + \Delta t))$$

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

This is a canonical transformation,
when Δt is infinitesimal.



Exact Hamiltonian dynamics satisfies the symplectic condition.
(The symplectic condition contains Liouville's theorem.)



For finite Δt (Euler method), it breaks the symplectic condition,
and the volume of phase space is **not** conserved.
(Main reason for the energy drift.)

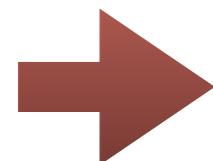
If we can construct discrete approximations satisfying
the symplectic condition, we obtain more stable methods!

Symplectic integrator

Symplectic integrator:

Discrete approximation of Hamilton dynamics
satisfying the symplectic condition.

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

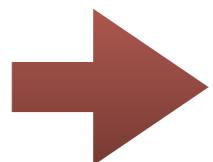


Because the volume of phase space is conserved,
the energy does not drift along this dynamics.
(if there is no numerical error.)

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:

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

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

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

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

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

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

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

Euler like equation
(but this is more stable!)

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

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

Exactly equal to
(Velocity) Verlet method

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

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

Control temperature (quick review)

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: $K = \sum_i \frac{p_i^2}{2m_i}$

Under the canonical (NVT) ensemble

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



Define **effective temperature** of a snapshot:

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

Rescale velocities every time step as

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

Results of the velocity scaling

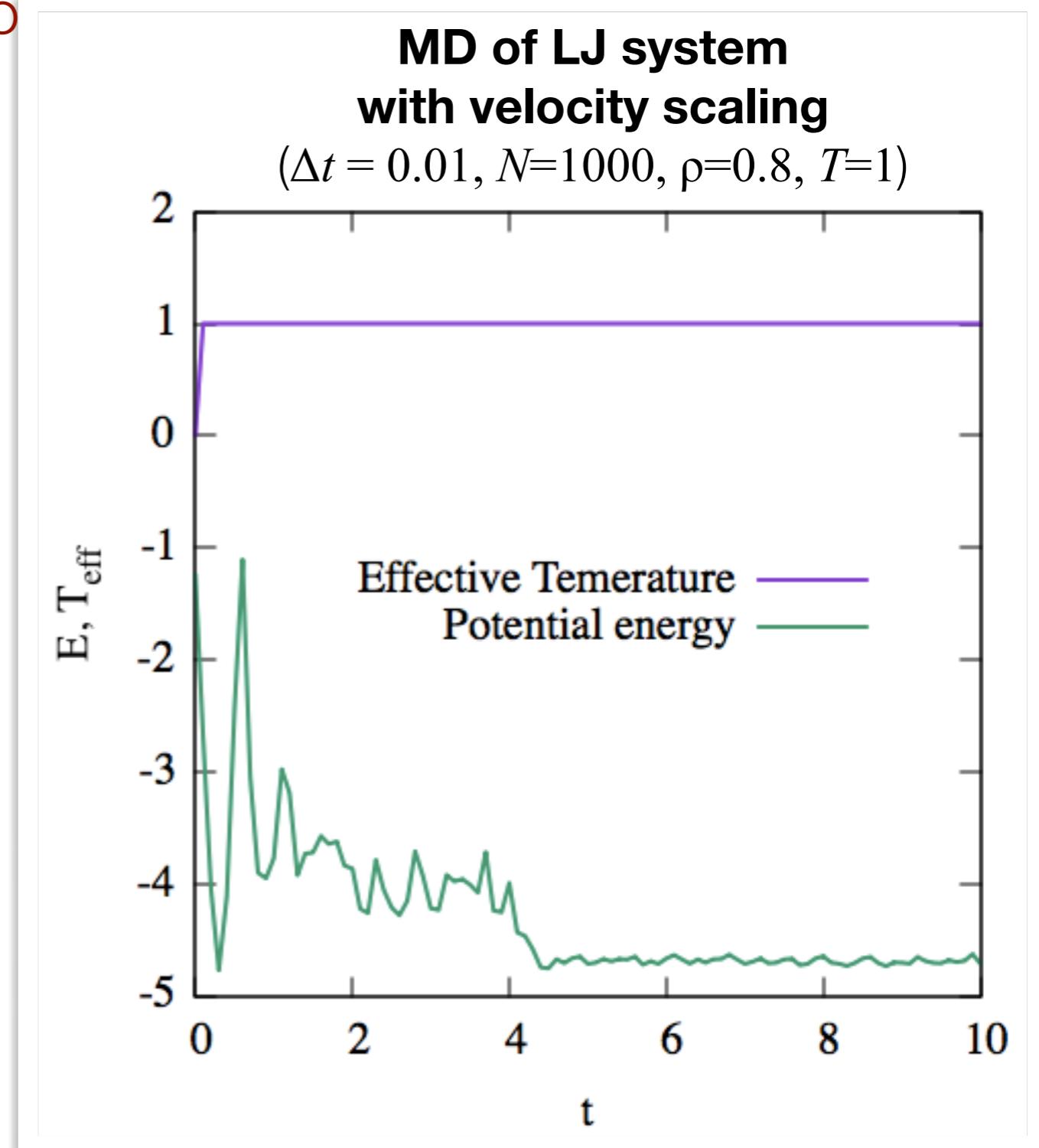
Total kinetic energy is artificially fixed to

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

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.



Temperature control: Langevin dynamics

Langevin dynamics

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

Dissipation

Random force

(Gaussian white noise)

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

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



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 thermostat

Nose thermostat

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

Extended Hamiltonian

System with a “heat bath”

$$\mathcal{H}_N = \sum_i \frac{(\mathbf{p}'_i)^2}{2m_i s^2} + V(\{\mathbf{q}_i\}) + \frac{P_s^2}{2Q} + gk_B T \ln s$$

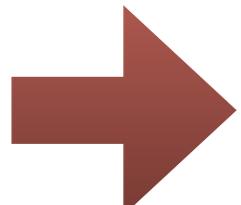
Original Hamiltonian
with scaled momentum

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

Heat-bath
s: scale factor for time

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

Canonical equation
(along t')



$$\frac{d\mathbf{p}'_i}{dt'} = -\frac{\partial V}{\partial \mathbf{q}_i} = \mathbf{F}_i(\{\mathbf{q}_i\})$$

$$\frac{d\mathbf{q}_i}{dt'} = \frac{\mathbf{p}'_i}{m_i s^2}$$

$$\frac{dP_s}{dt'} = \frac{1}{s} \left(\sum_i \frac{(\mathbf{p}'_i)^2}{m_i s^2} - gk_B T \right)$$

$$\frac{ds}{dt'} = \frac{P_s}{Q}$$

Temperature control: Nosé-Hoover method

Nosé-Hoover dynamics

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

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

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

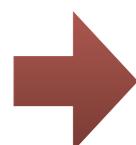
$$\frac{d\zeta}{dt} = \frac{gk_B}{Q} \left[\frac{1}{gk_B} \sum_i \frac{\mathbf{p}_i^2}{2m_i} - T \right] = \frac{1}{\tau^2} [T_{\text{eff}} - T]$$

$$\mathbf{p}_i = \frac{\mathbf{p}'_i}{s} \quad t = \frac{t'}{s}$$

$$g = 3N \text{ (# of DOF)}$$

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

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 $T_{\text{eff}} < T$)

* 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”)

$$\mathcal{H}_N = \mathcal{H} \left(\left\{ \frac{\mathbf{p}'_i}{s} \right\}, \{\mathbf{q}_i\} \right) + \frac{P_s^2}{2Q} + gk_B T \ln s$$

MD on (q, p', \mathbf{t}') dynamics yields NVE ensemble of H_N

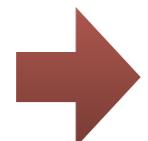
$$\begin{aligned} \rightarrow \lim_{\tau' \rightarrow \infty} \frac{1}{\tau'} \int_0^{\tau'} dt' O\left(\left\{ \frac{\mathbf{p}'_i}{s} \right\}, \{\mathbf{q}_i\}\right) &= \frac{\int d\mathbf{p}'_i d\mathbf{q}_i dP_s ds O\left(\left\{ \frac{\mathbf{p}'_i}{s} \right\}, \{\mathbf{q}_i\}\right) \delta(E - \mathcal{H}_N)}{\int d\mathbf{p}'_i d\mathbf{q}_i dP_s ds \delta(E - \mathcal{H}_N)} \\ s^{3N} \text{ comes from } \mathbf{p}'_i = s\mathbf{p}_i &\quad = \frac{\int d\mathbf{p}_i d\mathbf{q}_i dP_s ds s^{3N} O(\{\mathbf{p}_i\}, \{\mathbf{q}_i\}) \delta(E - \mathcal{H} - \frac{P^2}{2Q} - gk_B T \ln s)}{\int d\mathbf{p}_i d\mathbf{q}_i dP_s ds s^{3N} \delta(E - \mathcal{H} - \frac{P^2}{2Q} - gk_B T \ln s)} \end{aligned}$$

from

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

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

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



Canonical ensemble if $g = 3N + 1$

$(f(x_0) = 0)$

Nosé-Hoover dynamics becomes NVT ensemble 2

Time average on $\textcolor{brown}{t}$:

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

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

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

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

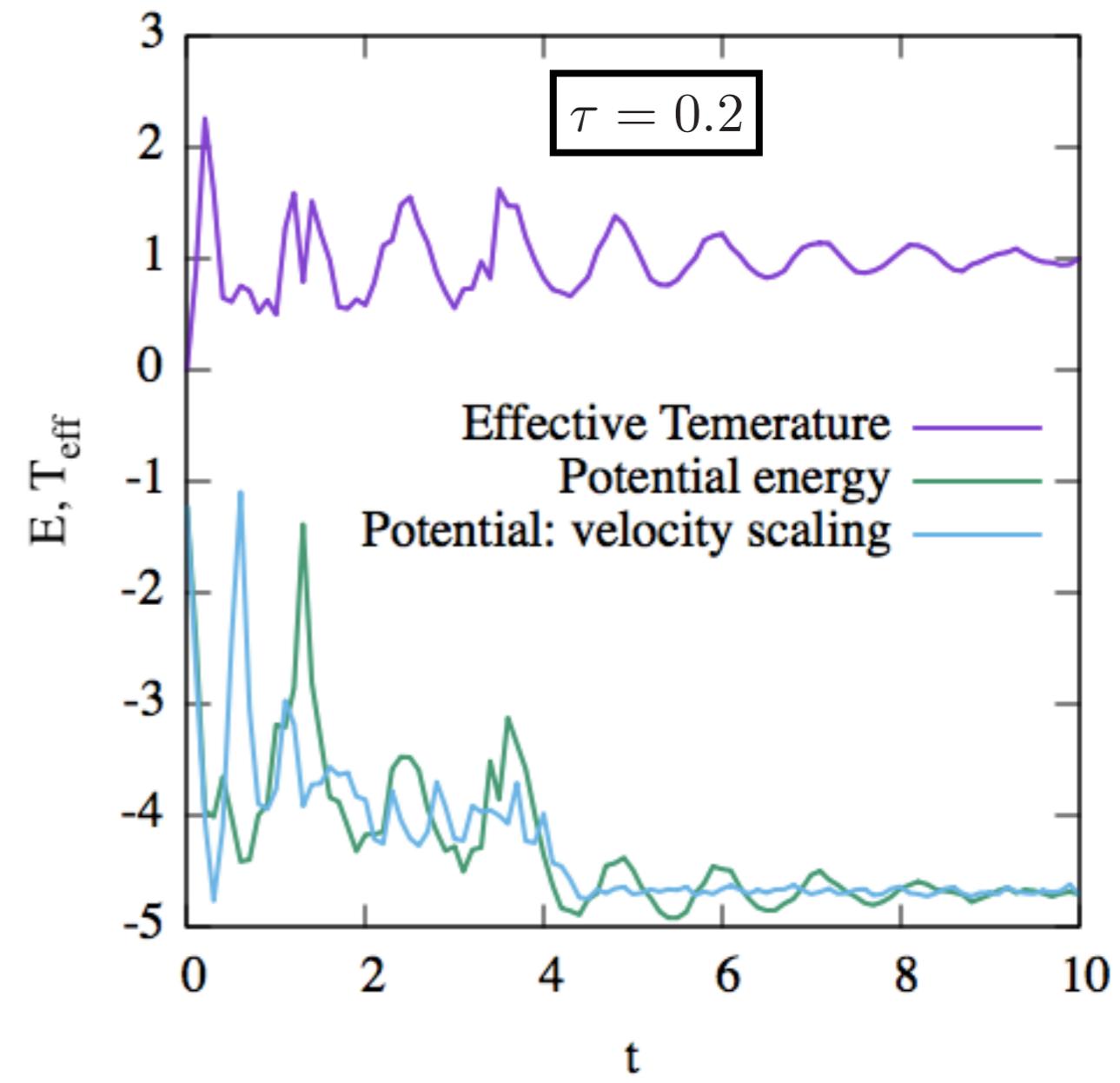
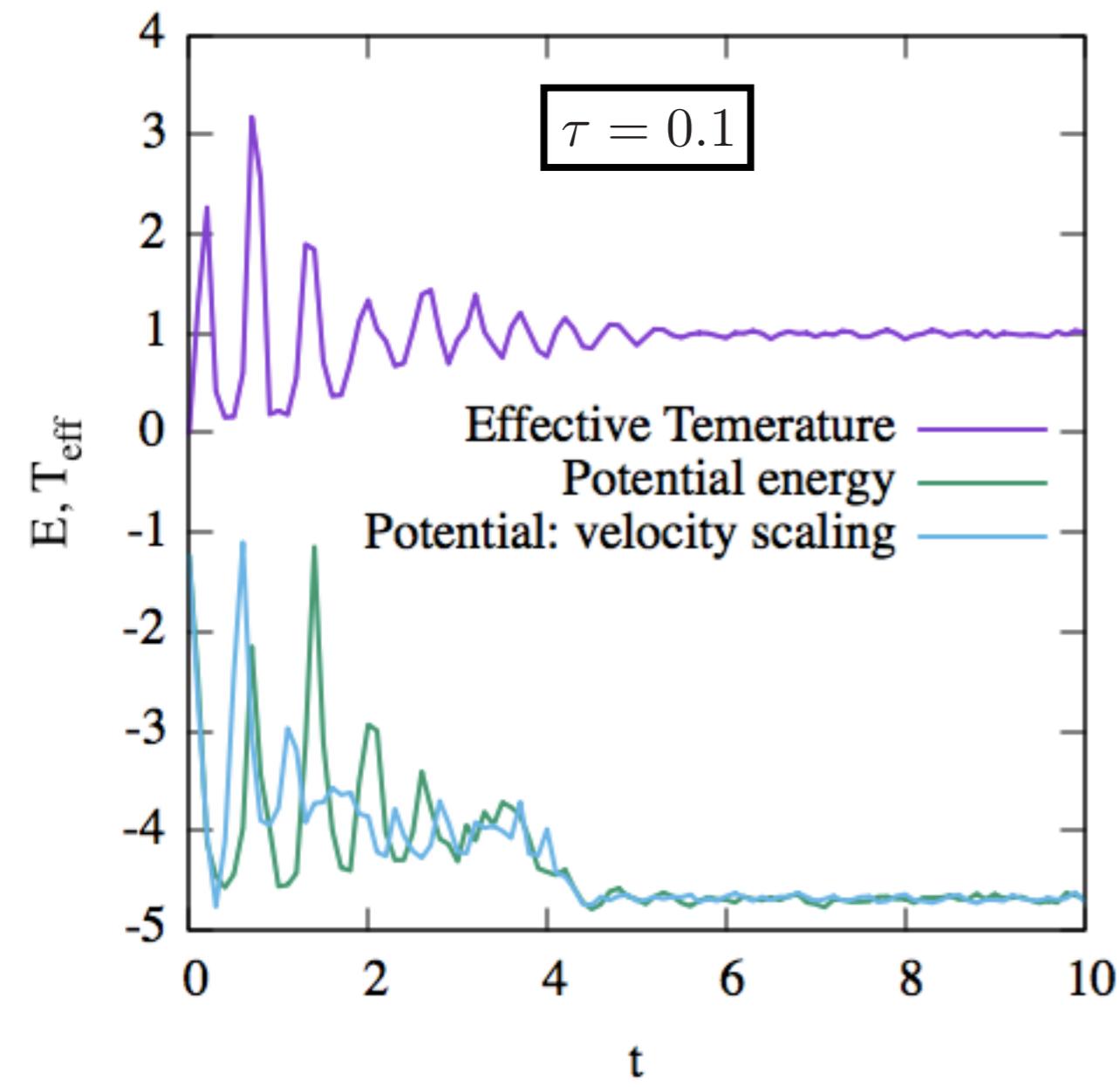
\rightarrow $\boxed{\text{Canonical ensemble if } g = 3N}$

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

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



Control pressure (will be skipped)

Pressure control: Andersen method

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

Extended Hamiltonian

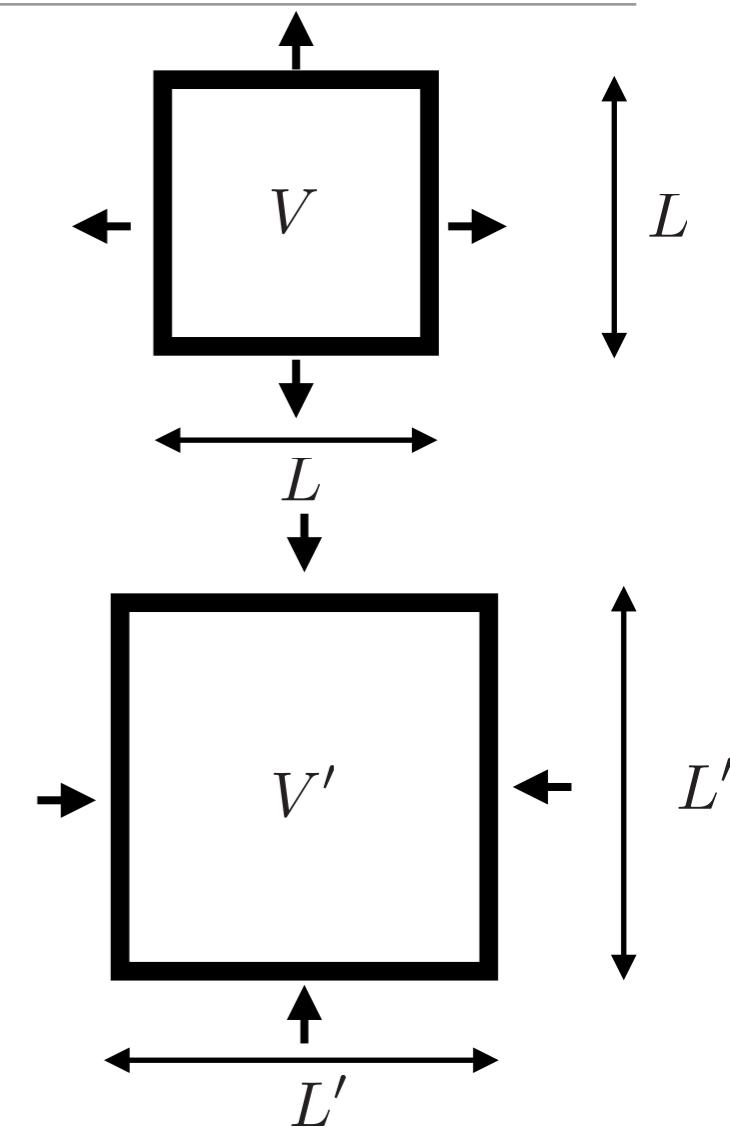
System with a “piston”

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

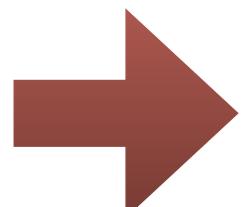
Original Hamiltonian with scaled coordinate and momentum

Piston

$$\begin{aligned}\tilde{q}_i &= V^{-\frac{1}{3}} q_i \\ \tilde{p}_i &= V^{\frac{1}{3}} p_i\end{aligned}$$



Canonical equation



$$\begin{aligned}\frac{d\tilde{q}_i}{dt} &= \frac{\tilde{p}_i}{m_i V^{\frac{2}{3}}} & \frac{dV}{dt} &= \frac{P_V}{M} \\ \frac{d\tilde{p}_i}{dt} &= V^{\frac{1}{3}} \mathbf{F}_i(\{V^{\frac{1}{3}}\tilde{q}_i\}) & \frac{dP_V}{dt} &= \frac{1}{3V} \sum_i \left[\frac{\tilde{p}_i^2}{m_i V^{\frac{2}{3}}} + \mathbf{F}_i \cdot (V^{\frac{1}{3}}\tilde{q}_i) \right] - P\end{aligned}$$

Pressure control: Andersen method

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

In original coordinates

$$\begin{aligned}\frac{d\mathbf{q}_i}{dt} &= \frac{\mathbf{p}_i}{m_i} + \frac{\dot{V}}{3V}\mathbf{q}_i & \frac{dV}{dt} &= \frac{P_V}{M} \\ \frac{d\mathbf{p}_i}{dt} &= \mathbf{F}_i - \frac{\dot{V}}{3V}\mathbf{p}_i & \frac{dP_V}{dt} &= \frac{1}{3V} \sum_i \left[\frac{\mathbf{p}_i^2}{m_i} + \mathbf{F}_i \cdot \mathbf{q}_i \right] - P \\ &&&\text{---} \\ &&= P_{\text{eff}} - P & P_{\text{eff}} : \text{virial theorem}\end{aligned}$$

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.

$H = \text{Enthalpy}$

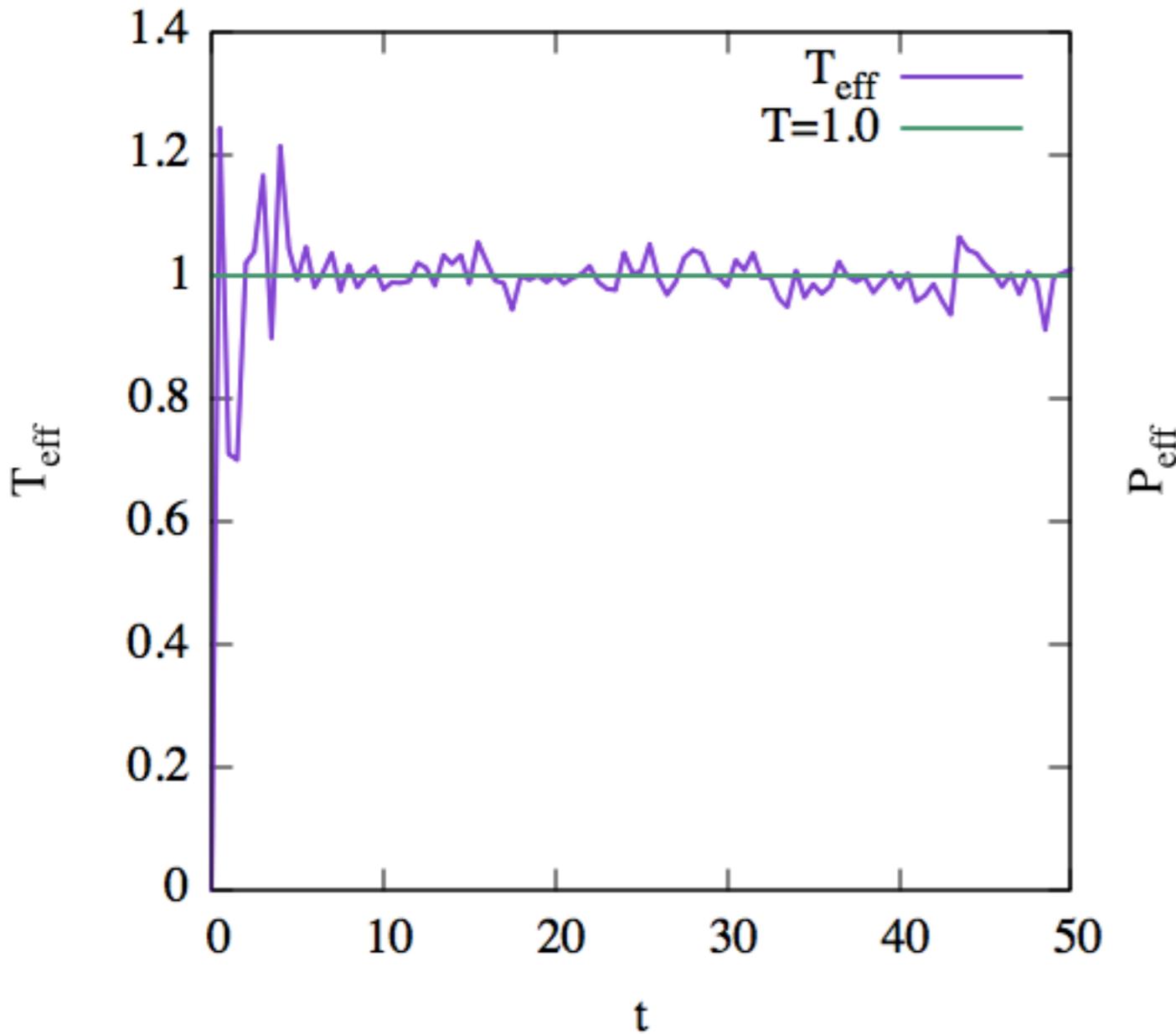
NPT ensemble

MD of LJ system

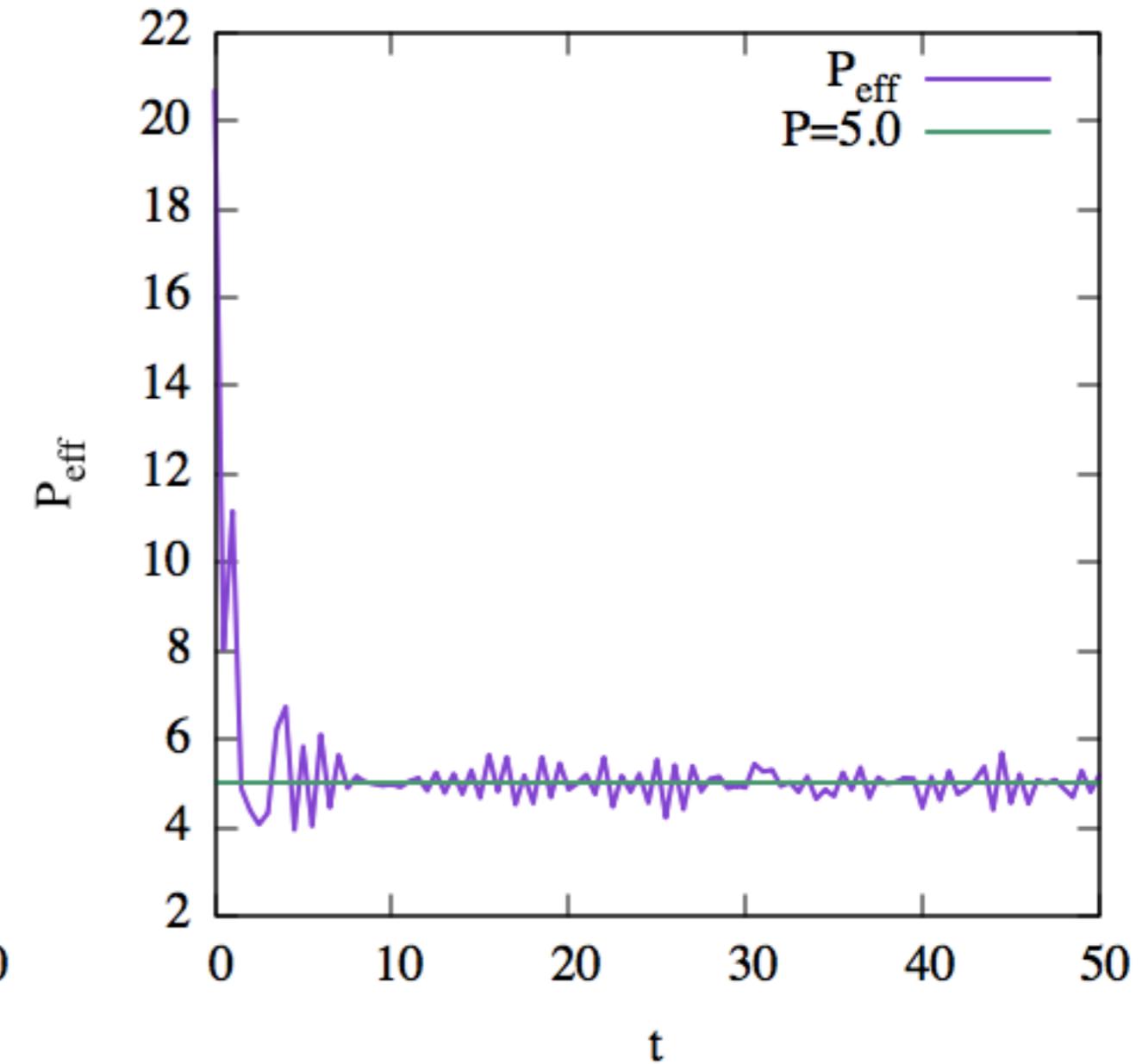
($\Delta t = 0.005, N=1000, T=1, P=5$)

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

Temperature



Pressure



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** (or **python3**).
 - To run the sample code you need
 - numpy, and numba (numba is used for speed up)
 - Jupyter notebook version contains auto-correlation analysis

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.

Extended Ensemble method for Monte Carlo Methods

Contents

- Back ground
 - Density of states and the histogram method
- Extended ensemble methods using information of the density of states
 - Multi Canonical Method
 - Wang-Landau method (will be skipped)
- Another extended ensemble: Replica exchange method
- Report problem

Density of state and histogram method

Origin of exponentially long relaxation time

Partition function of the canonical ensemble

$$Z = \int d\Gamma e^{-\beta \mathcal{H}(\Gamma)} = \int dE \frac{\rho(E)}{\text{Density of state}} e^{-\beta E} = \int dE e^{-\frac{\beta F(E)}{\text{Free energy}}}$$

Probability distribution for energy

$$\rightarrow P(E) = \frac{1}{Z} e^{-\beta F(E)}$$

Note! Free energy is **extensive**: $F(E) \propto N$

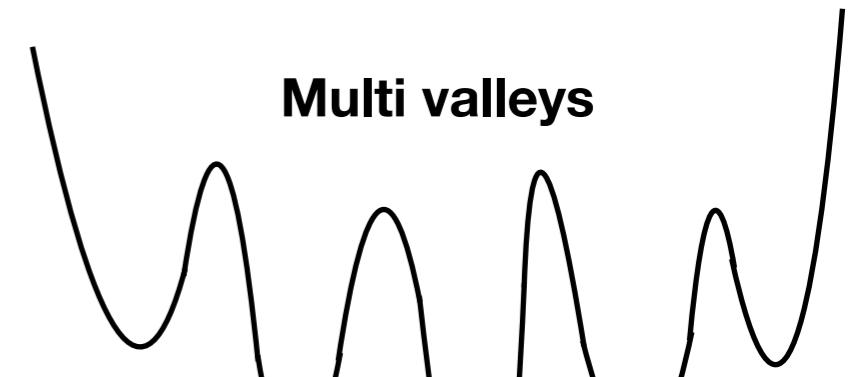
- “Transition probability” is proportional to the exponential of Free-energy difference: $\exp(-\Delta F/T)$
- Usual algorithm of MC (and MD) changes the state (or the energy) **gradually**.

\rightarrow If there are **local minima**, the relaxation time could be **exponentially large** as the size is increased.

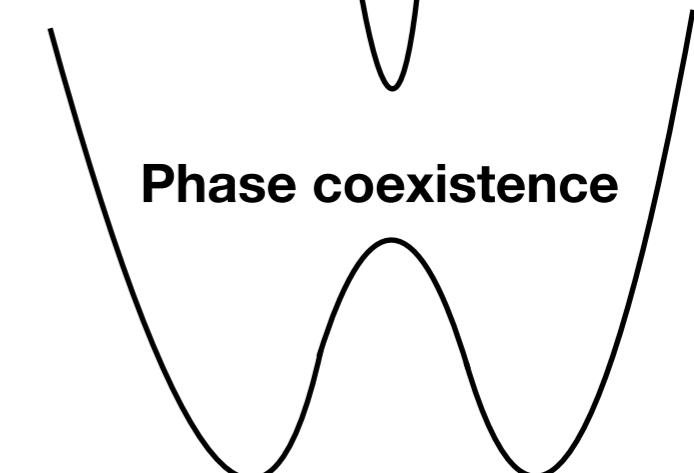
“Free energy”

$$F(E) \equiv E - k_B T \log \rho(E)$$

Multi valleys



Phase coexistence



Density of state

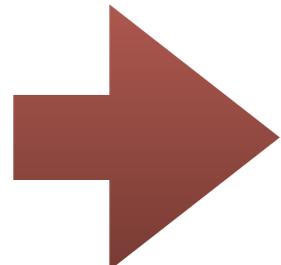
$$\begin{aligned} Z &= \int d\Gamma e^{-\beta \mathcal{H}(\Gamma)} = \int dE \rho(E) e^{-\beta E} \\ &= \int dE \int dM \rho(E, M) e^{-\beta E} \end{aligned}$$

$$\begin{array}{ll} \int d\Gamma & \sim O(N)\text{-dimensional integral} \\ \int dE & \sim 1\text{-dimensional} \\ \int dE \int dM & \sim 2\text{-dimensional} \end{array}$$

- If we know the exact $\rho(E)$ (or $\rho(E, M)$), the calculation of partition function is reduced to 1 or (a few) -dimensional integral.
- Even if we only know an approximate density of state,

$$\tilde{\rho}(E) \simeq \rho(E)$$

we can improve the sampling efficiency by using its information.



- Histogram method
- Multi canonical method
- Wang-Landau method

Energy Histogram

Energy histogram:

In MC or MD calculations

$h(E_i)$:# of samples (snap shots) with energy in

$$E_i - \Delta E/2 \leq E < E_i + \Delta E/2$$

$$\rightarrow P(E)\Delta E \simeq \frac{1}{N_h} h(E)$$

e.g. NVT ensemble:

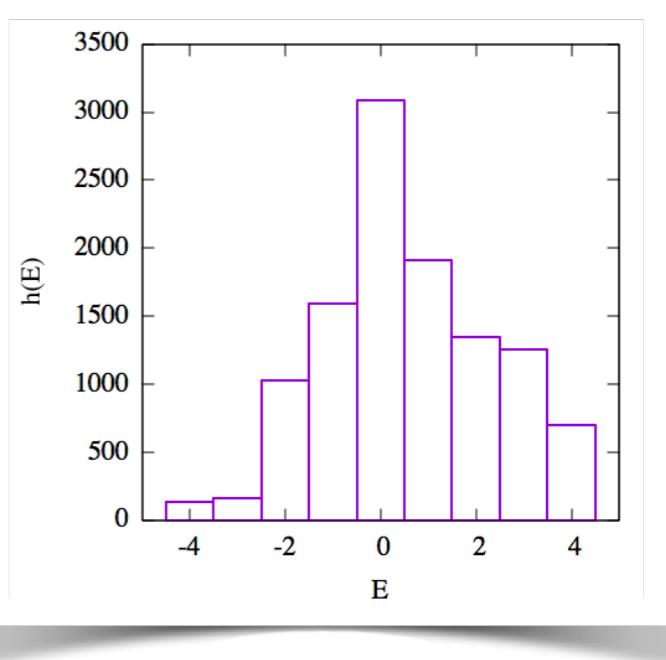
Total # of samples

$$N_h \equiv \sum_i h(E_i)$$

$$P(E) = \frac{1}{Z(\beta)} \rho(E) e^{-\beta E} \rightarrow \rho(E) \simeq \frac{Z(\beta)}{N_h \Delta E} h(E) e^{\beta E}$$

We can calculate (approximate) density of state from usual MC or MD simulations!

Because we don't know the partition function,
DOS is determined up to the proportional coefficient.



Histogram method (reweighting method)

Energy expectation value of different temperatures

$$\langle E \rangle_{\beta'} = \frac{\int dE \rho(E) E e^{-\beta' E}}{\int dE \rho(E) e^{-\beta' E}} \simeq \frac{\sum_i E_i h(E_i) e^{-(\beta' - \beta) E_i}}{\sum_i h(E_i) e^{-(\beta' - \beta) E_i}}$$

Any expectation values can also be calculated by the histogram method.

$$\rho(E) \simeq \frac{Z(\beta)}{N_h \Delta E} h(E) e^{\beta E}$$

$$\langle O \rangle_{\beta'} \simeq \frac{\sum_i O(E_i) h(E_i) e^{-(\beta' - \beta) E_i}}{\sum_i h(E_i) e^{-(\beta' - \beta) E_i}}$$

Average at energy E_i

$$O(E_i) \equiv \sum_{E(\Gamma_j) \in E_i} O(\Gamma_j)$$

Limitation of histogram method

Reweighted histogram becomes less accurate when T' is far from the original T .

“Tail” of the original histogram has only small # of snapshots. → large noise

Central limit theorem

Width of energy distribution: $\propto \sqrt{N}$

Average of energy: $\propto N$

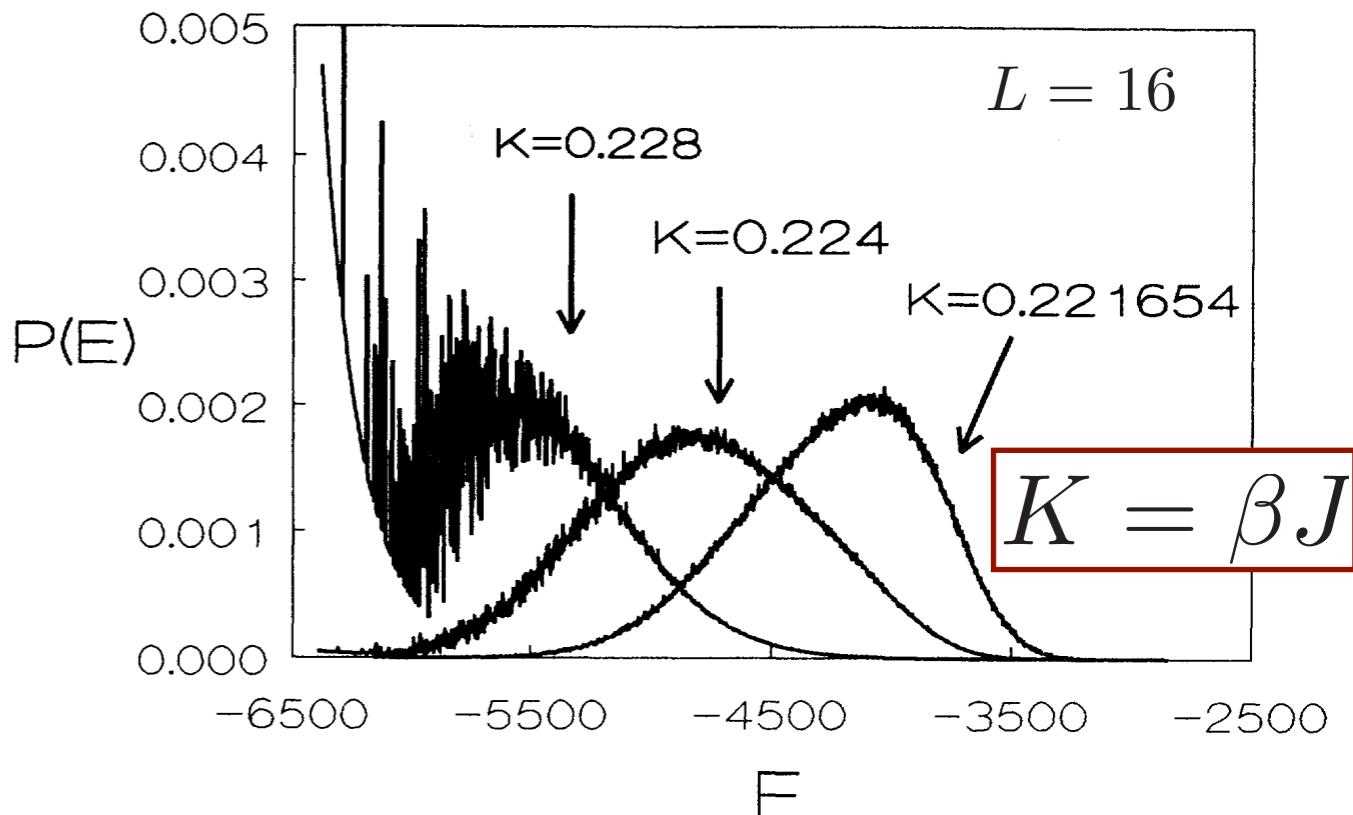
Distribution becomes narrower as N is increased!

Reliable temperature region for reweighting:

$$\Delta T \propto \frac{1}{\sqrt{N}}$$

Energy distribution of 3d-Ising model

A. M. Ferrenberg and D. P. Landau, Phys. Rev. B 44, 5081 (1991)



MC simulation at $K=0.221654$

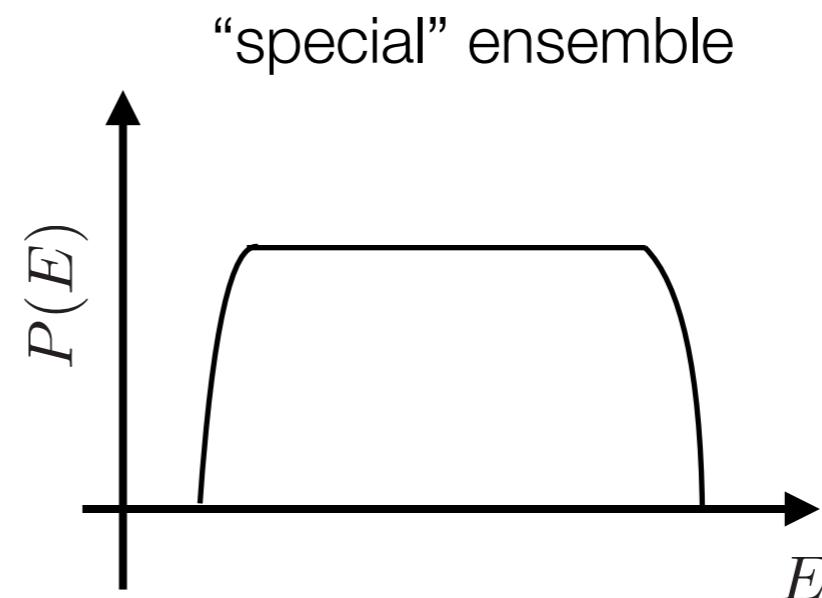
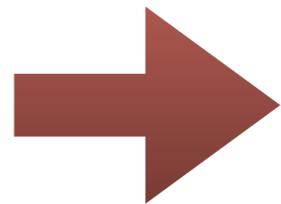
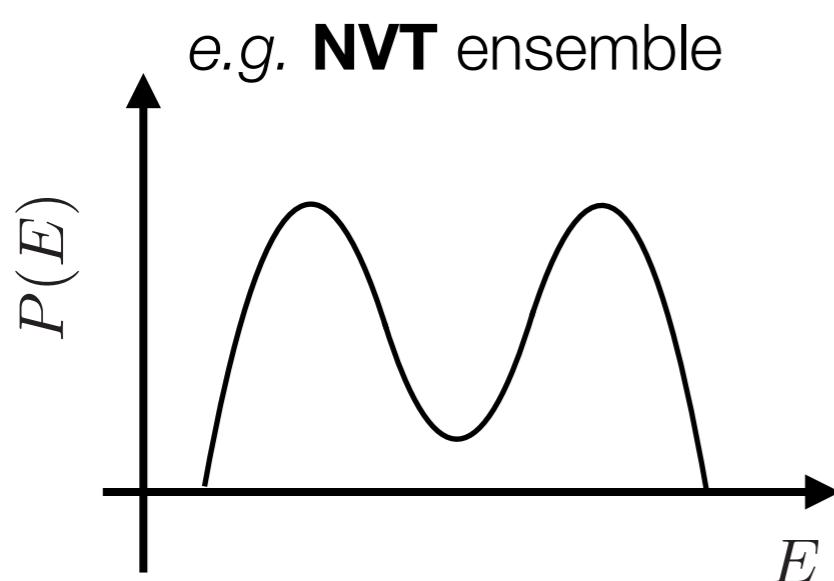
 Reweighting to
 $K=0.224$ and $K=0.228$

Multi Canonical methods

Idea of Multi-Canonical method

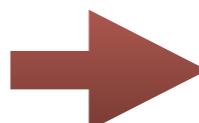
B.A. Berg and T. Neuhaus (1992)

If we can prepare a special ensemble where the energy distribution is “flat”, we can efficiently sample all relevant states.



$$P(E) \propto \rho(E)e^{-\beta E}$$

$$\tilde{P}(E) \propto \rho(E)e^{-S(E)} = \text{const.}$$



Special ensemble is related to log of DOS!

$$S(E) = \log \rho(E)$$

How to obtain the special ensemble?

Special ensemble is log of DOS!

$$S(E) = \log \rho(E)$$

DOS is unknown!

We can obtain $S(E)$ approximately by iterative calculations.

“Image” of an iterative algorithm:

1. Run MC simulation on a **high temperature** and calculate energy histogram.

$$h(E) \sim \rho(E)e^{-\beta E}$$

2. Based on the energy histogram, extract approximate $S(E)$.

$$S^0(E) = \beta E + \log h(E)$$

3. **Loop n**

1. Run MC simulation under $S^{(n)}(E)$ and calculate histogram $h^{(n)}(E)$

2. Calculate next $S^{(n+1)}(E)$ as

$$S^{(n+1)}(E) = S^{(n)}(E) + \log h^{(n)}(E)$$

How to obtain the special ensemble?

3. Loop n

1. Run MC simulation under $S^{(n)}(E)$ and calculate histogram $h^{(n)}(E)$
2. Calculate next $S^{(n+1)}(E)$ as

$$S^{(n+1)}(E) = S^{(n)}(E) + \log h^{(n)}(E)$$

- The histogram $h^{(n)}(E)$ is expected to be $h^{(n)}(E) \sim \rho(E)e^{-S^{(n)}(E)}$
- When $S^{(n)}(E)$ becomes close to $\log \rho(E)$, the histogram becomes almost flat.
→ We can **efficiently sample** the histogram and DOS.
- By using accurate $S^{(n)}(E)$ we can calculate expectations values under the canonical ensemble by using reweighting technique.

$$\langle O \rangle_\beta = \frac{\int dE O(E) \rho(E) e^{-S(E)} e^{-\beta E + S(E)}}{\int dE \rho(E) e^{-S(E)} e^{-\beta E + S(E)}} = \frac{\langle O e^{-\beta E + S(E)} \rangle_S}{\langle e^{-\beta E + S(E)} \rangle_S}$$

Detailed algorithm (will be skipped)

B.A. Berg, Nucl. Phys. B (Proc. Supple.) **63A-C**, 982 (1998)

Suppose $S(E)$ looks like: $S(E) = \beta(E)E - \alpha(E)$

(Energy dependent temperature)



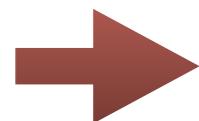
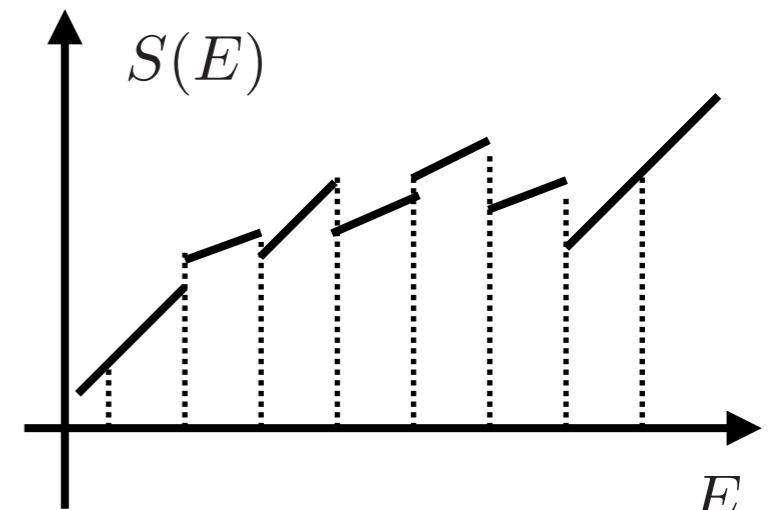
$$S(E) \simeq \beta_i E - \alpha_i$$

for $E_i - \Delta E/2 \leq E \leq E_i + \Delta E/2$

In a specific interval, we want to optimize β and α ,
i.e. $P(E)$ becomes flat.

By defining

$$\beta_i \equiv \frac{S(E_{i+1}) - S(E_i)}{\Delta E}$$



$$\alpha_{i-1} = \alpha_i + (\beta_{i-1} - \beta_i)E_i$$

We fix $\alpha_{i_{max}} = 0$

Detailed algorithm (will be skipped)

B.A. Berg, Nucl. Phys. B (Proc. Suple.) **63A-C**, 982 (1998)

Iteration :how to determine next β and α

In order to make the histogram flat,

$$S^{(n+1)}(E) = S^{(n)}(E) + \log h^{(n)}(E)$$

→ $\tilde{\beta}_i^{(n+1)} = \beta_i^{(n)} + \log \frac{h_{i+1}^{(n)}}{h_i^{(n)}}$

This estimator could be suffered from large statistical error

→ Gradual change from the previous β

$$\beta_i^{(n+1)} = (1 - c_i)\beta_i^{(n)} + c_i\tilde{\beta}_i^{(n+1)}$$

*For optimal c_i ,
see the reference

α is calculated from β

→ $\alpha_{i-1}^{(n+1)} = \alpha_i^{(n+1)} + (\beta_{i-1}^{(n+1)} - \beta_i^{(n+1)})E_i$

Example of application

q -state Potts model on the square lattice

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \delta_{S_i, S_j} \quad S_i = 0, 1, 2, \dots, q-1$$

Phase transition at

$$T_c/J = \frac{1}{\log(1 + \sqrt{q})}$$

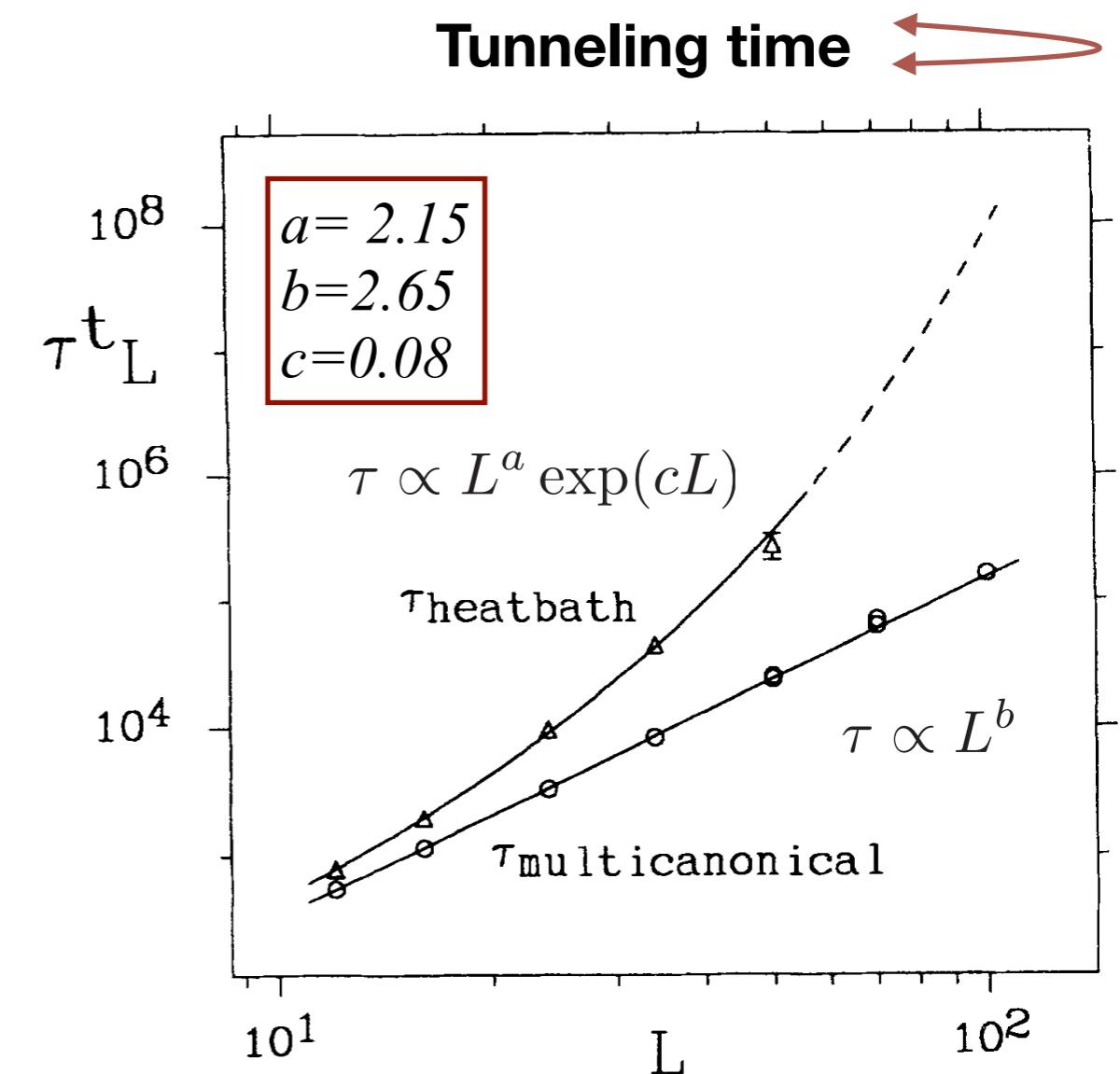
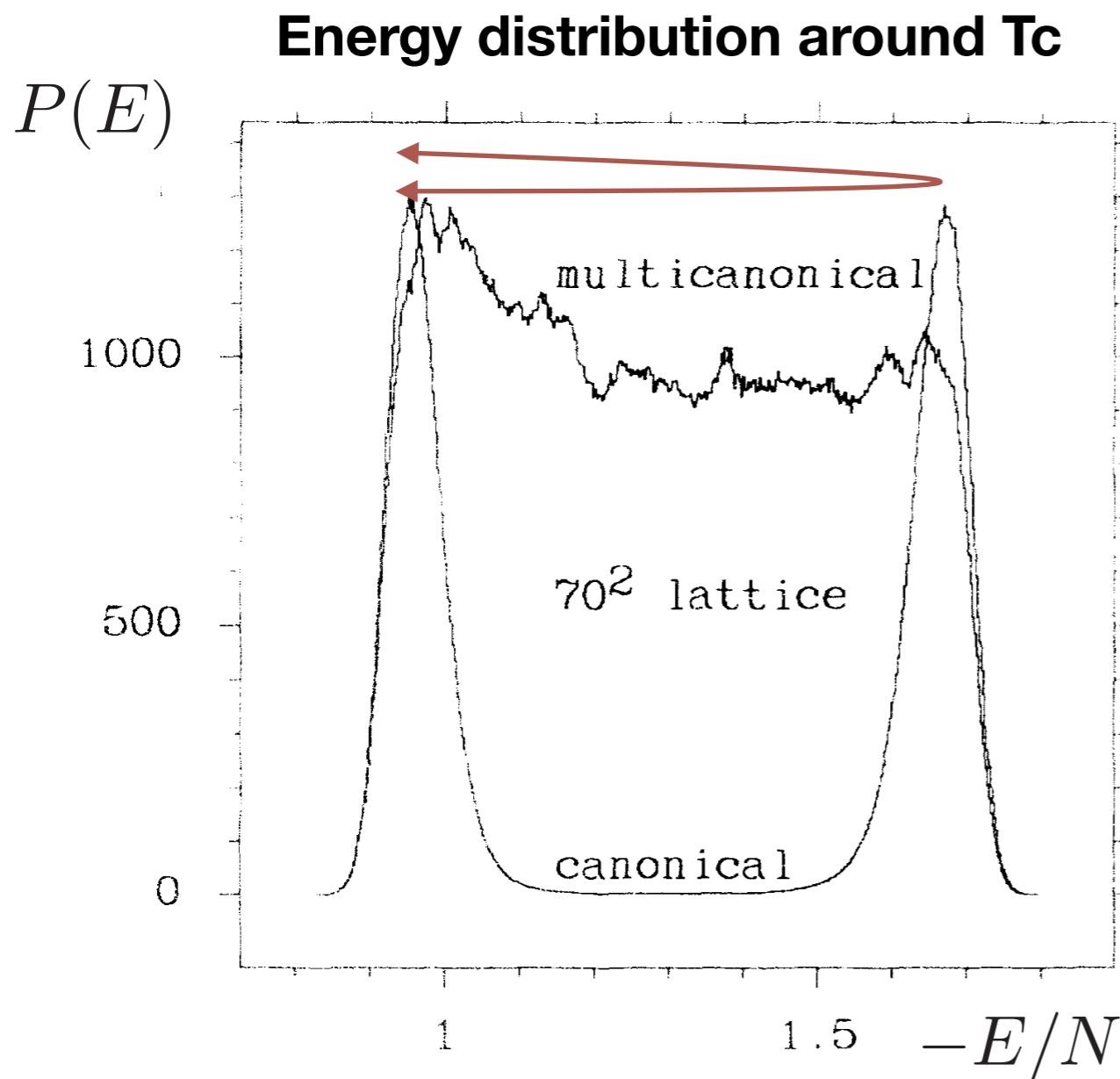
$q = 2$: Equivalent to Ising model

$q \leq 4$: Continuous phase transition

$q > 5$: 1st order phase transition

Multi Canonical method for q=10 Potts model

B.A. Berg and T. Neuhaus, Phys. Rev. Lett. **68**, 9 (1992)



By Multi canonical method, the tunneling time is reduced to **the power of L !**

Wang-Landau method (will be skipped)

Wang-Landau method

F. Wang and D. P. Landau (2001)

Another method to obtain the density of state:

Random walk on the energy space

Markov Chain Monte Carlo with the probability

$$W_{\Gamma \rightarrow \Gamma'} = \min \left(\frac{g(E(\Gamma))}{g(E(\Gamma'))}, 1 \right)$$

$g(E)$:estimate of DOS

if $g(E) = \rho(E)$ 

This MCMC give us
completely flat histogram

Wang-Landau method: update of $g(E)$

F. Wang and D. P. Landau (2001)

Initially, we don't know DOS. → Set an initial guess, e.g. $g(E) = 1$

Along MCMC, we update $g(E)$ of the $E(\Gamma)$ as

$$g_{new}(E) = g(E) \times f \quad (\log g_{new}(E) = \log g(E) + \log f)$$

If the multiplication factor is “gradually” reduced to $f=1$,

$g(E)$ eventually converges to $\rho(E)$.

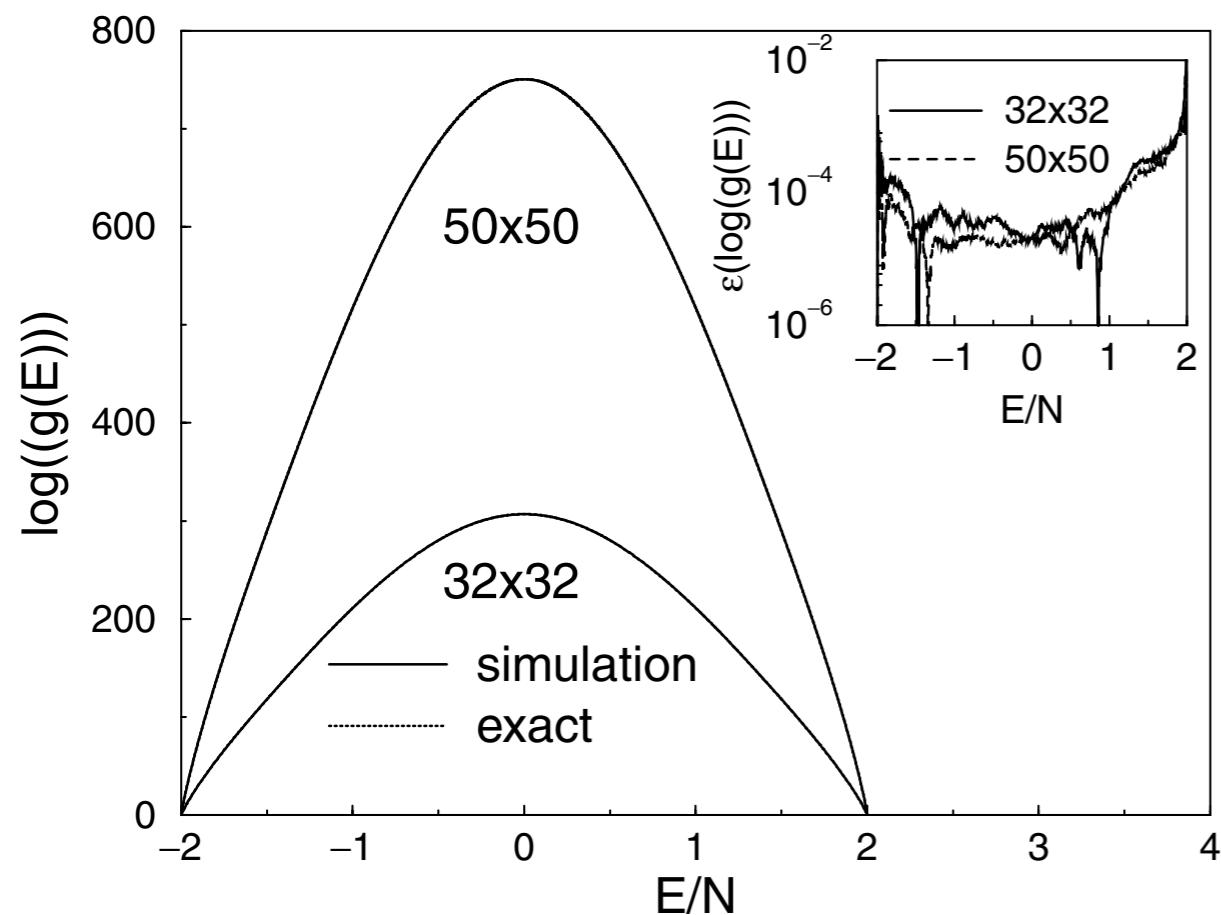
“gradual” change of f :

1. Initially $f=f_0$ (e.g. $f_0 = e^1$)
2. Loop i
 - If (the histogram $h(E)$ becomes “flat”?)
 - Then, we decrease f_i as
$$f_{i+1} = (f_i)^x \quad (\text{e.g. } x = 1/2),$$
and reset the histogram.
3. Repeat until f_i becomes enough small (e.g. $f \sim \exp(10^{-8})$)

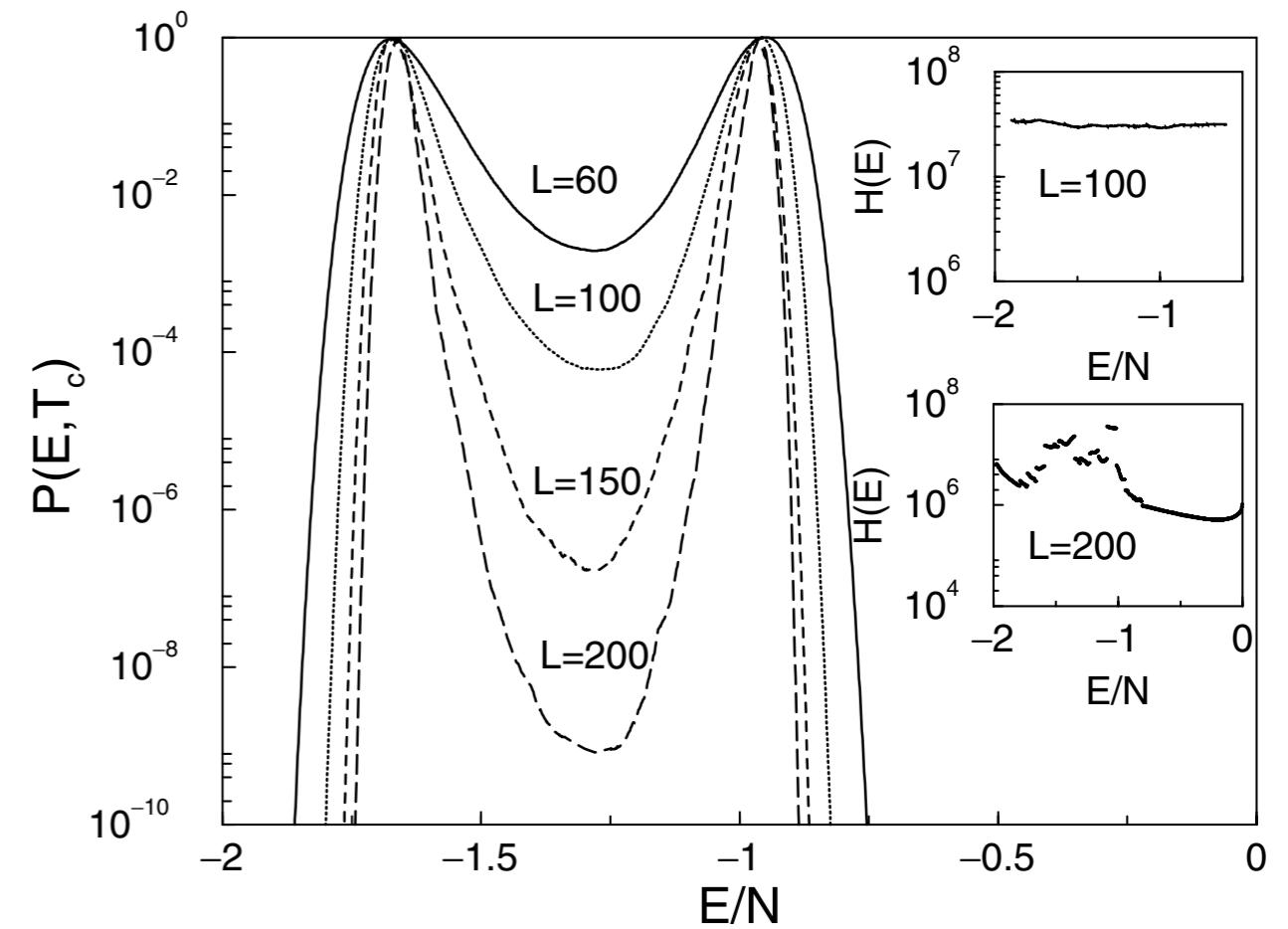
Power of Wang-Landau method

F. Wang and D. P. Landau, Phys. Rev. Lett. **86**, 2050 (2001)

Density of state of 2D-Ising model



Density of state of $q=10$ Potts model



We can obtain very accurate density of state
by Wang-Landau method!

Replica Exchange method

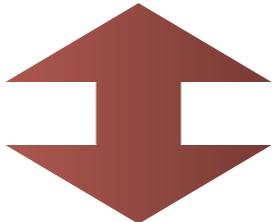
K.Hukushima and K. Nemoto, J. Phys. Soc. Jpn. **65**, 1604 (1996).

Replica exchange (parallel tempering)

A different types of extended ensemble:

Usual MC or MD considers one parameter and one realization:

$$T, \Gamma = \{S_i\}, \{q_i, p_i\}$$



Replica exchange method considers
multiple parameters together with **multiple realizations**:

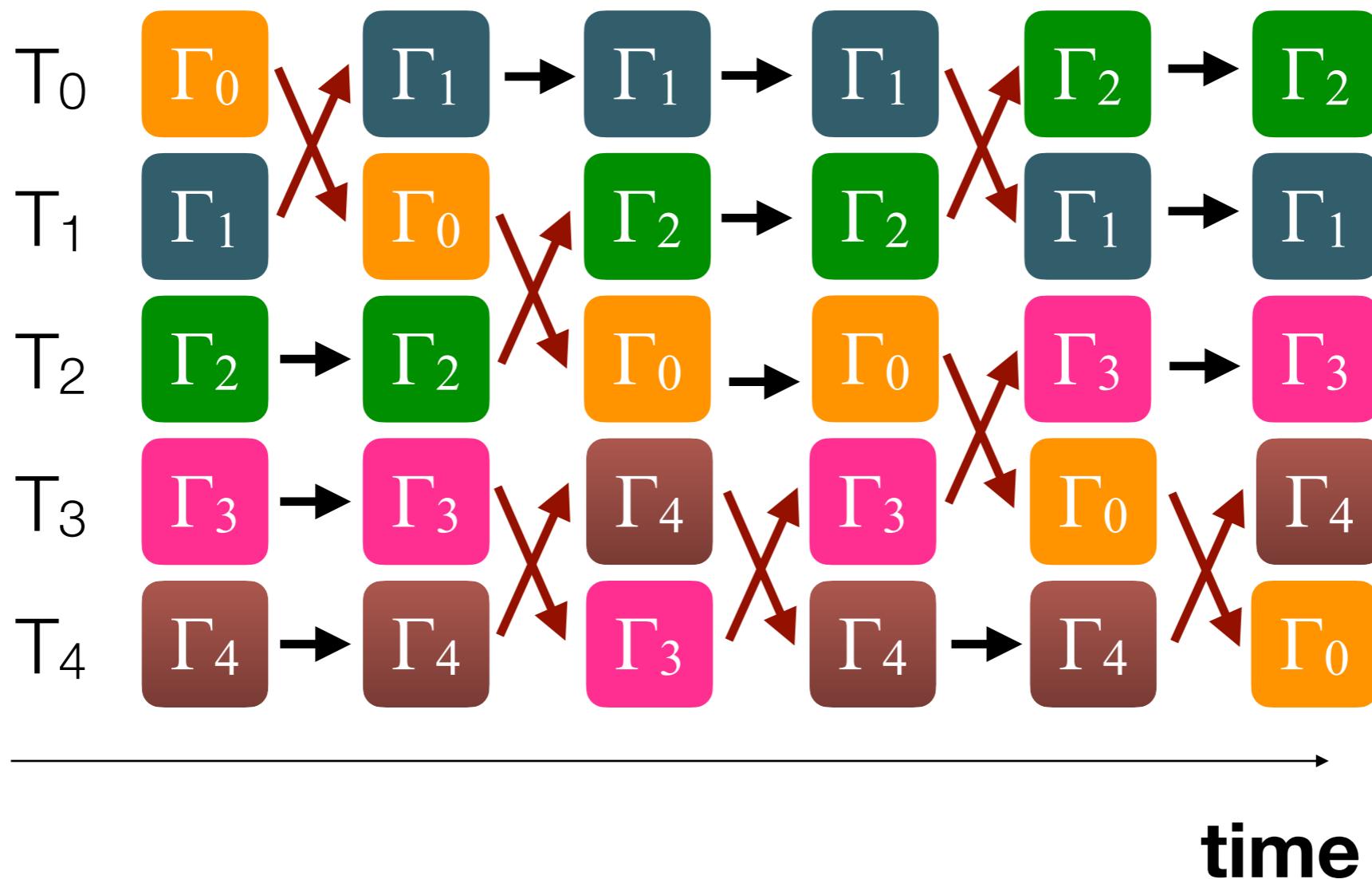
$$\{T_0, T_1, \dots, T_M\}, \{\Gamma_0, \Gamma_1, \dots, \Gamma_M\},$$

→ Try to sample “(M+1)-dimensional” joint-distribution

$$P(\Gamma_0, \Gamma_1, \dots, \Gamma_M; T_0, T_1, \dots, T_M)$$

“Replica exchange”

Along simulation, we “exchange” the relationship between parameter and realization

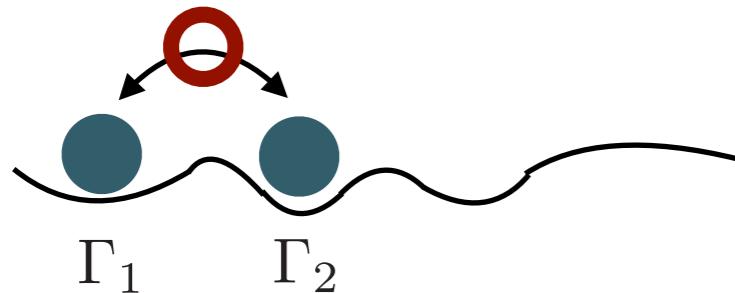


Purpose of replica exchange

Free energy landscape depends on the parameter

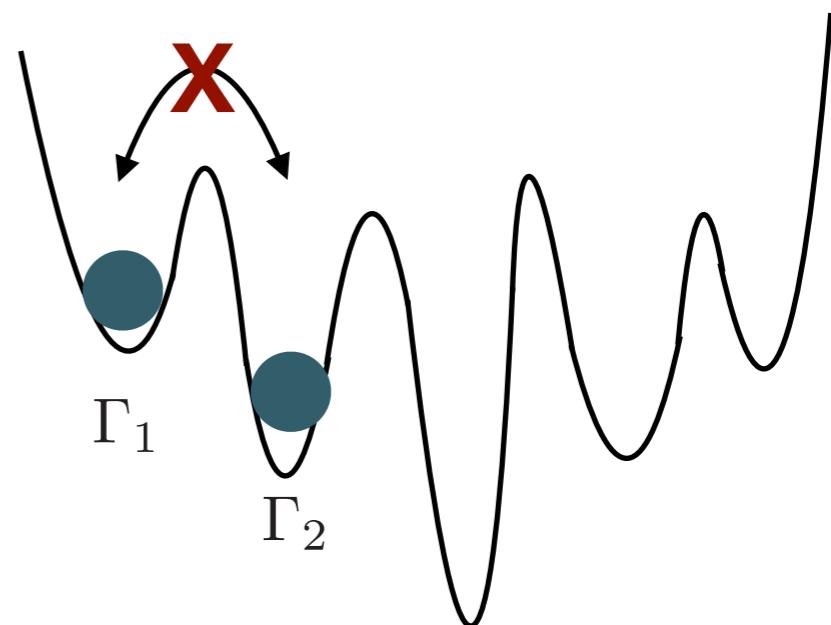
High temperature: T_h

Γ easily moves to other points!

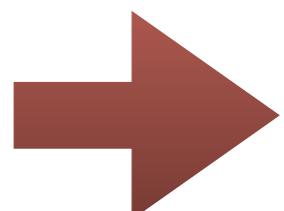


Low temperature: T_l

Γ hardly moves to other minima!



Make a pass like:



$$\{\Gamma_1, T_l\} \rightarrow \{\Gamma_1, T_h\} \rightarrow \{\Gamma_2, T_h\} \rightarrow \{\Gamma_2, T_l\}$$

low

high

high

low

* Parameter is **not necessarily** a temperature.

Markov Chain Monte Carlo for Replica Exchange

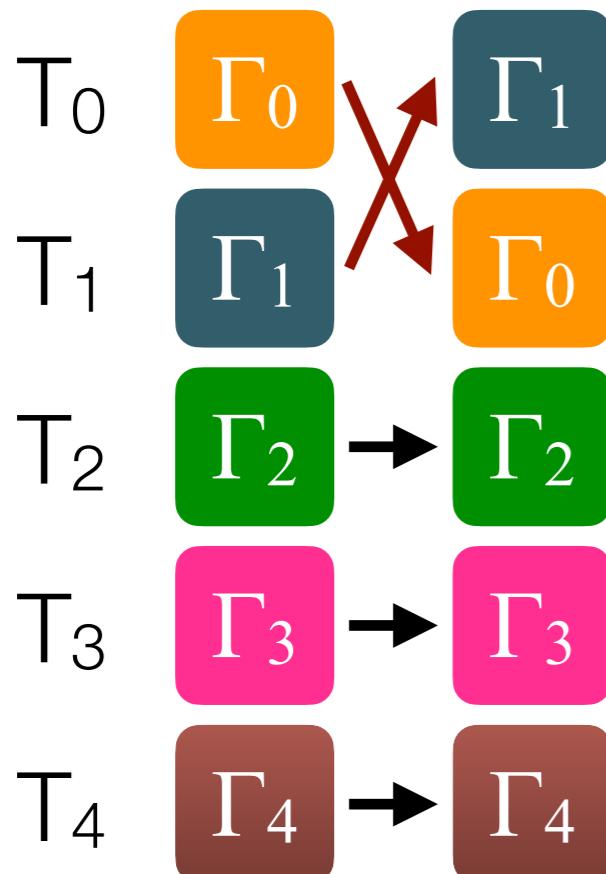
Target steady state distribution:

$$P(\Gamma_0, \Gamma_1, \dots, \Gamma_M; T_0, T_1, \dots, T_M) \propto e^{-\sum_i^M \beta_i E_i}$$
$$E_i \equiv \mathcal{H}(\Gamma_i)$$

Metropolis method:

\mathcal{T} :sequence of temperatures

$$\mathcal{T} = \{T_1, T_0, T_2, \dots\}$$



$$\{T_0, \Gamma_0\}, \{T_1, \Gamma_1\} \rightarrow \{\textcolor{red}{T}_1, \Gamma_0\}, \{\textcolor{red}{T}_0, \Gamma_1\}$$
$$\mathcal{T}_{01} \qquad \qquad \qquad \mathcal{T}_{10}$$

Transition probability

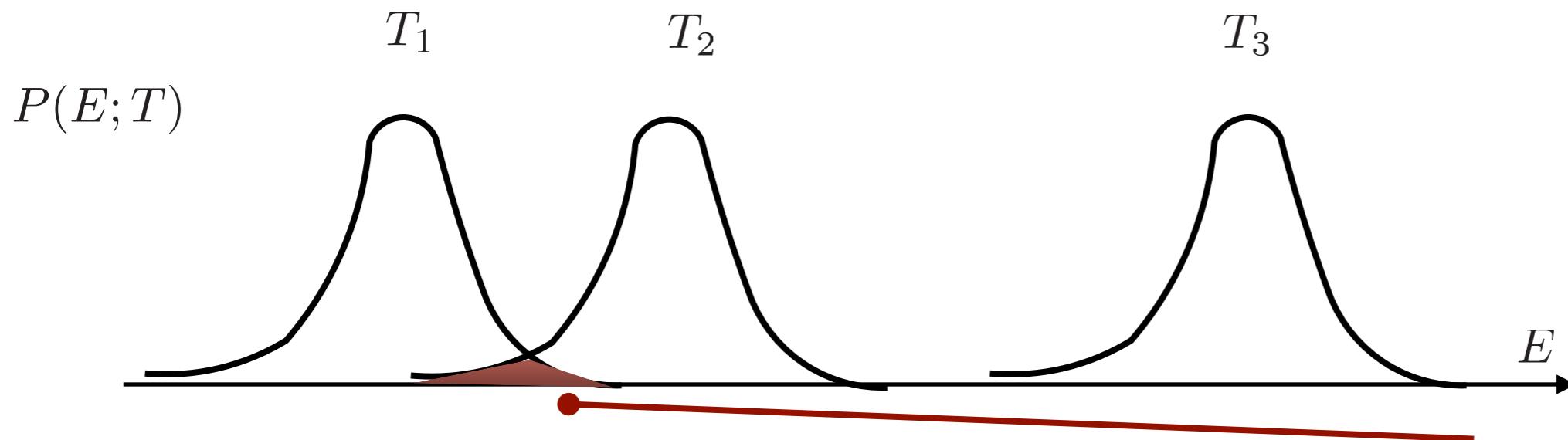
$$W_{\mathcal{T}_{01} \rightarrow \mathcal{T}_{10}} = \min \left(1, \frac{P(\{\Gamma_i\}; \mathcal{T}_{10})}{P(\{\Gamma_i\}; \mathcal{T}_{01})} \right)$$

$$\frac{P(\{\Gamma_i\}; \mathcal{T}_{10})}{P(\{\Gamma_i\}; \mathcal{T}_{01})} = \frac{e^{-\beta_1 E_0 - \beta_0 E_1}}{e^{-\beta_0 E_0 - \beta_1 E_1}}$$
$$= e^{(\beta_0 - \beta_1)(E_0 - E_1)}$$

Select of temperature sequence

$$\frac{P(\{\Gamma_i\}; \mathcal{T}_{10})}{P(\{\Gamma_i\}; \mathcal{T}_{01})} = e^{(\beta_0 - \beta_1)(E_0 - E_1)} = \frac{P(E_1; T_0)P(E_0; T_1)}{P(E_0; T_0)P(E_1; T_1)}$$

Energy distribution at T
 $P(E; T)$



Almost all exchange occurs in the energy region of “overlap”.

$\{\Gamma_1, T_1\}, \{\Gamma_2, T_2\} \rightarrow \{\Gamma_1, \textcolor{red}{T}_2\}, \{\Gamma_2, \textcolor{red}{T}_1\}$:acceptable!

$\{\Gamma_2, T_2\}, \{\Gamma_3, T_3\} \rightarrow \{\Gamma_2, \textcolor{red}{T}_3\}, \{\Gamma_3, \textcolor{red}{T}_2\}$:almost rejected!

For efficient exchange, we have to choose a sequence of temperatures so that the energy distributions have finite overlap!

Usually we only exchange the nearest neighbor pairs of temperatures

Select of temperature sequence: Example

Suppose $C = \frac{dE}{dT} = \text{const.}$

$$\frac{P(\{\Gamma_i\}; \mathcal{T}_{10})}{P(\{\Gamma_i\}; \mathcal{T}_{01})} = e^{(\beta_0 - \beta_1)(E_0 - E_1)}$$

→ Temperature sequence satisfying almost “flat” transition probability

$$(\beta_i - \beta_{i+1})(E_i - E_{i+1}) = \text{const.}$$

$$\leftrightarrow C \frac{(T_{i+1} - T_i)^2}{T_{i+1} T_i} = \text{const.}$$

→ $T_{i+1} = \alpha T_i$:**Temperatures are geometric sequence!**
 $\alpha \sim 1 + O(1/\sqrt{C})$

Important notice:

Heat capacity C is an extensive quantity: $C \sim O(N)$

→ In order to keep finite overwrap, we need to increase temperature point M as

$$M \propto \sqrt{N} \quad (T_{max} = T_M = \alpha^M T_{min})$$

Relaxation time of the replica exchange

In order to confirm the equilibration of the whole system,
usually we need two criterions.

1. The correlation time at **the highest temperature** is sufficiently short,
e.g. $\tau=O(1)$
 If a replica visits the highest temperature, it can **easily change its state Γ .**
2. **All replicas** make several ($\sim O(10)$) round trips between
the lowest and the highest temperatures
 The ensemble at the lower temperature is **in the equilibrium**.

The second part determines the relaxation time of the method.

$$\tau_{\text{RE}} \sim \text{round trip time}$$

* If the replica exchange is a random walk:

$$\text{round trip time} \propto M^2$$

Summary of replica exchange

Algorithm:

1. Make a temperature set $\{T_1, T_2, \dots, T_M\}$
2. Loop n
 - (1) Do MC or MD for M replicas: $\{\Gamma_1, \Gamma_2, \dots, \Gamma_M; T_1, T_2, \dots, T_M\}$
 - (2) Calculate the energies of replicas
 - (3) Try replica exchange based on, e.g. Metropolis method
 - Usually we alternatively try replica exchange such as even n ; $\{1 \leftrightarrow 2\}, \{3 \leftrightarrow 4\}, \{5 \leftrightarrow 6\}, \dots$
 - odd n ; $\{2 \leftrightarrow 3\}, \{4 \leftrightarrow 5\}, \{6 \leftrightarrow 7\}, \dots$
 - Note: each exchange trial is independent
 - (4) Observe the quantities for $\{\Gamma_1, \Gamma_2, \dots, \Gamma_M; T_1, T_2, \dots, T_M\}$



If we already have a MC or MD programs,
it is very easy to introduce the replica exchange method!

Next (5/25) (will be given by Yamaji-sensei)

Classical

Quantum

- 1st: Many-body problems in physics
- 2nd: Why many-body problem is hard to solve
- 3rd: Classical statistical models and numerical simulation**
- 4th: Classical Monte Carlo method and its applications**
- 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