Lecture 17, 18, 19
CH-4114
Molecular Simulation

"Everything that living things do can be understood in terms of the jigglings and wigglings of atoms."

- Richard P. Feynman

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Thermostat:
Velocity Rescaling, Berendsen, Nosé-Hoover

Velocity rescaling method

Instantaneous Temperature from Kinetic Energy

In molecular dynamics, the **instantaneous temperature** of a system with N particles is obtained from the kinetic energy (KE):
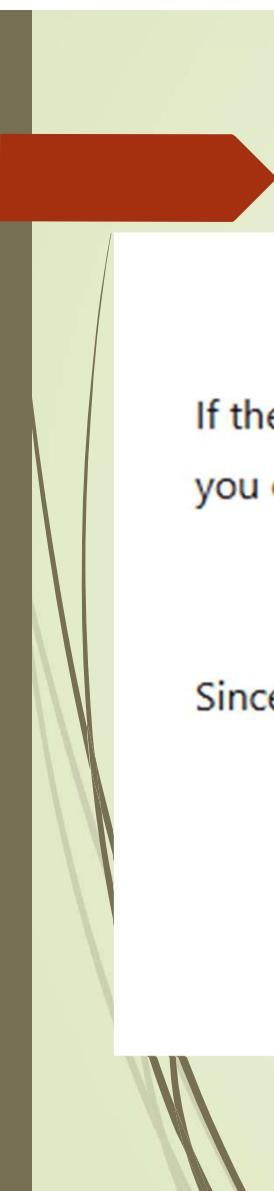
$$E_k = \frac{1}{2} \sum_{i=1}^{N} m_i v_i^2 = \frac{3}{2} N k_B T$$

So,

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

At any time t, you can compute the temperature $T(t)$ from the velocities.

Idea: Maintain constant temperature by rescaling velocities

If the current temperature $T(t)$ deviates from the desired temperature T_0, you can **rescale all velocities** by a constant factor λ:

$$\mathbf{v}'_i = \lambda \mathbf{v}_i$$

Since kinetic energy depends on v^2, the new kinetic energy (and hence the new temperature) changes as:

$$E'_k = \frac{1}{2} \sum_i m_i (\lambda v_i)^2 = \lambda^2 E_k$$

$$\Rightarrow T' = \lambda^2 T$$

Determine the scaling factor λ

We want the new temperature T' to equal the **desired target temperature** T_0.

So:

$$T_0 = \lambda^2 T(t)$$

$$\boxed{\lambda = \sqrt{\frac{T_0}{T(t)}}}$$

That's it — the simplest possible way to control temperature:

multiply all particle velocities by this factor λ at every MD step.

What happens during the simulation

At each time step:

1. Compute instantaneous $T(t)$ from velocities.
2. Compute scaling factor $\lambda = \sqrt{T_0/T(t)}$.
3. Multiply all velocities by λ.
4. Continue to the next step.

This ensures the **instantaneous temperature** matches T_0 exactly after every rescaling.

Limitations to be aware of

Mathematical effect on equations of motion

However, this procedure **overrides** the natural dynamics — you are continuously forcing the system to have the exact temperature.

Therefore, the **equations of motion become irreversible.**

That means:

- Energy and momentum conservation are broken.
- The system **does not** represent a physical ensemble (not canonical or microcanonical).
- "Transition probabilities" do not satisfy **detailed balance**, so it's not correct for statistical sampling.

Temperature control — Langevin as a thermostat

Molecular World: Imagine a particle in a "noisy soup"

Imagine a **single particle** (say, a dust grain or an atom) moving in a **liquid**.
It is constantly bombarded by solvent molecules:
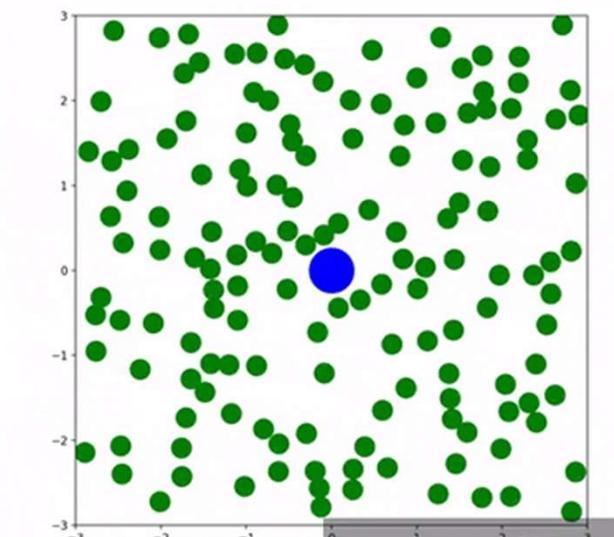
- Each hit changes its velocity a little, randomly.
- At the same time, friction from the fluid slows it down.

So the motion is not purely Newtonian anymore — it's a mix of:

- **Systematic forces** (e.g., spring force, potential gradient),
- **Friction (drag)** that resists motion, and
- **Random kicks** from solvent collisions.

This random–damped motion is exactly what **Langevin dynamics** models.

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The Langevin equation (1D form first)

For a particle of mass m at position $x(t)$, the Langevin equation is:

$$m\frac{d^2x}{dt^2} = F(x) - \gamma m\frac{dx}{dt} + R(t)$$

The Langevin equation (1D form first)

For a particle of mass m at position $x(t)$, the **Langevin equation** is:

$$m\frac{d^2x}{dt^2} = F(x) - \gamma m\frac{dx}{dt} + R(t)$$

or, equivalently,

$$m\dot{v} = F(x) - \gamma mv + R(t)$$

where each term means:

Term	Meaning	Physical role
$F(x)$	Deterministic force (e.g., −dU/dx)	Drives the system along potential
$-\gamma mv$	Friction (drag)	Dissipates kinetic energy
$R(t)$	Random force ("noise")	Injects random energy from the environment

Here γ (gamma) is the **friction coefficient** — it measures how strongly the particle is coupled to the "bath".

Why the random and friction terms go together

If we only had drag (friction), the particle would just **slow down and stop.**

But in real life, solvent collisions also **kick it around randomly,** so that on average, its kinetic energy matches the **temperature of the environment.**

This balance between friction and random kicks leads to **thermal equilibrium** — the system temperature T.

Mathematically, the random force satisfies:

$$\langle R(t) \rangle = 0$$

$$\langle R(t)R(t') \rangle = 2\gamma m k_B T \, \delta(t - t')$$

This is called the **fluctuation–dissipation theorem** — it ensures that the amount of random "noise" exactly compensates for the frictional "dissipation," maintaining the correct average thermal energy.

Physical meaning of γ (friction coefficient)

- If γ is **very small** → friction and noise are weak → dynamics are close to Newtonian. The system behaves almost like microcanonical dynamics.
- If γ is **very large** → velocity changes almost instantaneously due to friction. The motion becomes **overdamped** → inertial effects vanish. Then we get **Brownian dynamics**:

$$\gamma\dot{x} = \frac{F(x)}{m} + \text{noise}$$

Temperature control — Langevin as a thermostat

In molecular dynamics simulations, the Langevin equation acts as a thermostat.

- The random term injects heat → keeps average kinetic energy $\approx \frac{3}{2}Nk_BT$.
- The friction term removes excess energy → prevents runaway heating.

Together, they ensure the system samples the **canonical (NVT) ensemble**, i.e., correct temperature distribution.

Berendsen thermostat

Step 1. Start from the Langevin equation (heat bath coupling)
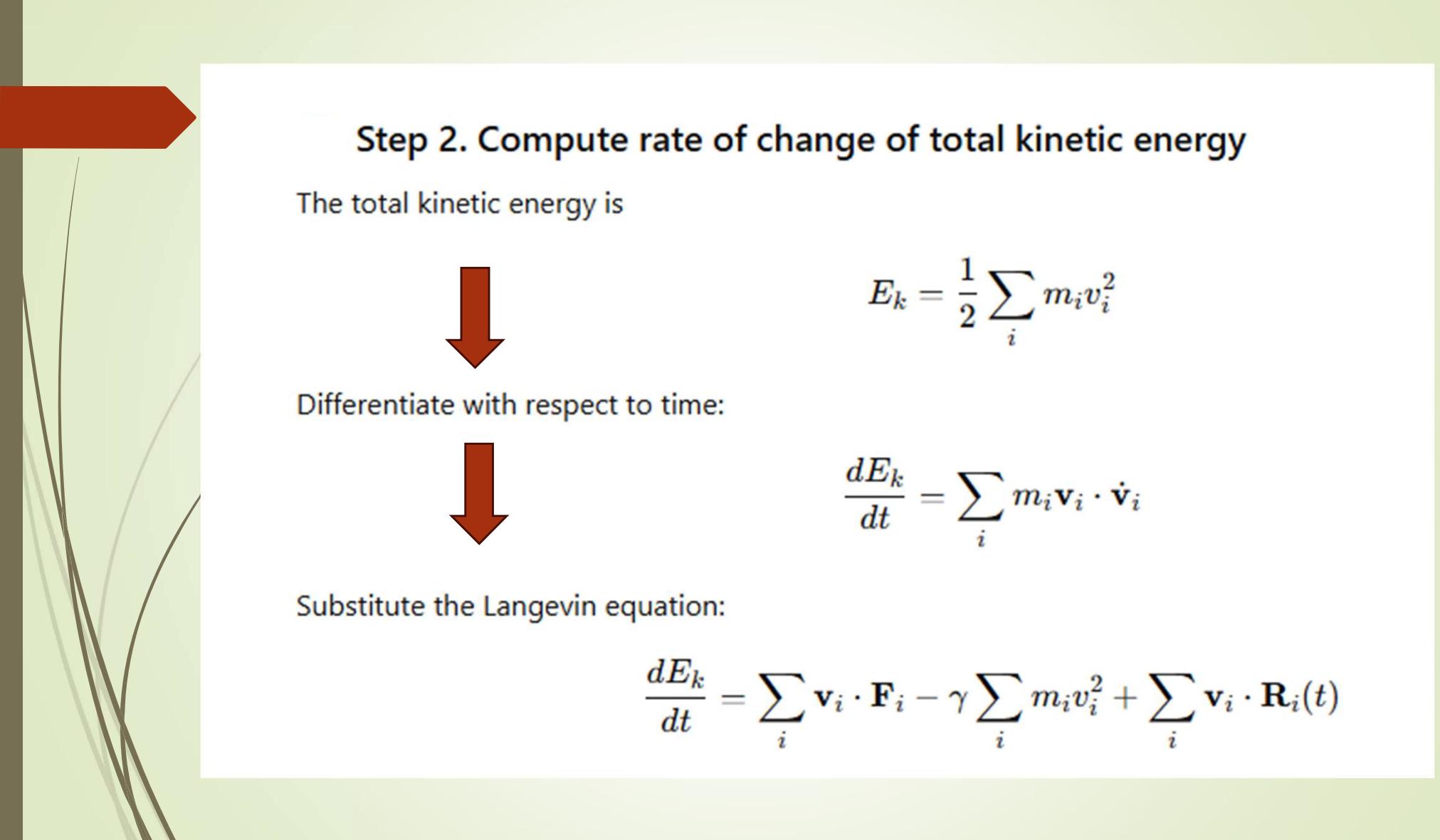
The **Berendsen thermostat** starts conceptually from the **Langevin equation**, where each particle is weakly coupled to a fictitious heat bath at temperature T_0:

$$m_i \dot{\mathbf{v}}_i = \mathbf{F}_i - \gamma m_i \mathbf{v}_i + \mathbf{R}_i(t)$$

where:

- $\mathbf{F}_i$: systematic (deterministic) force on particle i
- γ: friction coefficient (coupling strength)
- $\mathbf{R}_i(t)$: random force (Gaussian noise)
- $\langle R_{i\alpha}(t) R_{j\beta}(t') \rangle = 2\gamma m_i k_B T_0 \delta_{ij} \delta_{\alpha\beta} \delta(t - t')$

This ensures that the system exchanges energy with the bath, keeping it near T_0.

Step 2. Compute rate of change of total kinetic energy

The total kinetic energy is

$$E_k = \frac{1}{2} \sum_i m_i v_i^2$$

Differentiate with respect to time:

$$\frac{dE_k}{dt} = \sum_i m_i \mathbf{v}_i \cdot \dot{\mathbf{v}}_i$$

Substitute the Langevin equation:

$$\frac{dE_k}{dt} = \sum_i \mathbf{v}_i \cdot \mathbf{F}_i - \gamma \sum_i m_i v_i^2 + \sum_i \mathbf{v}_i \cdot \mathbf{R}_i(t)$$

Step 3. Average over stochastic noise

Since the random force $\mathbf{R}_i(t)$ is **uncorrelated** with the velocities and forces (white noise assumption), its average contribution vanishes:

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

So, the average rate of change of kinetic energy becomes:

$$\left\langle \frac{dE_k}{dt} \right\rangle = \sum_i \mathbf{v}_i \cdot \mathbf{F}_i - 2\gamma \left(E_k - \frac{3}{2} N k_B T_0 \right)$$

Here, $\frac{3}{2} N k_B T_0$ is the expected kinetic energy of the system if it were at temperature T_0.

The first term → rate of change of **potential energy**, i.e., mechanical energy exchange within the system (doesn't affect temperature directly).

Step 4. Connect kinetic energy to temperature

Define instantaneous temperature T from kinetic energy:

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

Differentiate:

$$\frac{dT}{dt} = \frac{2}{3 N k_B} \frac{dE_k}{dt}$$

Plug the previous result in:

$$\frac{dT}{dt} = -\frac{2\gamma}{1} (T - T_0)$$

Step 5. Define coupling time constant

Let's define a **temperature relaxation time** τ_T as

$$\tau_T = \frac{1}{2\gamma}$$

Then the equation becomes:

$$\frac{dT}{dt} = \frac{1}{\tau_T}(T_0 - T)$$

Step 6. Solve for T(t)

This differential equation has an exponential relaxation solution:

$$T(t) = T_0 + [T(0) - T_0]e^{-t/\tau_T}$$

So the system temperature relaxes exponentially toward the bath temperature T_0.

Step 7. Velocity rescaling form (used in MD)

Since $E_k \propto v^2 \propto T$, controlling T means **rescaling velocities** at each time step:

Let λ be the scaling factor for velocities at time t:

$$\mathbf{v}'_i = \lambda \mathbf{v}_i$$

Then $T' = \lambda^2 T$.

The change in temperature over one time step Δt according to the exponential relaxation is approximately:

$$T' = T + \frac{\Delta t}{\tau_T}(T_0 - T)$$

Replacing $T' = \lambda^2 T$, we get:

$$\lambda^2 T = T + \frac{\Delta t}{\tau_T}(T_0 - T)$$

$$\boxed{\lambda = \sqrt{1 + \frac{\Delta t}{\tau_T}\left(\frac{T_0}{T} - 1\right)}}$$

Step 8. Implementing the Berendsen thermostat

Each MD step:

1. Compute instantaneous temperature T from current velocities.

2. Compute $\lambda = \sqrt{1 + \frac{\Delta t}{\tau_T}\left(\frac{T_b}{T} - 1\right)}$

3. Rescale velocities: $\mathbf{v}_i \leftarrow \lambda \mathbf{v}_i$

- If τ_T is large → weak coupling → system evolves almost naturally.
- If τ_T is small → strong coupling → faster temperature adjustment (but less physical).

Advantages and limitations

Advantages:

- Simple and efficient implementation.
- Fast equilibration to desired temperature.
- Adjustable coupling strength τ_T.

Disadvantages:

- Does **not generate a true canonical ensemble** (distribution of kinetic energy is narrower).

Background: **Nosé-Hoover Thermostat**

What Nosé Tried to Do

Nosé wanted to derive canonical (constant T) dynamics from a purely Hamiltonian system — i.e., one that conserves energy but still samples a temperature-controlled ensemble.
To achieve that, he introduced an **extended system** with:
- Physical coordinates and momenta: $\mathbf{r}_i, \mathbf{p}_i$
- A *thermostat variable s* (which scales time)
- A *conjugate momentum* p_s for *s*
- A *mass parameter Q* for the thermostat

Nosé extended Hamiltonian

Nosé introduced an extra degree of freedom s (a scale factor for time/momenta) with conjugate momentum p_s and an associated mass parameter Q. The extended Hamiltonian is:

$$\mathcal{H}_{\mathrm{N}} = \sum_i \frac{\mathbf{p}_i^2}{2m_i s^2} + U(\{\mathbf{q}\}) + \frac{p_s^2}{2Q} + gk_B T \ln s.$$

Remarks:

- The s factor rescales momenta, so the physical kinetic energy depends on s.
- The $gk_B T \ln s$ term ensures the correct weighting that leads to canonical sampling for the physical variables (after transforming to real time and integrating out the extended variables).

➢ qi,pi : coordinates and momenta of particle i(physical variables).
➢ m_i :mass of particle i.
➢ $U(\{\mathbf{q}\})$:potential energy.
➢ k_B :Boltzmann constant.
➢ Target (bath) temperature: T.
➢ g: number of degrees of freedom coupled to the thermostat (commonly $g = 3N$minus constraints).
Goal: modify dynamics so that the *physical* coordinates sample the canonical ensemble at temperature T.

Equations of motion in extended (Nosé) time τ

Treating $\mathcal{H}_\mathrm{N}$ as a Hamiltonian with time parameter τ, Hamilton's equations give:

$$\frac{d\mathbf{q}_i}{d\tau} = \frac{\partial \mathcal{H}_\mathrm{N}}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m_i s^2}$$

$$\frac{d\mathbf{p}_i}{d\tau} = -\frac{\partial \mathcal{H}_\mathrm{N}}{\partial \mathbf{q}_i} = -\nabla_i U(\{\mathbf{q}\})$$

$$\frac{ds}{d\tau} = \frac{\partial \mathcal{H}_\mathrm{N}}{\partial p_s} = \frac{p_s}{Q}$$

$$\frac{dp_s}{d\tau} = -\frac{\partial \mathcal{H}_\mathrm{N}}{\partial s} = \sum_i \frac{\mathbf{p}_i^2}{m_i s^3} - \frac{g k_B T}{s}.$$

These are equations in the fictitious time τ. To connect to real MD time t we need a transformation.

Real-time transformation — Why we need it

In Nosé's extended system, the **velocity of particle** i is:

$$\frac{d\mathbf{r}_i}{d\tau} = \frac{\mathbf{p}_i}{m_i s^2}$$

But in *real dynamics*, we want:

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

So, to fix this, Nosé defined:

$$dt = s\, d\tau \quad \Rightarrow \quad \frac{d}{dt} = \frac{1}{s}\frac{d}{d\tau}$$

That's the **real-time transformation**.
It makes physical velocities and accelerations meaningful again.

It is convenient to define a friction-like variable, $\zeta \equiv \frac{p_s}{Q}$.

Using the real-time derivative and expressing everything in physical variables leads to the Nosé–Hoover form.

4 — Nosé–Hoover equations (standard form)

Transforming to real time t and switching to momenta/velocities appropriate for MD gives the familiar Nosé–Hoover equations:

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m_i} = \mathbf{v}_i$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \zeta\, \mathbf{p}_i \quad \Longleftrightarrow \quad m_i \dot{\mathbf{v}}_i = \mathbf{F}_i - \zeta\, m_i \mathbf{v}_i$$

$$\dot{\zeta} = \frac{1}{Q}\left(\sum_i \frac{\mathbf{p}_i^2}{m_i} - g k_B T\right) = \frac{1}{Q}\left(2 E_k - g k_B T\right)$$

A little work around- Homework

where $\mathbf{F}_i = -\nabla_i U$, and $E_k = \frac{1}{2}\sum_i m_i v_i^2$ is the instantaneous kinetic energy.

These are deterministic ODEs in real physical time t.

Temperature control interpretation

Differentiate the kinetic energy using Eqns (1–3):

$$\frac{dE_k}{dt} = \sum_i m_i \mathbf{v}_i \cdot \dot{\mathbf{v}}_i = \sum_i \mathbf{v}_i \cdot \mathbf{F}_i - 2\zeta E_k.$$

Ignoring the work term $\sum \mathbf{v}_i \cdot \mathbf{F}_i$ (it redistributes energy between kinetic and potential), the thermostat term $-2\zeta E_k$ controls the kinetic energy. From Eq. (3):

$$\dot{\zeta} = \frac{2E_k - gk_BT}{Q}.$$

Thus ζ adjusts so as to push E_k (hence temperature) toward the target value $gk_BT/2$. Linearizing around equilibrium yields a characteristic relaxation time scale

$$\tau_T \sim \sqrt{\frac{Q}{gk_BT}}.$$

So Q plays the role of a "mass" for the thermostat: larger $Q \Rightarrow$ slower thermostat; smaller $Q \Rightarrow$ tighter (faster) control — but very small Q can produce nonphysical oscillations.

Summary

1. Nosé introduced an **extended Hamiltonian** with a scaling variable s and mass Q.

2. Transforming to real time and eliminating p_s leads to the **Nosé–Hoover equations**:

$$\dot{\mathbf{q}}_i = \mathbf{v}_i,$$

$$m_i\dot{\mathbf{v}}_i = \mathbf{F}_i - \zeta m_i\mathbf{v}_i,$$

$$\dot{\zeta} = \frac{1}{Q}\left(2E_k - gk_BT\right).$$

3. Q controls the thermostat speed: $\tau_T \sim \sqrt{Q/(gk_BT)}$.

4. If the extended dynamics is ergodic, the physical variables sample the canonical ensemble; if not, chains or stochastic thermostats are used.