

# **Lecture 8**

# Lagrangian Formulation of Classical Mechanics

Lagrangian:

$$\mathcal{L}(\mathbf{R}^N, \dot{\mathbf{R}}^N) = K(\dot{\mathbf{R}}^N) - U(\mathbf{R}^N)$$

Euler Lagrange Equation:

$$\frac{d}{dt} \left( \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} \right) - \frac{\partial \mathcal{L}}{\partial \mathbf{R}_I} = 0$$

$$\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial}{\partial \dot{\mathbf{R}}_I} \left( \frac{1}{2} \sum_I^N M_I \dot{\mathbf{R}}_I^2 \right) \\ = M_I \ddot{\mathbf{R}}_I$$

$$\frac{d}{dt} \left( \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} \right) = M_I \ddot{\mathbf{R}}_I$$

$$\frac{\partial \mathcal{L}}{\partial \mathbf{R}_I} = - \frac{\partial U}{\partial \mathbf{R}_I}$$

$$= \mathbf{F}_I$$

Then,

$$\frac{d}{dt} \left( \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} \right) - \frac{\partial \mathcal{L}}{\partial \mathbf{R}_I} = M_I \ddot{\mathbf{R}}_I - \mathbf{F}_I \\ = 0$$

$$\frac{dE}{dt} = \frac{d}{dt} \left[ \sum_{I=1}^N \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + U(\mathbf{R}^N) \right]$$

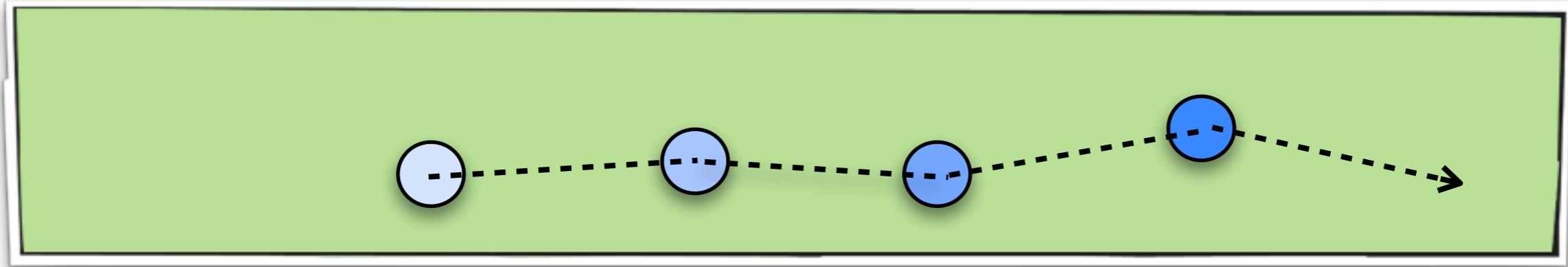
$$= \sum_{I=1}^N M_I \dot{\mathbf{R}}_I \cdot \ddot{\mathbf{R}}_I + \sum_{I=1}^N \frac{dU}{d\mathbf{R}_I} \cdot \frac{d\mathbf{R}_I}{dt}$$

$$= \sum_{I=1}^N \dot{\mathbf{R}}_I \cdot [M_I \ddot{\mathbf{R}}_I - \mathbf{F}_I]$$

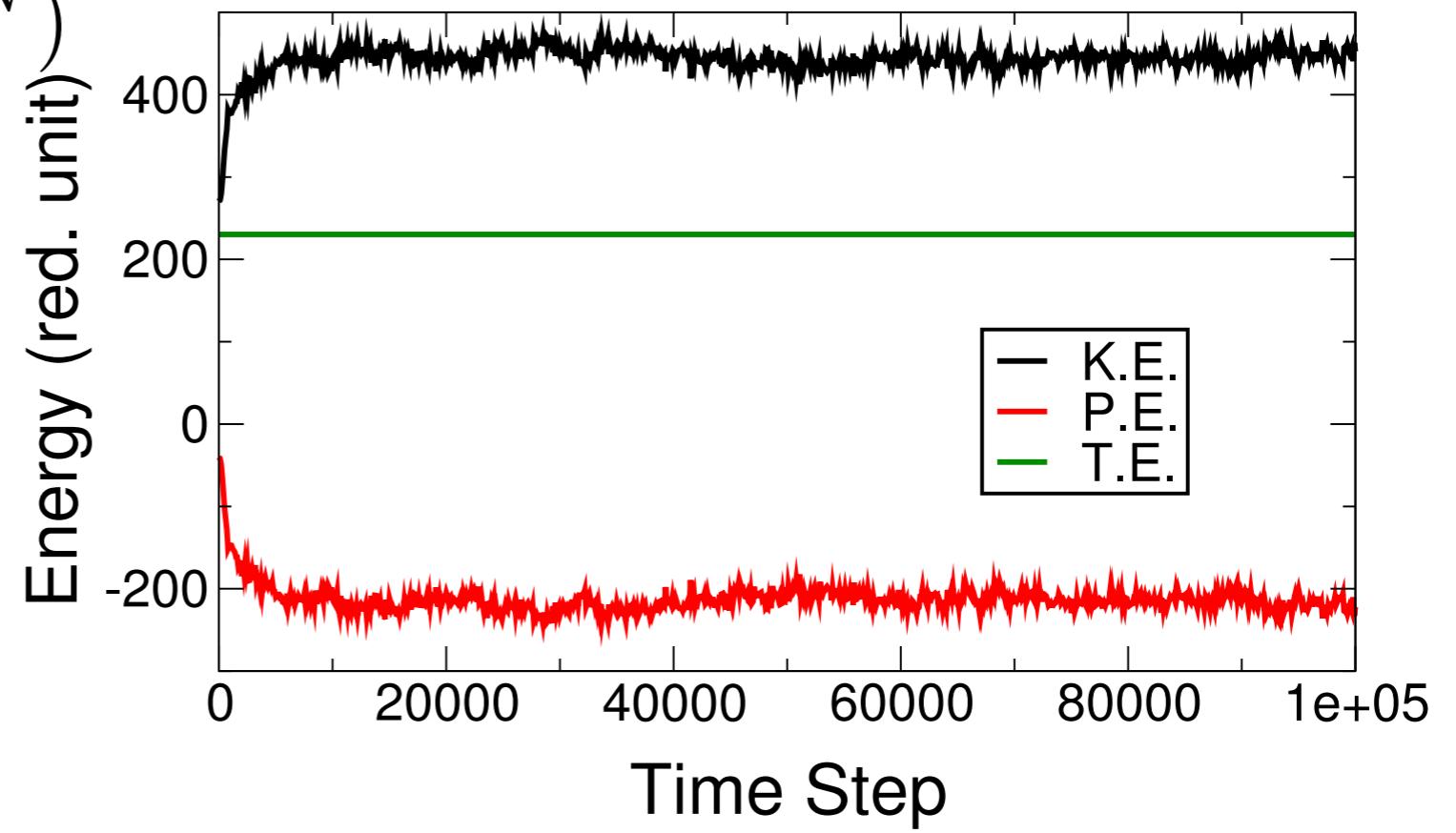
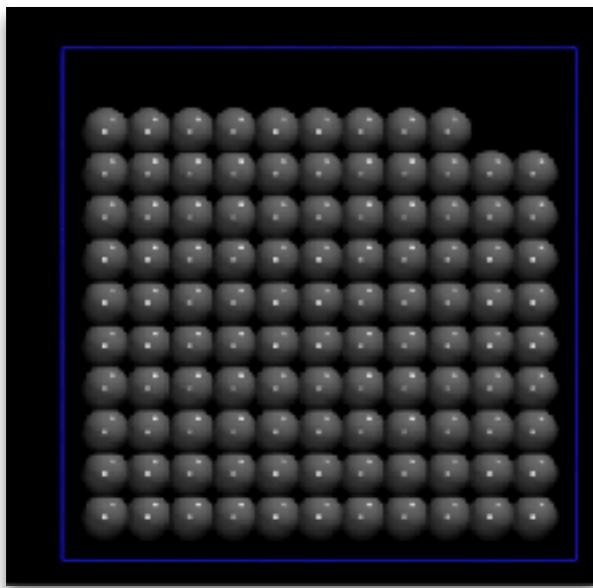
$$= 0$$

Total energy conservation

# Total Energy



$$E = \sum_{I=1}^N \frac{\mathbf{P}_I^2}{2M_I} + U(\mathbf{R}^N)$$



# Hamiltonian Mechanics

$$H(\mathbf{R}, \mathbf{P}) = K(\mathbf{P}) + U(\mathbf{R})$$

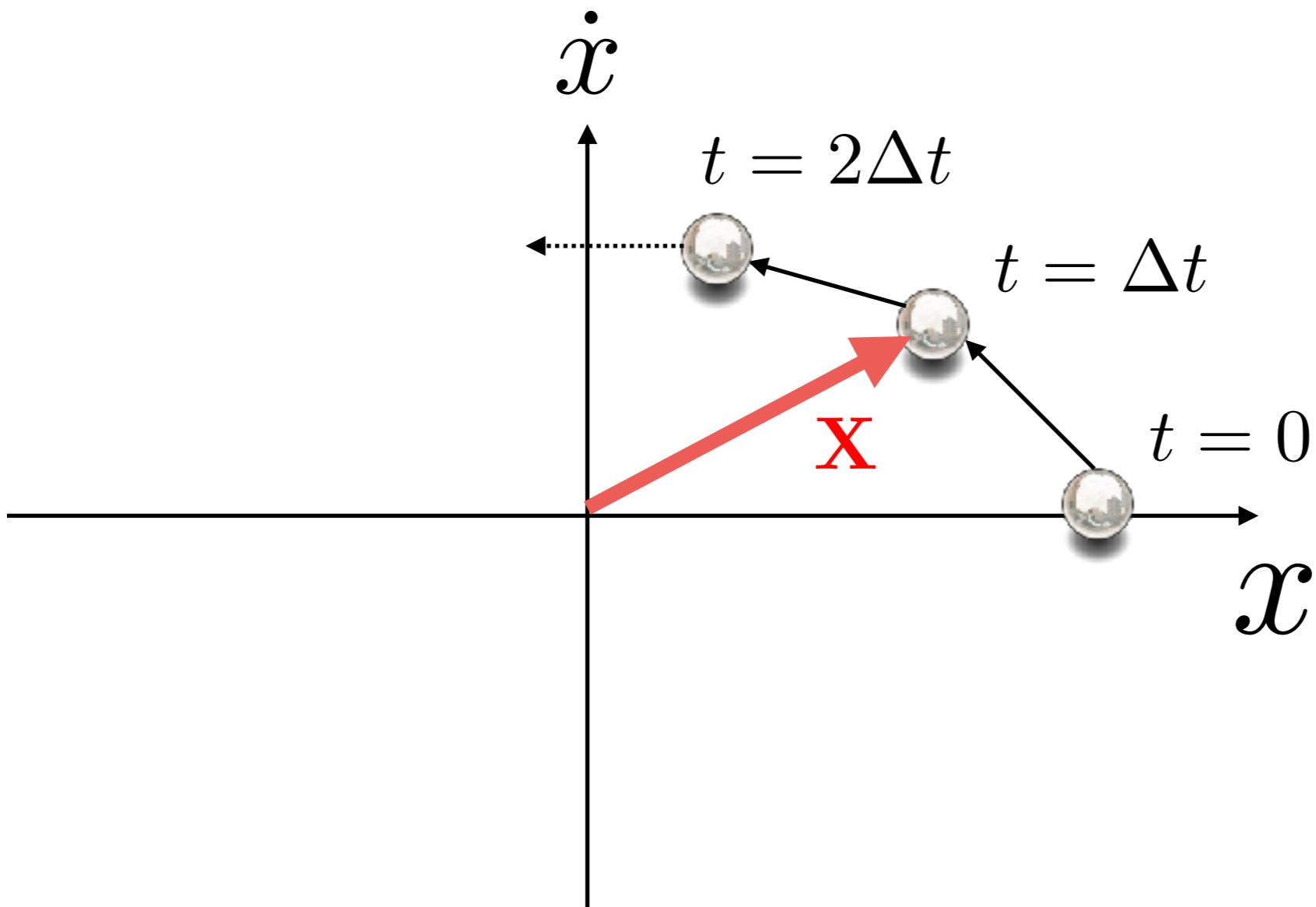
$$\dot{\mathbf{P}}_I = -\frac{\partial H}{\partial \mathbf{R}_I}$$

$$\dot{\mathbf{R}}_I = \frac{\partial H}{\partial \mathbf{P}_I}$$

EOMs

Derive EOMs for a 1-D simple harmonic oscillator.

# Microscopic states from trajectory

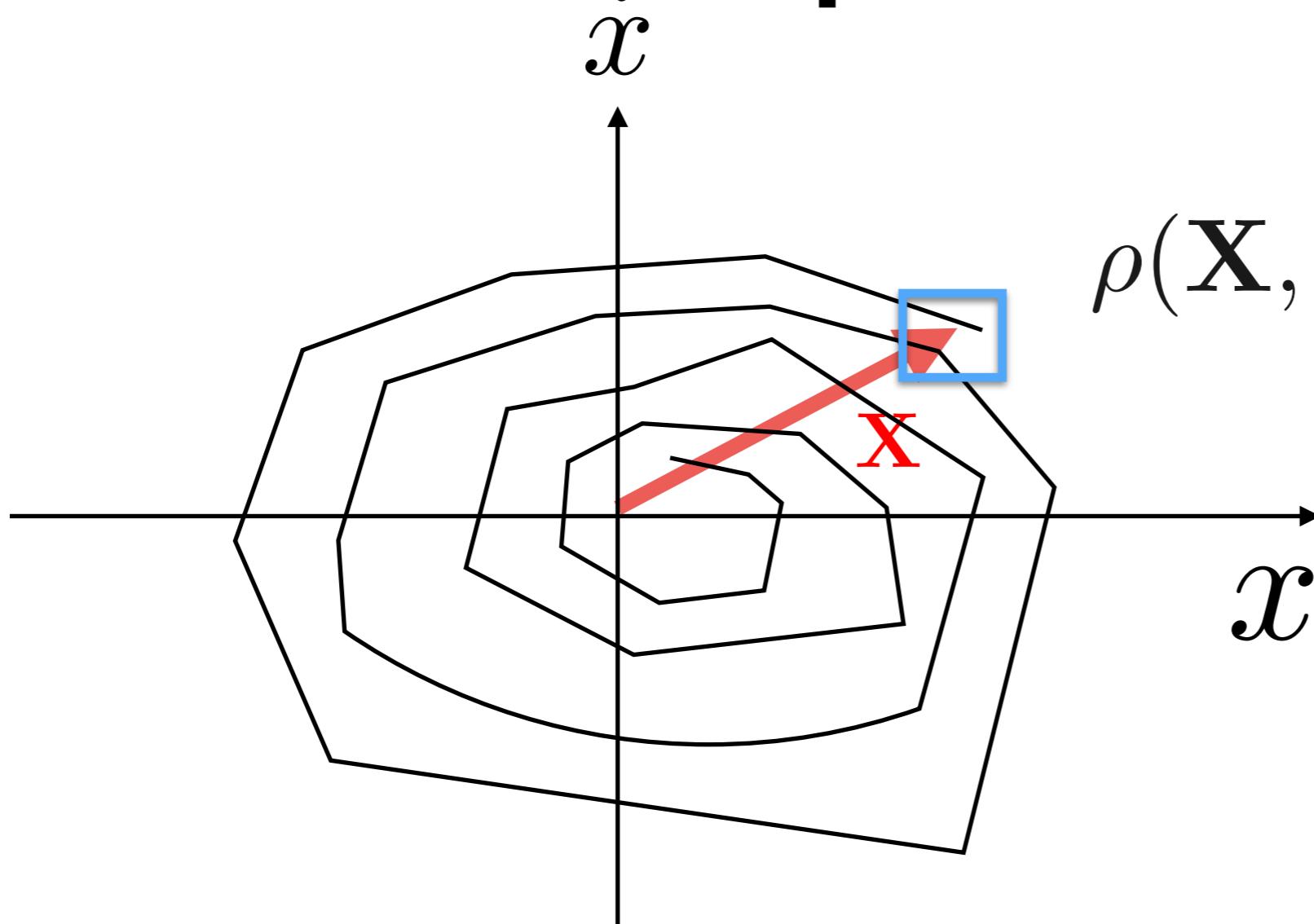


$$A = \langle a \rangle = \frac{1}{\mathcal{N}} \sum_i^{\mathcal{N}} a(\mathbf{X}_i)$$

$$\bar{a} = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t dt' a(\mathbf{X}_i(t'))$$

**Ergodic hypothesis:**  $A = \bar{a}$

# Phase space density



$$\rho(\mathbf{X}, t)$$

probability  
density  
of phase space  
vectors  
of all the ensemble  
members  
at a time  $t$

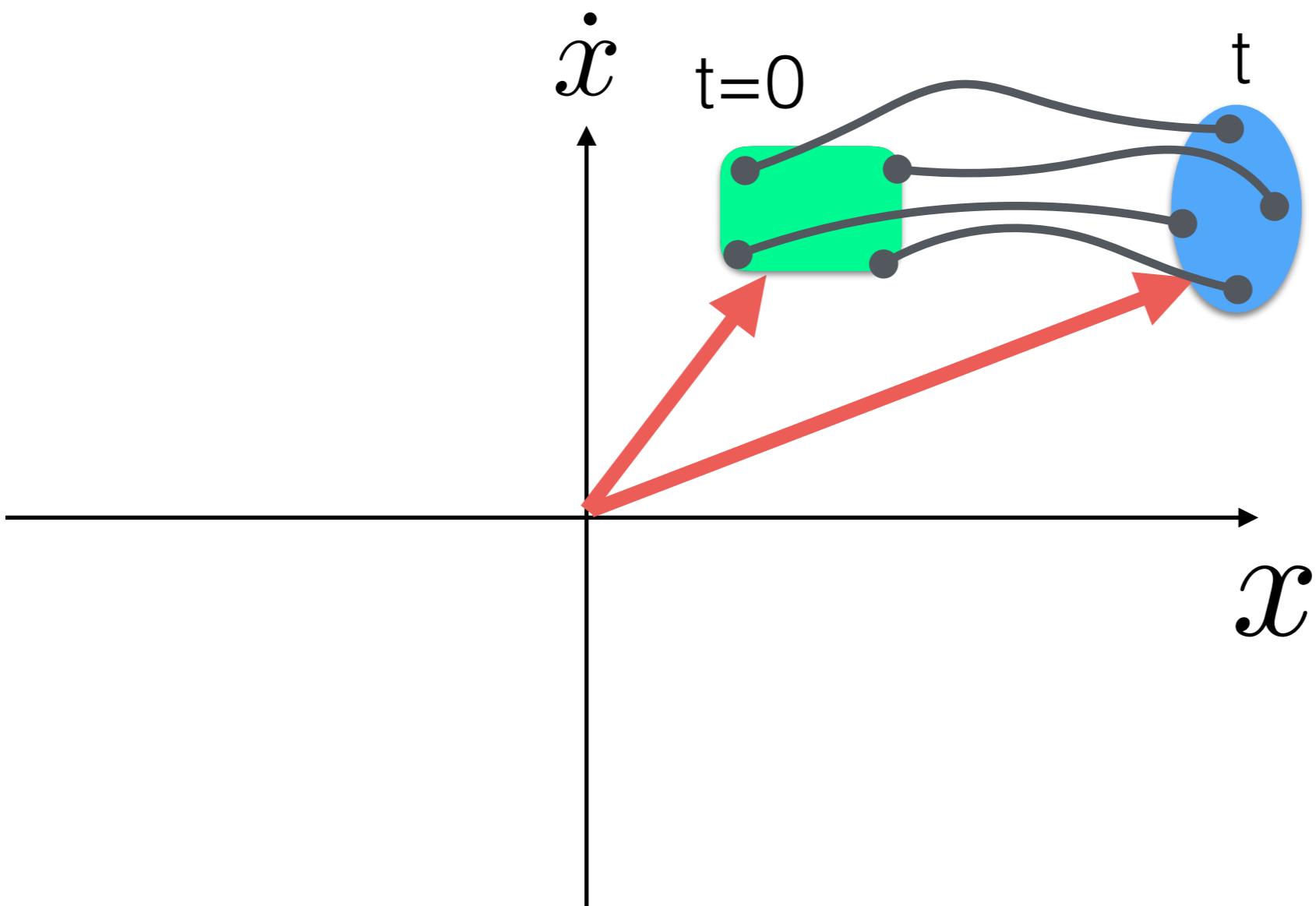
$$\int d\mathbf{X} \rho(\mathbf{X}, t) = 1$$

$$\frac{d\rho}{dt} = 0$$

Liouville's Theorem:  
# representative points  
in a given volume is  
constant.

Ensemble average is  
independent of time

$$d\mathbf{X}_0 = d\mathbf{X}_t$$



Phase space volume occupied by a set of points will be preserved in time

$$\rho(\mathbf{X}_0, 0) d\mathbf{X}_0 = \rho(\mathbf{X}_t, t) d\mathbf{X}_t$$

Thus, ensemble averages can be carried out at any point of time

# A general solution to Liouville's Equation

$$\rho(\mathbf{X}) = \frac{1}{\mathcal{Z}} \mathcal{F}[H(\mathbf{X})]$$

$$H(\mathbf{X}) = K(\mathbf{P}^N) + U(\mathbf{R}^N)$$

Hamiltonian

$$\mathcal{Z} = \int d\mathbf{X} \mathcal{F}[H(\mathbf{X})]$$

normalisation

Then, ensemble average is

$$A = \langle a(\mathbf{X}) \rangle = \frac{1}{\mathcal{Z}} \int d\mathbf{X} a(\mathbf{X}) \mathcal{F}[H(\mathbf{X})]$$

averaging can be computed at any instance of time

# Microcanonical Ensemble (NVE)

- N, V, and E are constants for the members of the ensemble
- Here,

$$F[H(\mathbf{X})] = \frac{1}{\Omega} \delta(H(\mathbf{X}) - E)$$

$$\Omega = C \int d\mathbf{X} \delta(H(\mathbf{X}) - E)$$

partition function: measures the number of micro states with constant energy

# NVE: Connection to Thermodynamics

$$S = k_B \ln \Omega(N, V, E)$$

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{N,V} \quad \frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{N,E} \quad \frac{\mu}{T} = - \left( \frac{\partial S}{\partial N} \right)_{V,E}$$

$$A = \langle a \rangle = \frac{\int d\mathbf{X} a(\mathbf{X}) \delta(H(\mathbf{X}) - E)}{\int d\mathbf{X} \delta(H(\mathbf{X}) - E)}$$

# Canonical Ensemble (NVT)

$$\rho(\mathbf{X}) = \frac{C_N}{Q} \exp\left(-\frac{H(\mathbf{X})}{k_B T}\right)$$

$$Q(N, V, T) = C_N \exp\left(-\frac{H(\mathbf{X})}{k_B T}\right)$$

$$C_N = \frac{1}{N! h^{3N}}$$

Note: here the Hamiltonian dynamics is not energy conserving

# NVT: Connection to Thermodynamics

Helmholtz free energy:

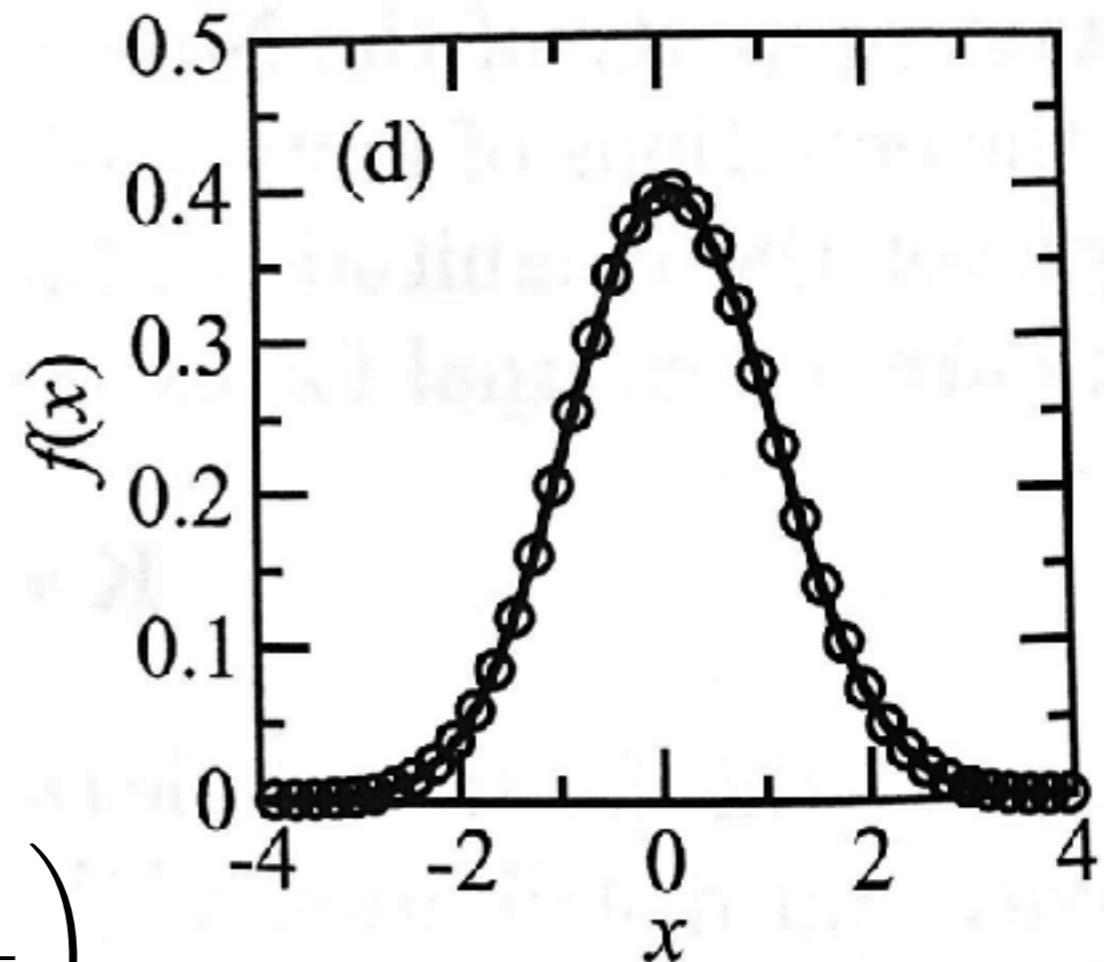
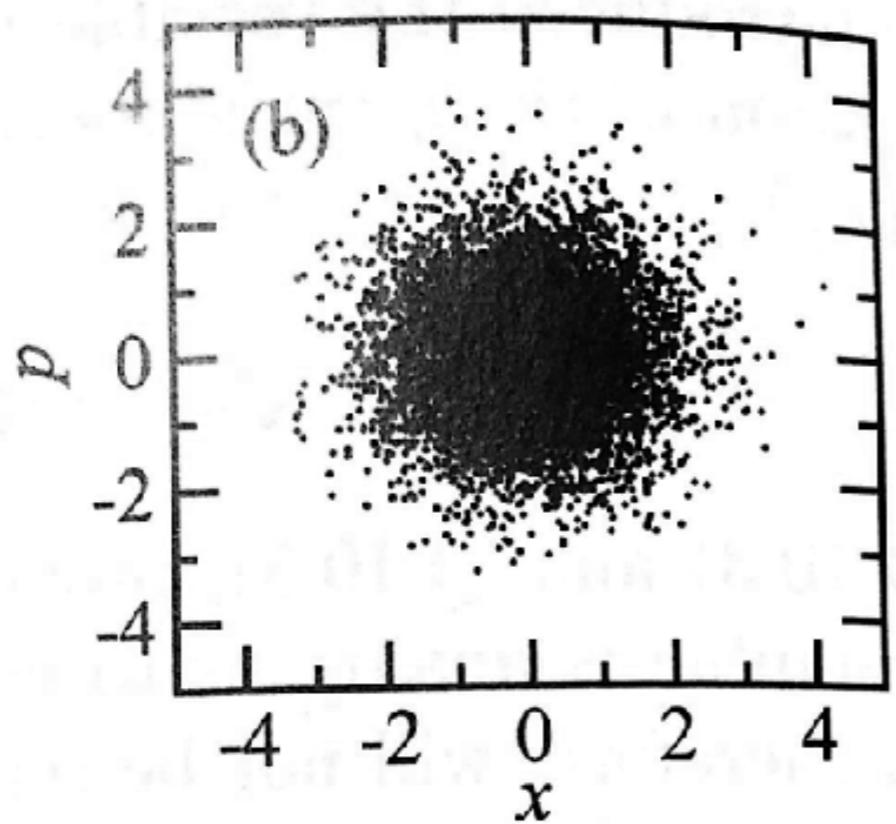
$$F = -k_B T \ln Q(N, V, T)$$

$$S = k_B \ln Q + k_B T \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V}$$

...

# NVT ensemble from MD simulation

- connecting to a thermostat to achieve Boltzmann distribution



$$f(p) = \frac{1}{\sqrt{2\pi m k_B T}} \exp\left(-\frac{p^2}{2m k_B T}\right)$$

# Equilibrium distribution

- Boltzmann distribution of velocities, coordinates
- Every degree of freedom is thermalised uniformly

no. of degrees of freedom

$$\frac{1}{N_f} \left\langle \sum_I^N \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 \right\rangle = \frac{1}{2} k_B T$$

Here T is the average temperature (macroscopic measure)

# Temperature

$$\frac{1}{N_f} \left\langle \sum_I^N \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 \right\rangle = \frac{1}{2} k_B T$$

Defining instantaneous temperature from above:

$$T(t) = \sum_{I=1}^N \frac{M_I \dot{\mathbf{R}}_I^2(t)}{k_B N_f}$$

Time average of  $T(t)$  gives the macroscopic temperature  $T$

$$\dot{\mathbf{R}}_I = \sqrt{\frac{T}{T'(t)}} \dot{\mathbf{R}}'_I$$

Rescaling  
velocities to  
achieve target  
temperature  $T$

But rescaling doesn't ensure canonical distribution; why?

# **Lecture 9**

# Fluctuations

$$\sigma^2 = \frac{\langle T(t)^2 \rangle - \langle T(t) \rangle^2}{\langle T(t) \rangle^2} \quad T = \langle T(t) \rangle = \frac{1}{k_B N_f} \sum_{I,\alpha} \langle M_I V_{I,\alpha}^2 \rangle$$

$$\begin{aligned} \langle T(t)^2 \rangle &= \frac{1}{k_B^2 N_f^2} \sum_{I,\alpha} \sum_{J,\beta} \langle M_I^2 V_{I,\alpha}^2 V_{J,\beta}^2 \rangle \\ &= \frac{1}{k_B^2 N_f^2} \left[ \sum_{I,\alpha} \langle M_I^2 V_{I,\alpha}^4 \rangle + \sum_{I \neq J} \sum_{\alpha \neq \beta} \langle M_I V_{I,\alpha}^2 \rangle \langle M_J V_{J,\beta}^2 \rangle \right] \end{aligned}$$

$$\langle V_\alpha^4 \rangle = \int dV_\alpha \ V_\alpha^4 f(V_\alpha) = 3 \left( \frac{k_B T}{M} \right)^2$$

$$\langle V_\alpha^2 \rangle = \int dV_\alpha \ V_\alpha^2 f(V_\alpha) = \frac{k_B T}{M}$$

$$\Rightarrow \langle T(t)^2 \rangle = \frac{1}{k_B^2 N_f^2} [3N_f k_B^2 T^2 + N_f (N_f - 1) k_B^2 T^2]$$

$$= \frac{T^2}{N_f} [2 + N_f]$$

Now,  $\langle T(t) \rangle^2 = T^2$

$$\sigma^2 = \frac{2}{N_f}$$

This is not zero; thus temperature fluctuates  
It is system dependent

For large deg. of freedom, fluctuation of T is small

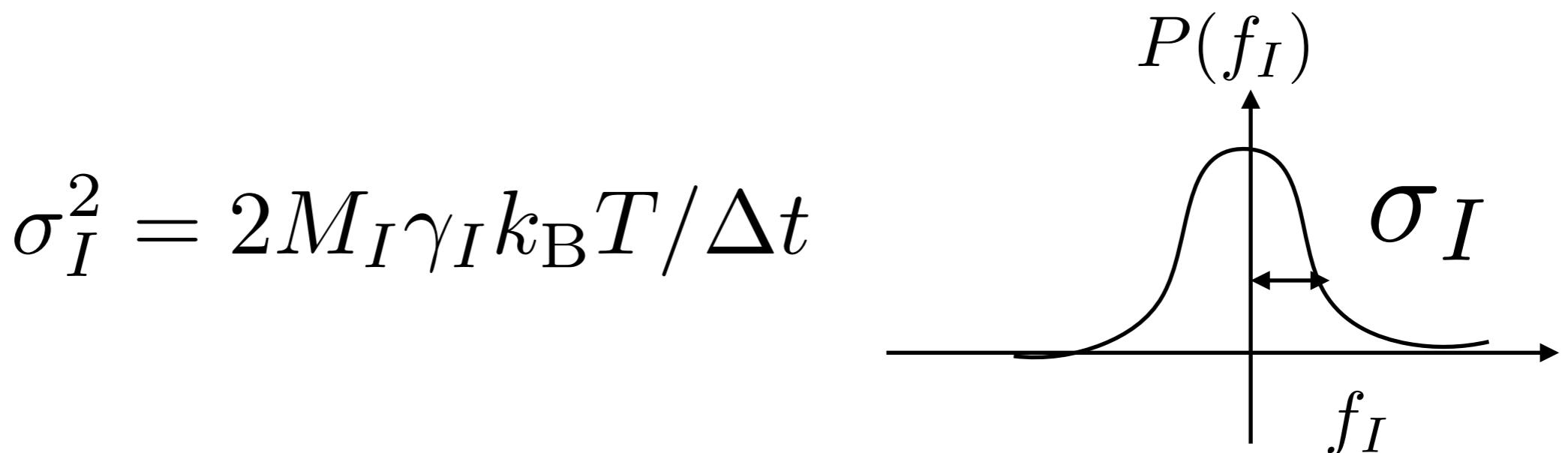
Also, one can show that variance for KE is 2/3 and thus is non-zero

Thus, constant KE ensemble (**i.e. isokinetic ensembles**) is not necessarily canonical!

# How to get canonical distribution from MD

- Modifying the equations of motion
- Langevin Thermostat:

$$\ddot{M_I \mathbf{R}_I} = \mathbf{F}_I - \gamma_I M_I \dot{\mathbf{R}}_I + f_I$$

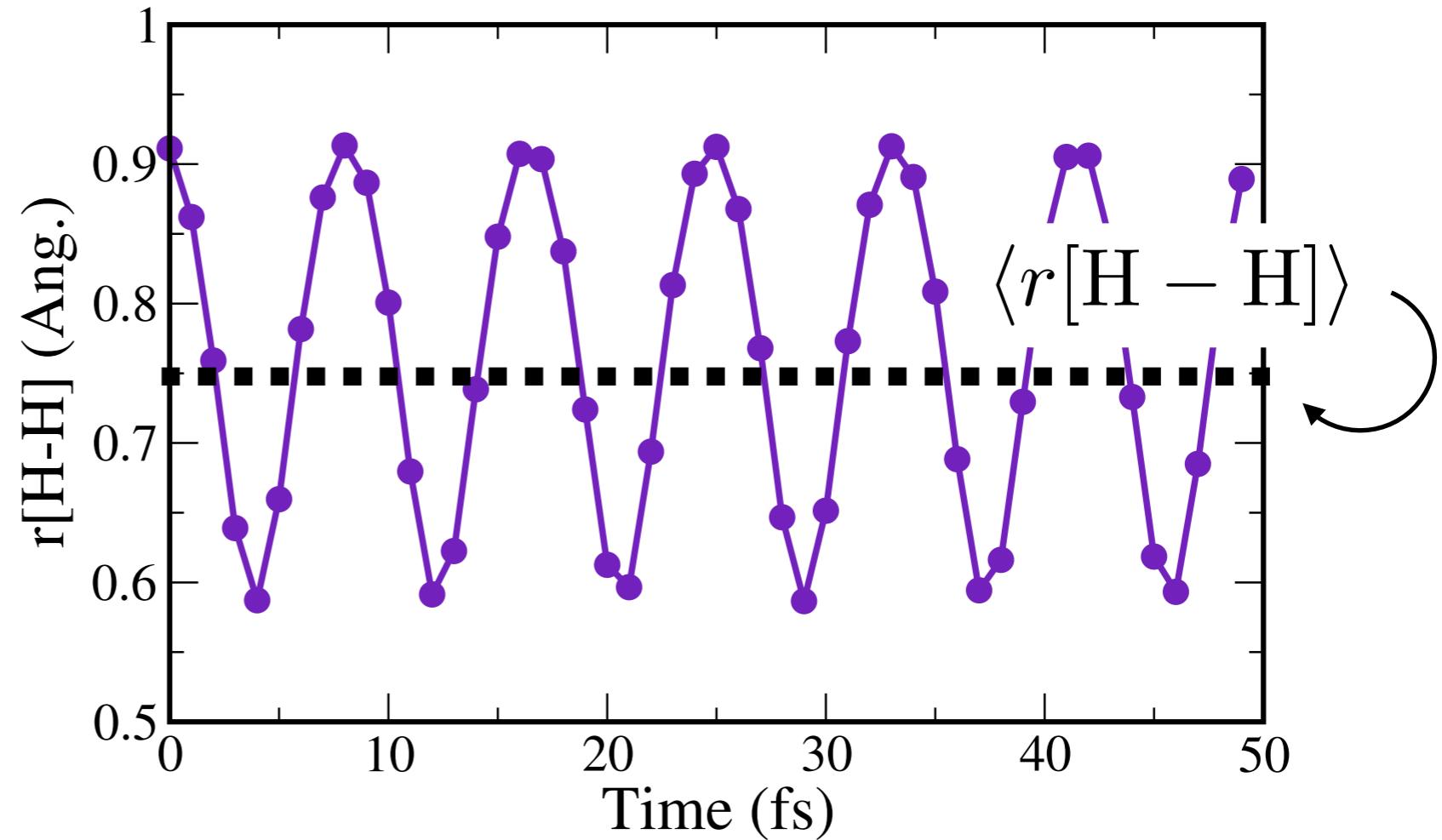
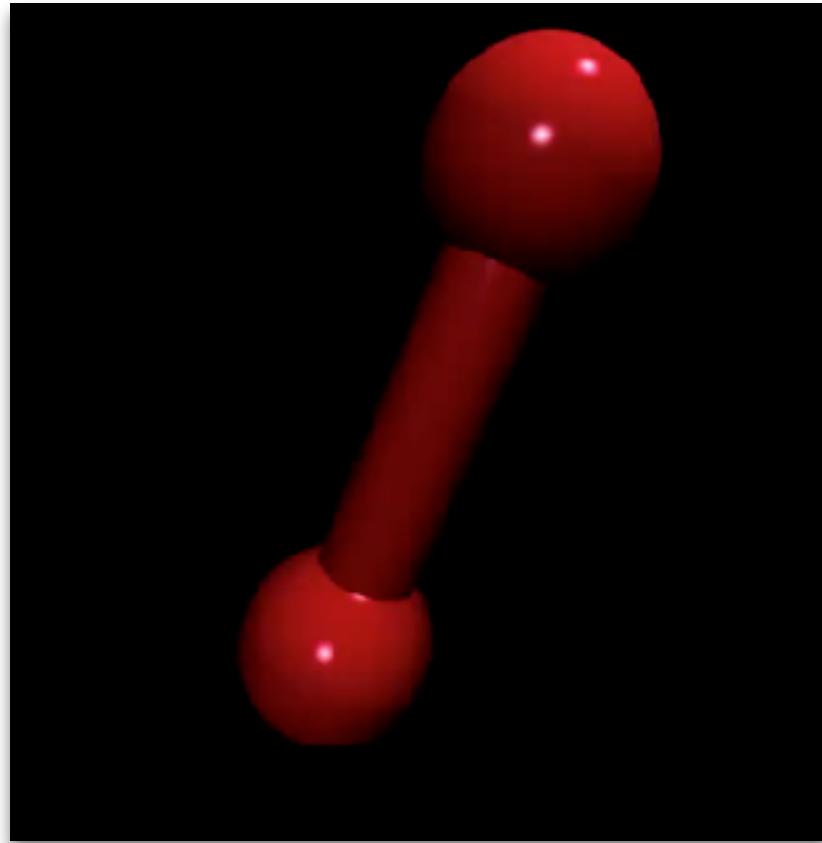


# Questions:

- What is the distribution of momentum and positions for a simple harmonic oscillator in micro-canonical ensemble?
- Implement Langevin thermostat in your MD code for 1D harmonic oscillator and test it.

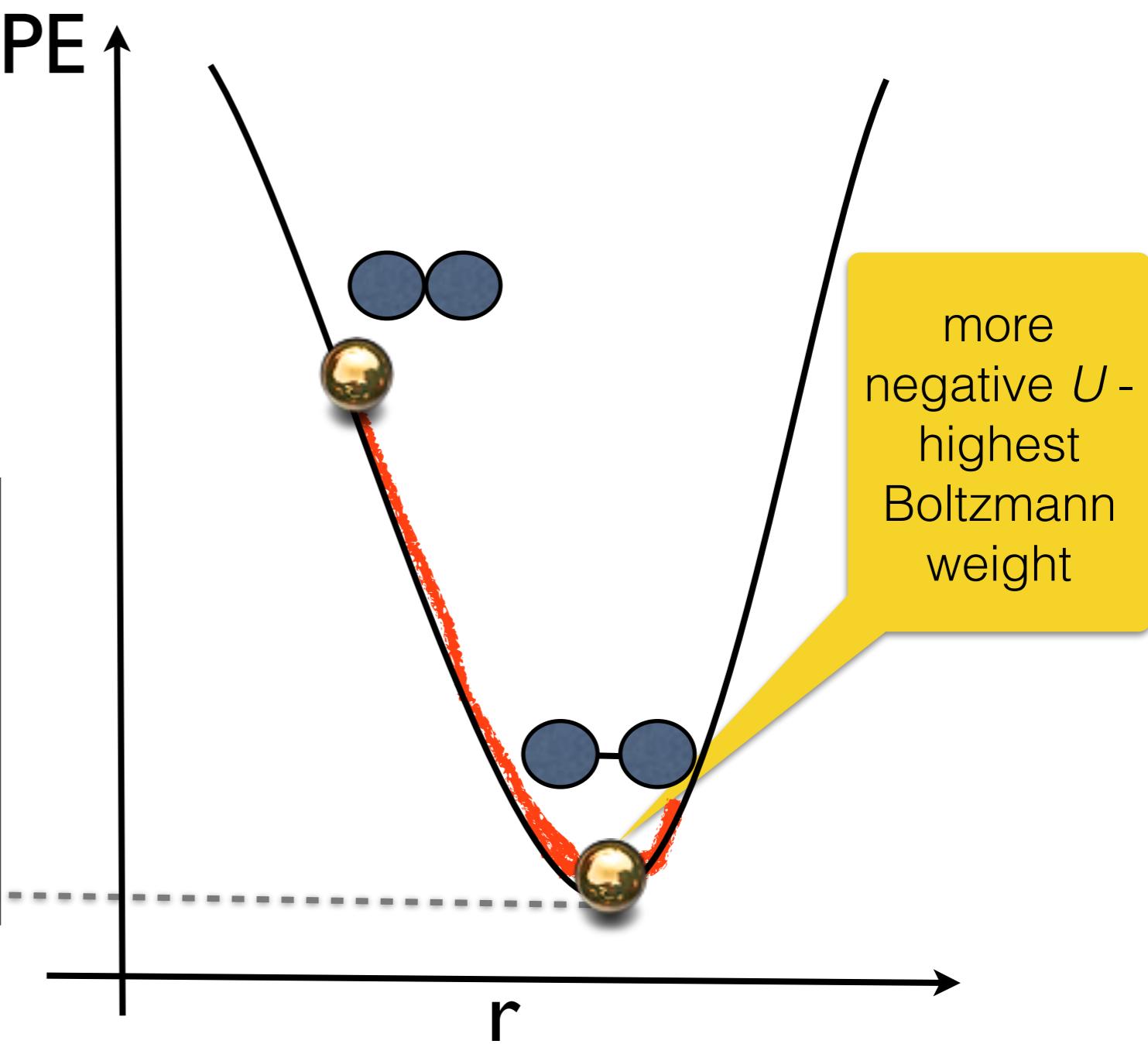
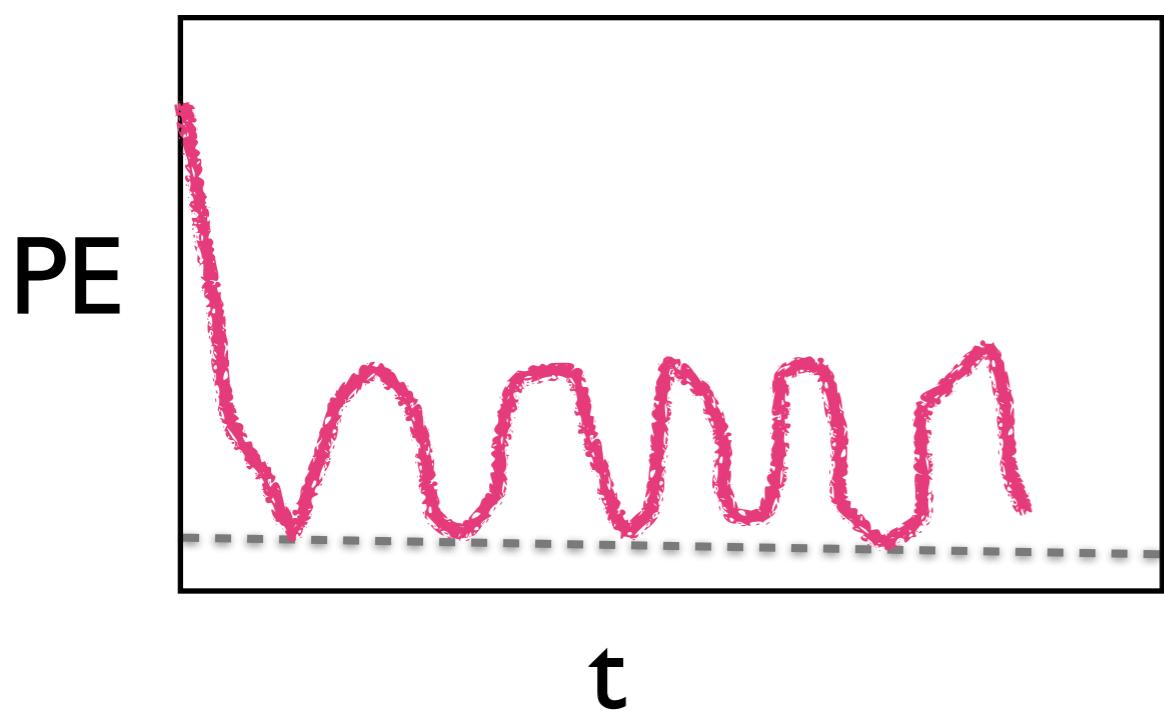
# Other Averages

- structural parameters: time averages



# Configurational Sampling at NVT

- Molecular dynamics simulations drive molecular system to equilibrium configurations



# Question:

- a. Consider a diatomic molecule in gas phase. If the bond between the atoms is described by harmonic molecular-mechanics potential, sketch how internuclear distance varies with time in NVE simulations
- b. Repeat the same exercise as in (a), but the temperature is increased (make the plots on the same graph).
- c. Repeat the same as in (a), but for an initial condition where the initial structure is at the minimum and the initial velocities are given for a temperature equal to zero.

- d. Repeat the same exercise as above in (c), but the initial temperate is not zero.
- e. Repeat the same exercise in (c), but the system is connected to a Langevin thermostat of temperature  $T > 0$ .

# Andersen Thermostat

- System is in contact with bath that leads to stochastic collisions
- Frequency of collision  $\nu$

Integrate EOMs to a time  $\Delta t$

A number of particles are selected to undergo collision with the heat bath with probability  $\nu \Delta t$

For these particles new velocities are drawn from Maxwell-Boltzmann distribution

```
DO ISTEP=1, NSTEP_MD  
    CALL VEL_VERLET_VEL(...)  
    CALL VEL_VERLET_POS(...)  
    CALL VEL_VERLET_VEL(...)  
    CALL TEMPERATURE(VEL, TEMP)  
    DO IATOM=1,NATOM  
        IF(RANF() < NU*DELTA_T )THEN  
            VEL(IATOM1:3)=GAUS_DIST(TEMP)  
        END IF  
    END DO  
END DO
```

uniform  
random  
numbers  
between 0  
and 1

# Berendsen Thermostat

*J. Chem. Phys.* **81**, 3684 (1984)

$$\frac{dT}{dt} = \frac{1}{\tau} (T - T(t))$$

velocity scaling:  $V_{I,\alpha}^{\text{new}} = \lambda V_{I,\alpha}^{\text{old}}$

$$\Delta E_{\text{KE}} = E_{\text{KE}}^{\text{new}} - E_{\text{KE}}^{\text{old}} = (\lambda^2 - 1) E_{\text{KE}}^{\text{old}} = (\lambda^2 - 1) \frac{3}{2} N k_{\text{B}} T$$

$$\Delta T = (\lambda^2 - 1) T$$

$$\frac{dT}{dt} \approx \frac{\Delta T}{\Delta t} \equiv \frac{(\lambda^2 - 1)}{\Delta t} = \frac{1}{\tau} (T - T(t))$$

$$\Rightarrow \lambda^2 = 1 + \frac{\Delta t}{\tau} \left( \frac{T}{T(t)} - 1 \right)$$

$$\tau \approx \Delta t$$

standard velocity  
rescaling

$\tau \gg \Delta t$  no scaling -> microcanonical

Usually, one uses  $\tau > 0.01$  ps

There is no proof that proper canonical distribution & dynamics is obtained by this thermostat

It is only numerically shown that canonical averages are coming out reasonable with the thermostat

# pseudo code:

```
DO ISTEP=1, NSTEP_MD
    CALL VEL_VERLET_VEL(....)
    CALL TEMPERATURE(VEL, TEMP)
    CALL LAMBDA(TAU, DT, TEMP, TO)
    VEL(:) = VEL(:) * LAMBDA
    CALL VEL_VERLET_POS(...)
    CALL VEL_VERLET_VEL(...)
END DO
```

# Home work

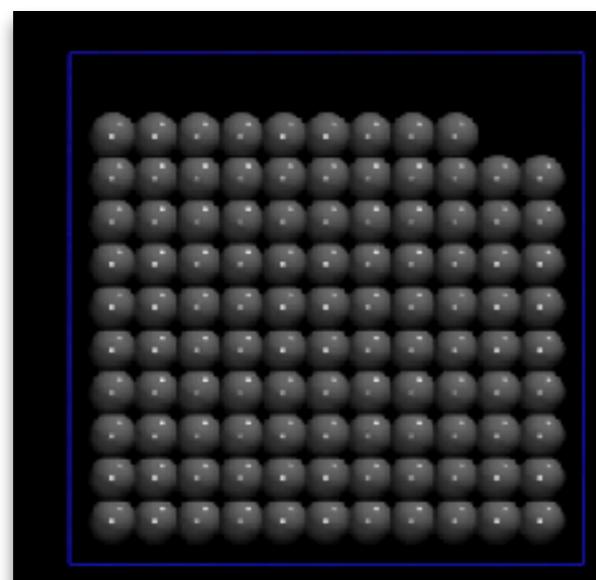
- Modify your NVE ensemble code to generate phase phase picture for Harmonic oscillator at NVT for some constant  $T>0$  of your choice using (a) velocity scaling (b) Andersen thermostat (c) Berendsen thermostat. Compare the correct phase space picture discussed in the lecture.

# Nosé Hoover Chain Thermostat

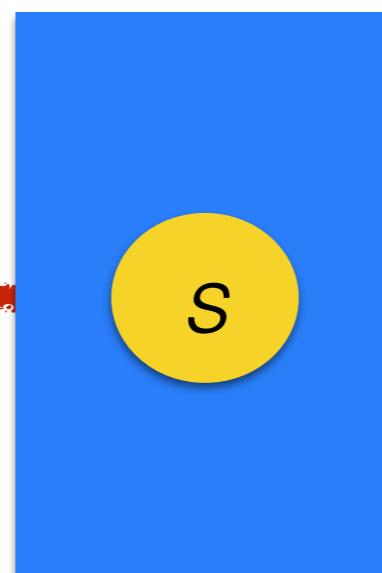
- Nosé-Thermostat (1983, 1984):

$$\mathcal{H}_N = \sum_{I=1}^N \frac{\mathbf{P}_I^2}{2M_I s^2} + U(\mathbf{R}^N) + \frac{p_s^2}{2Q} + gk_B T \ln s$$

$g$  and  $Q$  are some constant parameters



original system



Extended system

total dimensionality of the phase space is now increased by 2 ( $s$  and  $p_s$ )

$$\Omega = \int d^N \mathbf{R} d^N \mathbf{P} ds dp_s \delta \left( \sum_{I=1}^N \frac{\mathbf{P}_I^2}{2M_I s^2} + U(\mathbf{R}^N) + \frac{p_s^2}{2Q} + gk_B T \ln s - E \right)$$

(since the total energy of the extended system is conserved)

$$= \frac{e^{E/k_B T} \sqrt{2\pi Q k_B T}}{(dN + 1) k_B T} \int d^N \mathbf{P} d^N \mathbf{R} \exp [-\beta \mathcal{H}(\mathbf{R}^N, \mathbf{P}^N)]$$

(Here, d=dimensionality=3 & using g=dN+1=3N+1)

Thus, canonical distribution can be obtained for physical degrees of freedom

Unfortunately, integrating the equations of motion was not practical in MD simulations - thus not used as such

- Nosé-Hoover Thermostat:

$$\dot{\mathbf{R}}_I = \frac{\mathbf{P}_I}{M_I}$$

$$\dot{\mathbf{P}}_I = \mathbf{F}_I - \frac{p_\eta}{Q} \mathbf{P}_I$$

$$\dot{\eta} = \frac{p_\eta}{Q}$$

$$\dot{p}_\eta = \sum_I \frac{\mathbf{P}_I^2}{M_I} - gk_B T$$

This is by reformulating EOMs of Nosé

Integration requires  $\mathbf{P}_I$  and thus it has to be integrated iteratively!

Conserved quantity:

$$\mathcal{H}_{\text{NH}}(\mathbf{R}, \eta, \mathbf{P}, p_\eta) = \mathcal{H}(\mathbf{R}, \mathbf{P}) + \frac{p_\eta^2}{2Q} + dNk_B T\eta$$

The above gives canonical distribution for the physical system

- Nosé-Hoover Chains Thermostat:

$$\dot{\mathbf{R}}_I = \frac{\mathbf{P}_I}{M_I}$$

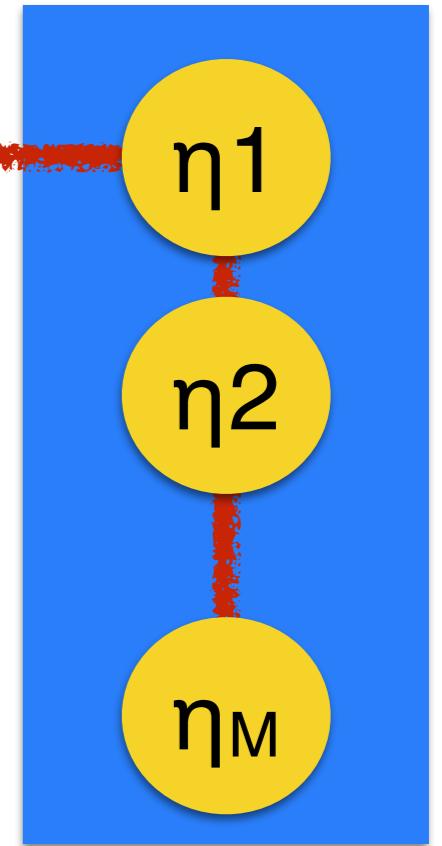
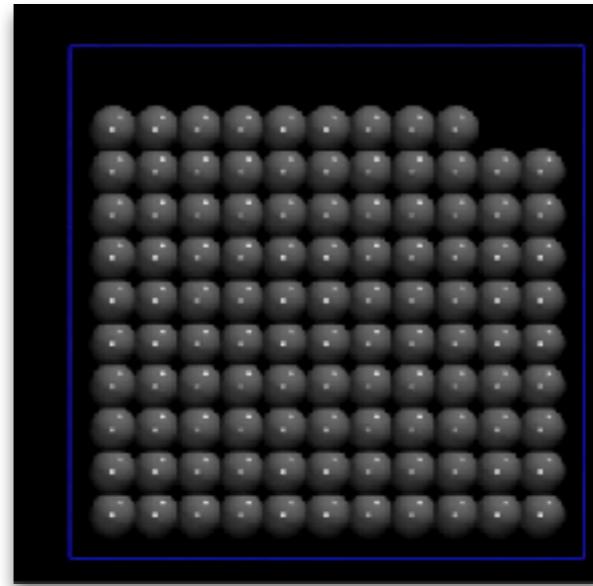
$$\dot{\mathbf{P}}_I = \mathbf{F}_I - \frac{p_{\eta_1}}{Q_1} \mathbf{P}_I$$

$$\dot{\eta}_j = \frac{p_{\eta_j}}{Q_j} \quad , j = 1, \dots, M$$

$$\dot{p}_{\eta_1} = \left[ \sum_I \frac{\mathbf{P}_I^2}{M_I} - dNk_B T \right] - \frac{p_{\eta_2}}{Q_2} p_{\eta_1}$$

$$\dot{p}_{\eta_j} = \left[ \frac{p_{\eta_{j-1}}^2}{Q_{j-1}} - k_B T \right] - \frac{p_{\eta_{j+1}}}{Q_{j+1}} p_{\eta_j} \quad , j = 2, \dots, M-1$$

$$\dot{p}_{\eta_M} = \left[ \frac{p_{\eta_{M-1}}^2}{Q_{M-1}} - k_B T \right]$$



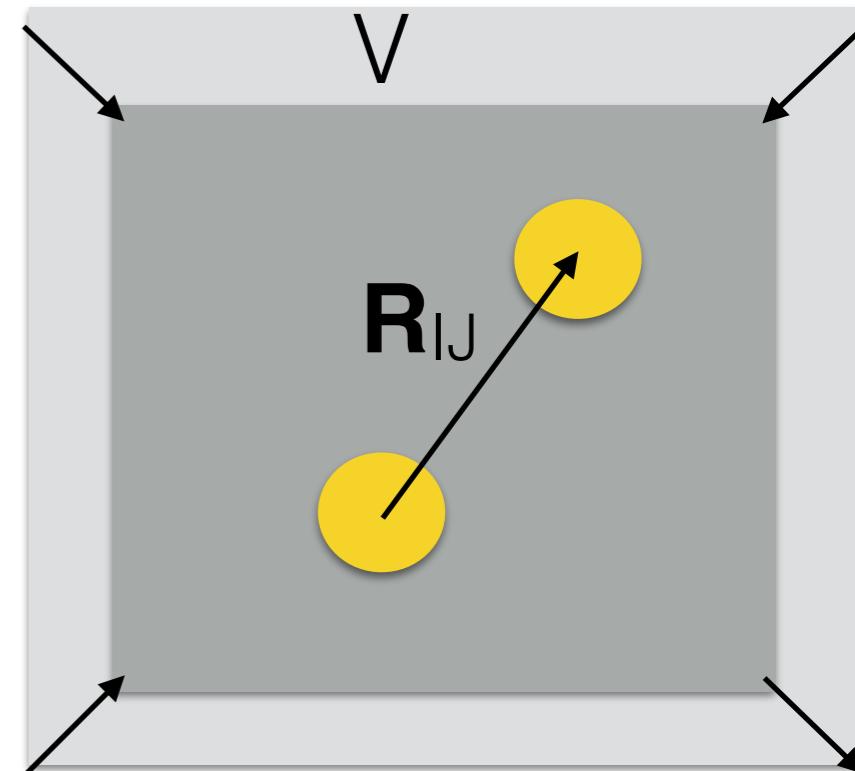
# Constant Pressure Simulations

- NPT ensemble
- To obtain equilibrium density
- Important for crystal structure predictions & phase changes
- Experiments are often done at constant temperature & pressure => thus this is a very important ensemble to simulate

# Pressure

$$P(t) = \frac{Nk_B T}{V} + \frac{1}{3V} \sum_I^N \sum_{J>I}^N \mathbf{R}_{IJ} \cdot \mathbf{F}_{IJ}$$

$$P = \langle P(t) \rangle$$



# NPH ensemble

## Molecular dynamics simulations at constant pressure and/or temperature<sup>a)</sup>

Hans C. Andersen

*Department of Chemistry, Stanford University, Stanford, California 94305*

(Received 10 July 1979; accepted 31 October 1979)

In the molecular dynamics simulation method for fluids, the equations of motion for a collection of particles in a fixed volume are solved numerically. The energy, volume, and number of particles are constant for a particular simulation, and it is assumed that time averages of properties of the simulated fluid are equal to microcanonical ensemble averages of the same properties. In some situations, it is desirable to perform simulations of a fluid for particular values of temperature and/or pressure or under conditions in which the energy and volume of the fluid can fluctuate. This paper proposes and discusses three methods for performing molecular dynamics simulations under conditions of constant temperature and/or pressure, rather than constant energy and volume. For these three methods, it is shown that time averages of properties of the simulated fluid are equal to averages over the isoenthalpic-isobaric, canonical, and isothermal-isobaric ensembles. Each method is a way of describing the dynamics of a certain number of particles in a volume element of a fluid while taking into account the influence of surrounding particles in changing the energy and/or density of the simulated volume element. The influence of the surroundings is taken into account without introducing unwanted surface effects. Examples of situations where these methods may be useful are discussed.

- Andersen used extended Lagrangian concept here (for the first time!)

$$\mathcal{L}(\mathbf{R}, \dot{\mathbf{R}}, V, \dot{V}) = \mathcal{L}_0(\mathbf{R}, \dot{\mathbf{R}}) - P_0V + \frac{1}{2}Q\dot{V}^2$$

Volume  $V$  as the extended variable

Coordinates as scaled:  $\mathbf{s}_I = \frac{\mathbf{R}_I}{V^{1/3}}$

Equations of motion for  $\mathbf{s}$  and  $V$  can be then derived

# Crystal Structure and Pair Potentials: A Molecular-Dynamics Study

M. Parrinello<sup>(a)</sup> and A. Rahman

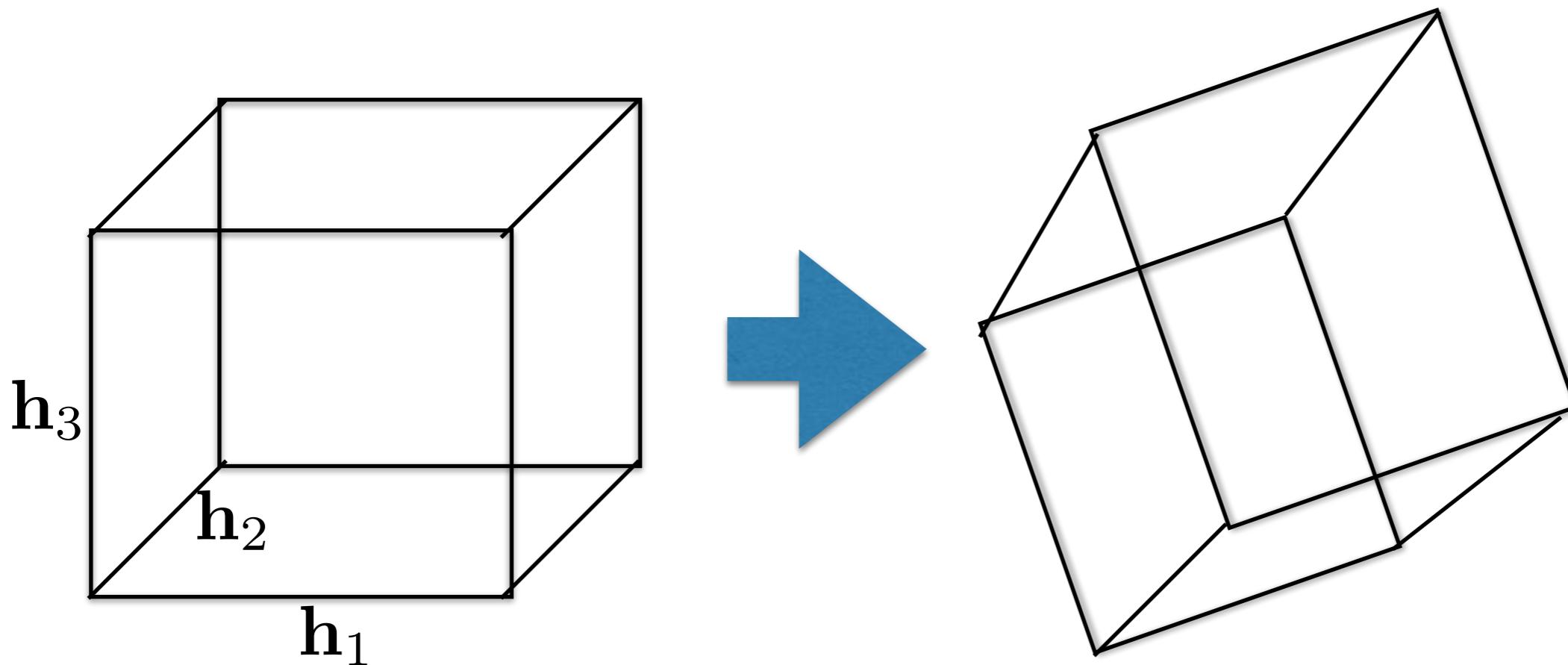
Argonne National Laboratory, Argonne, Illinois 60439

(Received 31 July 1980)

With use of a Lagrangian which allows for the variation of the shape and size of the periodically repeating molecular-dynamics cell, it is shown that different pair potentials lead to different crystal structures.

M. Parrinello and A. Rahman, Phys. Rev. Lett. 45, 1196 (1980).

## Beyond isotropic cell



They used  $h_1$ ,  $h_2$ ,  $h_3$  as variables

- Nose Hoover Chain Barostat is most appropriate: Extended variables are coupled to the cell variables (as in Nose Hoover thermostat) + another set of extended variables are coupled to nuclear degrees of freedom to maintain constant temperature

# Berendsen Barostat

- scales the cell vectors using

$$\mu = \left[ 1 + \frac{\Delta t}{\tau_P} (P_0 - P(t)) \right]^{1/3}$$

# Liouville Operators & Equations of Motion

# Integrating EOMs for Nose Hoover Chain Thermostat