

# Statistical mechanics

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# From the microscopic to the macroscopic level: the realm of statistical mechanics

## Computer simulations

Generates information at the  
**microscopic level**

Atomic positions  $\vec{q} = (\vec{q}_1, \vec{q}_2, \dots, \vec{q}_N)$

Momenta  $\vec{p} = (\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N)$

Can be thought of as coordinates of a  
multidimensional space of  $6N$  dimensions:  
**the phase space**

## Thermodynamic state

Defined by a small set of  
**macroscopic parameters**

Pressure  $P$

Temperature  $T$

Number of particles  $N$

Other thermodynamic  
properties may be derived  
through the knowledge of the  
equation of state and the  
fundamental equations of  
thermodynamics

# Statistical sampling from ensembles

- $\Gamma$  A particular point in phase space
- $\mathcal{A}$  A given property (for instance, the potential energy)
- $\mathcal{A}(\Gamma)$  Instantaneous value of the property when the system is at point  $\Gamma$

It is reasonable to assume that the experimentally observable macroscopic property  $\mathcal{A}_{\text{obs}}$  is really the time average of  $\mathcal{A}(\Gamma)$  taken over a long time interval

$$\mathcal{A}_{\text{obs}} = \langle \mathcal{A} \rangle_{\text{time}} = \langle \mathcal{A}(\Gamma(t)) \rangle_{\text{time}} = \lim_{t_{\text{obs}}} \frac{1}{t_{\text{obs}}} \int_0^{t_{\text{obs}}} \mathcal{A}(\Gamma(t)) dt$$

The equations governing this time evolution (Newton's equation of motion in a simple classical system) are well known

# Statistical sampling from ensembles

$$\mathcal{A}_{\text{obs}} = \langle \mathcal{A} \rangle_{\text{time}} = \langle \mathcal{A}(\Gamma(t)) \rangle_{\text{time}} = \lim_{t_{\text{obs}}} \frac{1}{t_{\text{obs}}} \int_0^{t_{\text{obs}}} \mathcal{A}(\Gamma(t)) dt$$

The equations governing this time evolution  
(Newton's equation of motion in a simple classical system)  
are well known

But we can not hope to extend the integration of the dynamical equations:

- For a truly macroscopic number  $10^{23}$
- To infinite time

We might be satisfied to average over:

- A system of the order of thousand of atoms **(length and size scale)**
- Over a long but finite time  $t_{\text{obs}}$  **(time scale)**

That is what we do in MD simulations:

The equations of motion is solved step

by step a large number of steps  $\tau_{\text{obs}} = t_{\text{obs}}/\delta t$

$$\mathcal{A}_{\text{obs}} = \langle \mathcal{A} \rangle_{\text{time}} = \frac{1}{\tau_{\text{obs}}} \sum_{\tau=1}^{\tau_{\text{obs}}} \mathcal{A}(\Gamma(\tau))$$

## Practical questions regarding the validity of the method

$$\mathcal{A}_{\text{obs}} = \langle \mathcal{A} \rangle_{\text{time}} = \frac{1}{\tau_{\text{obs}}} \sum_{\tau=1}^{\tau_{\text{obs}}} \mathcal{A}(\Gamma(\tau))$$

Whether or not a sufficient region of phase space is explored by the system trajectory within a feasible amount of computer time

Whether thermodynamic consistency can be attained between simulation with identical macroscopic parameters (density, energy,...) but different initial conditions

Such simulation runs are within the power of modern computers

# Ergodicity

- In MD we want to replace a full sampling on the appropriate statistical ensemble by a SINGLE very long trajectory.
- This is OK only if system is **ergodic**.
- **Ergodic Hypothesis**: *a phase point for any isolated system passes in succession through every point compatible with the energy of the system before finally returning to its original position in phase space. This journey takes a Poincare cycle.*
- *In other words, Ergodic hypothesis*: each state consistent with our knowledge is equally “likely”.
  - Implies the average value does not depend on initial conditions.
  - $\langle A \rangle_{\text{time}} = \langle A \rangle_{\text{ensemble}}$ , so  $\langle A_{\text{time}} \rangle = (1/N_{\text{MD}}) = \sum_{t=1, N} A_t$  is good estimator.
- **Are systems in nature really ergodic?** Not always!
  - Non-ergodic examples are glasses, folding proteins (in practice) and harmonic crystals (in principle).

# Ergodicity

$$\mathcal{A}_{\text{obs}} = \langle \mathcal{A} \rangle_{\text{ens}} = \langle \mathcal{A} | \rho_{\text{ens}} \rangle = \sum_{\Gamma} \mathcal{A}(\Gamma) \rho_{\text{ens}}(\Gamma)$$

$\rho_{\text{ens}}(\Gamma)$  is the phase space density

## Different aspects of ergodicity

- The system relaxes on a “reasonable” time scale towards a unique equilibrium state (microcanonical state)
- Trajectories wander irregularly through the energy surface eventually sampling all of accesible phase space.
- Trajectories initially close together separate rapidly (Sensitivity to initial conditions).

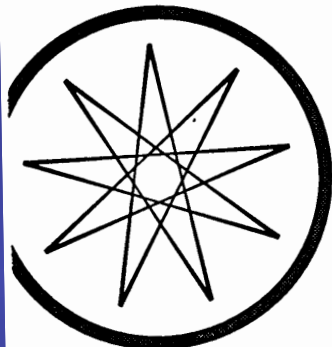
**Ergodic behavior makes possible the use of statistical methods on MD of small system.**

**Small round-off errors and other mathematical approximations should not matter.**

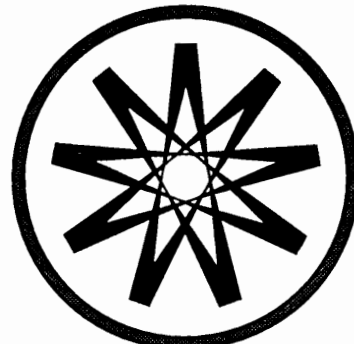


# Particle in a smooth/rough circle

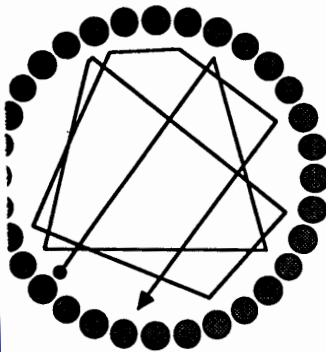
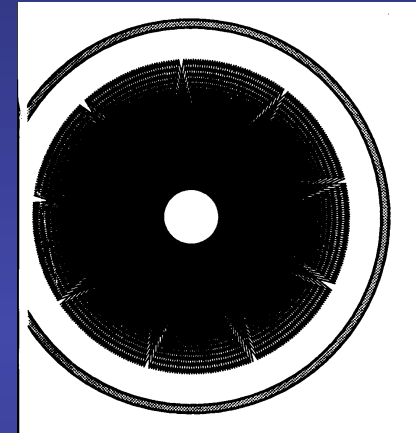
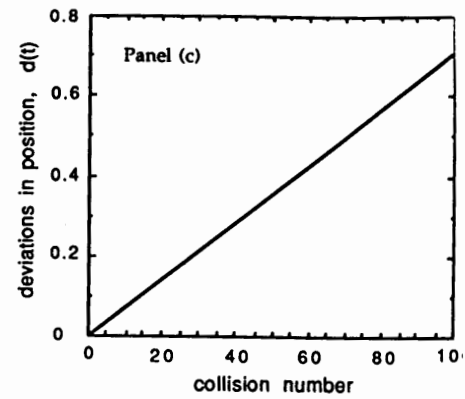
From J.M. Haile: MD Simulations



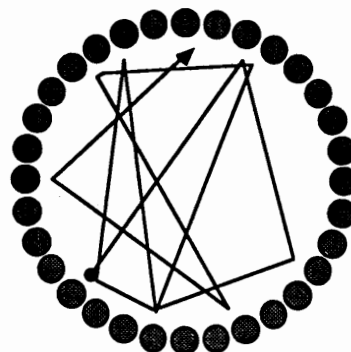
Panel (a): Parent Trajectory



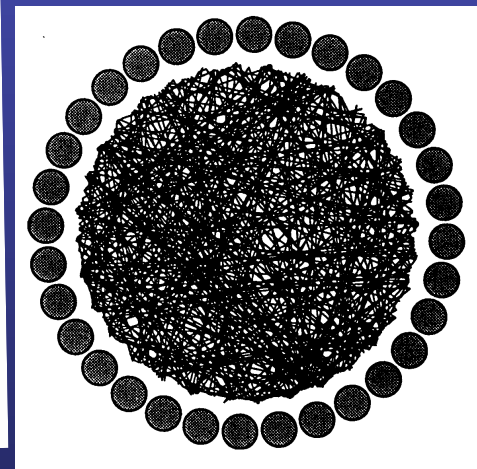
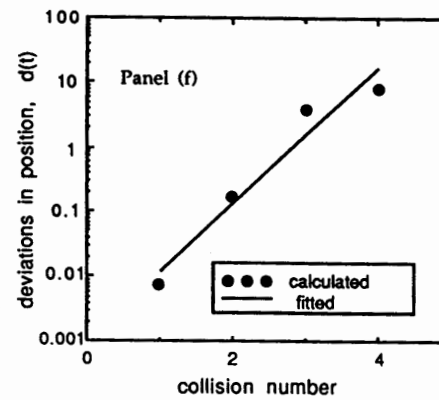
Panel (b): Perturbed Trajectory



Panel (d): Parent Trajectory



Panel (e): Perturbed Trajectory



# Simple thermodynamic averages: mechanical energy

The kinetic, potential, and total energies might be calculated  
using the phase functions already seen

$$\vec{q} = (\vec{q}_1, \vec{q}_2, \dots, \vec{q}_N)$$

$$\vec{p} = (\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N)$$

$$\mathcal{H}(\vec{q}, \vec{p}) = \mathcal{K}(\vec{p}) + \mathcal{V}(\vec{q})$$

$$\mathcal{K}(\vec{p}) \equiv \text{kinetic energy}$$

$$\mathcal{V}(\vec{q}) \equiv \text{potential energy}$$

$$E = \langle \mathcal{H} \rangle = \langle \mathcal{K} \rangle + \langle \mathcal{V} \rangle$$

**Average of kinetic energy**  
Sum of contribution from  
individual particle momenta

**Average of potential energy**  
Sum over all pairs, triplets, ...  
depending on the complexity of  
the potential energy function

**Simple thermodynamic averages:  
virial theorem in the form of “generalized equipartition”**

$$\left\langle p_k \frac{\partial \mathcal{H}}{\partial p_k} \right\rangle = k_B T$$

$$\left\langle q_k \frac{\partial \mathcal{H}}{\partial q_k} \right\rangle = k_B T$$

# Simple thermodynamic averages: temperature

Applying the previous formula to compute the average kinetic energy in the atomic case

$$\left\langle \sum_{i=1}^N \frac{|\vec{p}_i|^2}{m_i} \right\rangle = 2 \left\langle \sum_{i=1}^N \frac{|\vec{p}_i|^2}{2m_i} \right\rangle = 2 \langle \mathcal{K} \rangle$$

$$\left\langle \sum_{i=1}^N \frac{|\vec{p}_i|^2}{m_i} \right\rangle = \sum_{i=1}^N \sum_{\alpha=1}^3 \left\langle \frac{p_{i\alpha}^2}{m_i} \right\rangle = \sum_{i=1}^N \sum_{\alpha=1}^3 \left\langle p_{i\alpha} \frac{\partial \mathcal{H}}{\partial p_{i\alpha}} \right\rangle = 3Nk_B T$$

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

**Familiar equipartition energy: an average energy of  $\frac{1}{2}k_B T$  per degree of freedom**

# Simple thermodynamic averages: instantaneous temperature

We can define an “instantaneous kinetic energy function”  
from the momenta of the atoms at a given time step (not averaged)

$$\mathcal{T} = \frac{2\mathcal{K}}{3Nk_B} = \frac{1}{3Nk_B} \sum_{i=1}^N \frac{|\vec{p}_i|^2}{m_i}$$

whose average is equal to  $T$

For a system of  $N$  atoms subject to internal molecular constraints,  
the number of degrees of freedom will be  $3N - N_c$ , where  $N_c$  is the  
total number of independent internal constraints

$$\mathcal{T} = \frac{2\mathcal{K}}{(3N - N_c) k_B} = \frac{1}{(3N - N_c) k_B} \sum_{i=1}^N \frac{|\vec{p}_i|^2}{m_i}$$

In  $N_c$  we should include the fixed  
bond lengths, angles, or additional  
global constraints (on the center of  
mass motion, for instance)

# Simple thermodynamic averages: pressure

Let us assume that we are using Cartesian coordinates, and we use the Hamilton's equation of motion

$$\dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i}$$

$$\dot{\vec{p}}_i = -\nabla_{\vec{r}_i} \mathcal{V} = \vec{f}_i$$

$$\frac{\partial \mathcal{H}}{\partial \vec{r}_i} = \frac{\partial \mathcal{V}}{\partial \vec{r}_i} = \nabla_{\vec{r}_i} \mathcal{V} = -\vec{f}_i$$

$$-\frac{1}{3} \left\langle \sum_{i=1}^N \vec{r}_i \cdot \nabla_{\vec{r}_i} \mathcal{V} \right\rangle = -\frac{1}{3} \sum_{i=1}^N \sum_{\alpha=1}^3 \langle r_{i\alpha} \nabla_{r_{i\alpha}} \mathcal{V} \rangle = -\frac{1}{3} \sum_{i=1}^N \sum_{\alpha=1}^3 \langle r_{i\alpha} \frac{\partial \mathcal{H}}{\partial r_{i\alpha}} \rangle = -\frac{1}{3} 3Nk_B T = -Nk_B T$$

$$\uparrow$$
$$\left\langle q_k \frac{\partial \mathcal{H}}{\partial q_k} \right\rangle = k_B T$$

# Simple thermodynamic averages: pressure

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$$-\frac{1}{3} \left\langle \sum_{i=1}^N \vec{r}_i \cdot \nabla_{\vec{r}_i} \mathcal{V} \right\rangle = \frac{1}{3} \langle \vec{r}_i \cdot \vec{f}_i^{\text{tot}} \rangle = -Nk_B T$$

$\vec{f}_i^{\text{tot}}$  represents the sum of  
internal molecular forces and  
external forces

# Simple thermodynamic averages: pressure

The external forces are related to the external pressure.  
Considering the effect of the container walls on the system

$$\frac{1}{3} \left\langle \sum_{i=1}^N \vec{r}_i \cdot \vec{f}_i^{\text{ext}} \right\rangle = -PV$$

If we define the “internal virial”, where we now restrict our attention to the intermolecular forces, then

$$-\frac{1}{3} \sum_{i=1}^N \vec{r}_i \cdot \nabla_{\vec{r}_i} \mathcal{V} = \frac{1}{3} \sum_{i=1}^N \vec{r}_i \cdot \vec{f}_i = \mathcal{W}$$

$$-\frac{1}{3} \left\langle \sum_{i=1}^N \vec{r}_i \cdot \nabla_{\vec{r}_i} \mathcal{V} \right\rangle = \frac{1}{3} \left\langle \vec{r}_i \cdot \vec{f}_i^{\text{tot}} \right\rangle = \frac{1}{3} \left\langle \vec{r}_i \cdot \vec{f}_i^{\text{ext}} \right\rangle + \frac{1}{3} \left\langle \vec{r}_i \cdot \vec{f}_i \right\rangle = -PV + \langle \mathcal{W} \rangle = -Nk_{\text{B}}T$$

**So, finally**

$$PV = Nk_{\text{B}}T + \langle \mathcal{W} \rangle$$



# Simple thermodynamic averages: instantaneous pressure

As it happened with the temperature, we can define the instantaneous pressure function as

$$\mathcal{P} = \rho k_B T + \frac{\mathcal{W}}{V} = \mathcal{P}^{\text{id}} + \mathcal{P}^{\text{ext}}$$

whose average is simply  $P$

This definition of the instantaneous pressure is not unique. For instance, for a constant temperature ensemble we can define

$$\mathcal{P}' = \rho k_B T + \frac{\mathcal{W}}{V} = \langle \mathcal{P}^{\text{id}} \rangle + \mathcal{P}^{\text{ex}}$$

Both definitions of the instantaneous pressure give the same  $P$  when averaged, but their fluctuations in any ensemble would be different

Although the systems simulated we use periodic boundary conditions (and therefore there are no walls), the results are the same

# Simple thermodynamic averages: instantaneous pressure

For pairwise interaction, we can express  $\mathcal{W}$  in a form that is explicitly independent of the origin of coordinates

$$\sum_i \vec{r}_i \cdot \vec{f}_i = \sum_i \sum_{j \neq i} \vec{r}_i \cdot \vec{f}_{ij} = \frac{1}{2} \sum_i \sum_{j \neq i} (\vec{r}_i \cdot \vec{f}_{ij} + \vec{r}_j \cdot \vec{f}_{ji})$$

The indices  $i$  and  $j$  are equivalent

Newton's third law  $\vec{f}_{ji} = -\vec{f}_{ij}$  is used to switch the force indices

$$\sum_i \vec{r}_i \cdot \vec{f}_i = \frac{1}{2} \sum_i \sum_{j \neq i} \vec{r}_{ij} \cdot \vec{f}_{ij} = \sum_i \sum_{j > i} \vec{r}_{ij} \cdot \vec{f}_{ij}$$

where  $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$

## Simple thermodynamic averages: instantaneous pressure

In a simulation that uses periodic boundary condition, it is essential to use  $\vec{r}_{ij} \cdot \vec{f}_{ij}$

$$\begin{aligned}\mathcal{W} &= \frac{1}{3} \sum_i \sum_{j>i} \vec{r}_{ij} \cdot \vec{f}_{ij} = -\frac{1}{3} \sum_i \sum_{j>i} \vec{r}_{ij} \cdot \nabla_{\vec{r}_{ij}} v(\vec{r}_{ij}) \\ &= -\frac{1}{3} \sum_i \sum_{j>i} w(r_{ij})\end{aligned}$$

where the intermolecular pair virial function  $w(r) = r \frac{dv(r)}{dr}$

Like  $\mathcal{V}$ ,  $\mathcal{W}$  is limited by the range of the interactions, and hence  $\langle \mathcal{W} \rangle$  should be a well behaved, ensemble-independent function in most cases

# Simple thermodynamic averages: number of molecules and volume

Average number of particles

$$\langle N \rangle$$

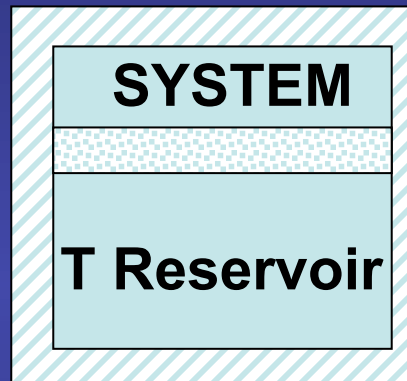
Average number of particles

$$\langle V \rangle$$

Are easily evaluated in the simulation of ensembles in which these quantities vary,  
and derived functions such as the enthalpy are easily calculated from the above

# Constant temperature molecular dynamics: the canonical ensemble $(N, V, T)$

A physical picture of a system corresponding to the canonical ensemble  $(N, V, T)$  involves weak interactions between molecules of the system and the particles of a heat bath at a specific temperature



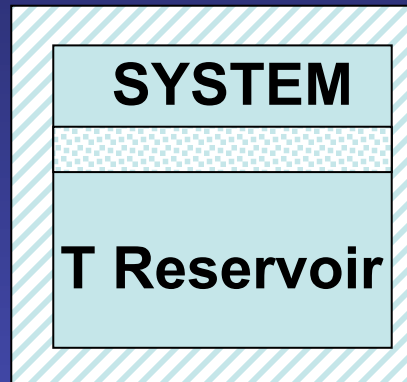
Simulate an “extended system”:

- the **real** system
- an **external (virtual)** system, acting as a **heat reservoir**

The **energy** is allowed to **flow dynamically from the reservoir to the system and back**. The **heat reservoir controls the temperature** of the given system, i. e., the temperature fluctuates around a target value.

The **reservoir** is simply included by an **extra degree of freedom,  $s$** , with momentum  $p_s$

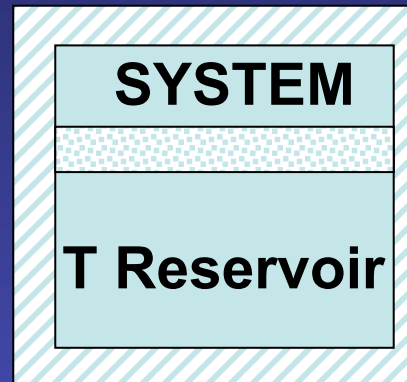
# Constant temperature molecular dynamics: variables of the Nose-Hoover thermostat



The **heat bath** is considered as an integral part of the system by addition of

- an **extra degree of freedom**,  $s$
- an **extra momentum**,  $p_s$
- a “**mass**”,  $Q > 0$ , [**dimensions: (energy)  $\times$  (times) $^2$** ] . This variable controls the rate of temperature fluctuations

## Constant temperature molecular dynamics: variables of the Nose-Hoover thermostat: the artificial variable



The extra degree of freedom (artificial parameter)  $s$ , plays the role of a time scaling parameter.

The time scale in the extended system,  $\tau$ , is scaled by the factor  $s$

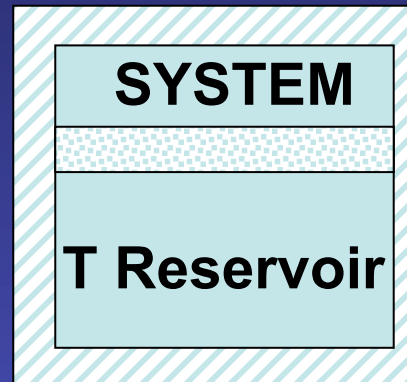
$d\tau = s dt$

Virtual time in the extended system

Real time

$$s = \frac{d\tau}{dt}$$

# Constant temperature molecular dynamics: variables of the Nose-Hoover thermostat: the artificial momentum



The atomic coordinates are identical in both systems

$$\vec{\rho}_i = \vec{r}_i$$

Atomic coordinates in the extended system      Atomic coordinates in the real system

$$\vec{\pi}_i = m_i \frac{d\vec{\rho}_i}{d\tau} = m_i \frac{d\vec{r}_i}{d\tau} = m_i \frac{d\vec{r}_i}{dt} \frac{dt}{d\tau} = m_i \vec{v}_i \frac{1}{s} = \frac{1}{s} \vec{p}_i$$

Momentum in the extended system

Momentum in the real system



# Constant temperature molecular dynamics: variables of the Nose-Hoover thermostat: the extended Lagrangian

The Lagrangian of the extended system is

$$\mathcal{L}(\vec{\rho}_i, \vec{\pi}_i, s, \frac{ds}{d\tau}) = \underbrace{\sum_{i=1}^N \frac{1}{2m_i} s^2 \vec{\pi}_i^2 - U(\vec{\rho}_1, \dots, \vec{\rho}_N)}_{\text{Kinetic energy minus the potential energy of the real system}} + \frac{1}{2} Q \left( \frac{ds}{d\tau} \right)^2 - g k_B T \ln s$$

Kinetic energy minus the potential energy of the real system

Kinetic energy of the thermostat

Extra potential

The extra potential is chosen to ensure that the algorithm produces a canonical ensemble

$$g = N_{df} + 1$$

$N_{df}$  Numbers of degree of freedom:

**3N**

**3N-3 if the total momentum is fixed**

**+1 because of the extra degree of freedom of the thermostat**

## Constant temperature molecular dynamics: the Lagrangian equations for the Nose-Hoover thermostat

$$\mathcal{L}(\vec{\rho}_i, \vec{\pi}_i, s, \frac{ds}{d\tau}) = \sum_{i=1}^N \frac{1}{2m_i} s^2 \vec{\pi}_i^2 - U(\vec{\rho}_1, \dots, \vec{\rho}_N) + \frac{1}{2} Q \left( \frac{ds}{d\tau} \right)^2 - g k_B T \ln s$$

The Lagrangian equations of motions are

$$\frac{d}{d\tau} \left( \frac{\partial \mathcal{L}}{\partial \dot{\vec{\rho}}_k} \right) - \left( \frac{\partial \mathcal{L}}{\partial \vec{\rho}_k} \right) = 0$$

$$\frac{\partial \mathcal{L}}{\partial \dot{\vec{\rho}}_k} = m_k s^2 \dot{\vec{\rho}}_k = s^2 \vec{\pi}_k$$

$$\frac{d}{d\tau} \frac{\partial \mathcal{L}}{\partial \dot{\vec{\rho}}_k} = \frac{d \left( m_k s^2 \dot{\vec{\rho}}_k \right)}{d\tau} = 2m_k s \frac{d\vec{\rho}_k}{d\tau} \frac{ds}{d\tau} + m_k s^2 \frac{d^2 \vec{\rho}_k}{d\tau^2} \quad \frac{\partial \mathcal{L}}{\partial \vec{\rho}_k} = - \frac{\partial U(\vec{\rho}_1, \dots, \vec{\rho}_N)}{\partial \vec{\rho}_k} = \tilde{\vec{F}}_k$$

$$\frac{d^2 \vec{\rho}_k}{d\tau^2} = \frac{\tilde{\vec{F}}_k}{m_k s^2} - \frac{2}{s} \frac{d\vec{\rho}_k}{d\tau} \frac{ds}{d\tau}$$

## Constant temperature molecular dynamics: the Lagrangian equations for the Nose-Hoover thermostat

$$\mathcal{L}(\vec{\rho}_i, \vec{\pi}_i, s, \frac{ds}{d\tau}) = \sum_{i=1}^N \frac{1}{2m_i} s^2 \vec{\pi}_i^2 - U(\vec{\rho}_1, \dots, \vec{\rho}_N) + \frac{1}{2} Q \left( \frac{ds}{d\tau} \right)^2 - gk_B T \ln s$$

The Lagrangian equations of motions are

$$\frac{d}{d\tau} \left( \frac{\partial \mathcal{L}}{\partial \dot{s}} \right) - \left( \frac{\partial \mathcal{L}}{\partial s} \right) = 0$$

$$\frac{\partial \mathcal{L}}{\partial \dot{s}} = Q \frac{ds}{d\tau}$$

$$\frac{d}{d\tau} \left( \frac{\partial \mathcal{L}}{\partial \dot{s}} \right) = Q \frac{d^2 s}{d\tau^2} \qquad \frac{\partial \mathcal{L}}{\partial s} = \sum_{i=1}^N \frac{s \vec{\pi}_i^2}{m_i} - \frac{gk_B T}{s}$$

$$\frac{d^2 s}{d\tau^2} = \frac{1}{Qs} \left( \sum_{i=1}^N \frac{s^2 \vec{\pi}_i^2}{m_i} - gk_B T \right)$$

# Constant temperature molecular dynamics: the Lagrangian equations for the Nose-Hoover thermostat

The Lagrangian equations of motions are

$$\frac{d^2 \vec{\rho}_k}{d\tau^2} = \frac{\vec{F}_k}{m_k s^2} - \frac{2}{s} \frac{d\vec{\rho}_k}{d\tau} \frac{ds}{d\tau}$$

$$\frac{d^2 s}{d\tau^2} = \frac{1}{Qs} \left( \sum_{i=1}^N \frac{s^2 \vec{\pi}_i^2}{m_i} - gk_B T \right)$$

The equations of motion are solved using the standard predictor-corrector method

These equations sample a microcanonical ensemble in the extended system.  
The extended system Hamiltonian is conserved

However, the energy of the real system is not constant. Accompanying the fluctuations of  $s$ , heat transfers occur between the system and a heat bath, which regulate the system temperature.

# Constant temperature molecular dynamics: Choice of $Q$ in the Nose-Hoover thermostat

Too high

Slow energy flow between the  
system and the reservoir

$Q \rightarrow 0$  regain conventional  
Molecular Dynamics

Too low

Long lived weakly damping  
oscillations of energy occur,  
resulting in poor equilibration