Course 06/2

Nosé-Hoover thermostats.

- Real variables vs virtual variables (scaling of time)
- Equations of Nosé-Hoover thermostat
- Setting of inertia parameter *Q*

Real variables vs virtual variables (scaling of time)

Real variables	Virtual Nosé variables
$r' = r$	r
$p' = p/s$	p
$dt' = dt/s$	dt

This implies that the scaling of momenta occurs through the scaling of time!

$$\left.\begin{aligned} p' &= m\frac{dr'}{dt'} = m\frac{dr}{dt'} \\ p' &= p/s = ms\frac{dr}{dt} \end{aligned}\right\} \quad dt' = dt/s$$

In the Nosé simulation, the integration is done at integer multiples of the virtual time step Δt. Given the relation $\Delta t' = \Delta t/s$, the real time step $\Delta t'$ fluctuates with s.

Time averages

So far

$$\bar{A} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} dt \; A\left(p^N(t)/s(t), r^N(t)\right)$$

virtual time   virtual time

Suppose that we want to sample at integer multiples of a real time step

$$\lim_{\tau' \to \infty} \frac{1}{\tau'} \int_0^{\tau'} dt' \; A\left(p^N(t')/s(t'), r^N(t')\right) = ?$$

real time   real time

Time averages in real time

Since $dt' = dt/s$, the following relation holds:

$$\int_0^{\tau'} dt' = \int_0^{\tau} dt \frac{1}{s(t)} \qquad \Rightarrow \qquad \tau' = \int_0^{\tau} dt \frac{1}{s(t)}$$

Let us now transform the time average calculated over the real time steps:

$$\lim_{\tau' \to \infty} \frac{1}{\tau'} \int_0^{\tau'} dt' \quad A\left(p^N(t')/s(t'), r^N(t')\right)$$

$$= \lim_{\tau' \to \infty} \frac{\tau}{\tau'} \frac{1}{\tau} \int_0^{\tau} dt \quad A\left(p^N(t)/s(t), r^N(t)\right) / s(t)$$

change of variable
$t' \rightarrow t$

$$= \frac{\lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} dt\, A\left(p^N(t)/s(t), r^N(t)\right) / s(t)}{\lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} dt \quad 1/s(t)} = \frac{\langle A(p^N/s, r^N)/s \rangle_{\text{Nosé}}}{\langle 1/s \rangle_{\text{Nosé}}}$$

Time averages in real time

But what is

$$\lim_{\tau' \to \infty} \frac{1}{\tau'} \int_0^{\tau'} dt' \; A\left(p^N(t')/s(t'), r^N(t')\right) = \frac{\langle A(p^N/s, r^N)/s \rangle_{\text{Nosé}}}{\langle 1/s \rangle_{\text{Nosé}}} \quad ?$$

For this, we use the partition function of the Nosé system:

$$\frac{\langle A(p^N/s, r^N)/s \rangle_{\text{Nosé}}}{\langle 1/s \rangle_{\text{Nosé}}} = \frac{\dfrac{\int dp_i'^N dr_i^N \; A(p'^N, r^N) \; \exp\left[-\dfrac{3N}{g}\beta\mathcal{H}^{\text{PHYS}}(p'^N, r^N)\right]}{\cancel{\int dp_i'^N dr_i^N \; \exp\left[-\dfrac{3N+1}{g}\beta\mathcal{H}^{\text{PHYS}}(p'^N, r^N)\right]}}}{\dfrac{\int dp_i'^N dr_i^N \; \exp\left[-\dfrac{3N}{g}\beta\mathcal{H}^{\text{PHYS}}(p'^N, r^N)\right]}{\cancel{\int dp_i'^N dr_i^N \; \exp\left[-\dfrac{3N+1}{g}\beta\mathcal{H}^{\text{PHYS}}(p'^N, r^N)\right]}}}$$

Time averages in real time: result

$$\frac{\langle A(p^N/s, r^N)/s(t)\rangle_{\text{Nosé}}}{\langle 1/s\rangle_{\text{Nosé}}} = \frac{\int dp_i'^N dr_i'^N A(p'^N, r^N)\exp\left[-\frac{3N}{g}\beta\mathcal{H}^{\text{PHYS}}(p'^N, r^N)\right]}{\int dp_i'^N dr_i^N \exp\left[-\frac{3N}{g}\beta\mathcal{H}^{\text{PHYS}}(p'^N, r^N)\right]}$$

$$= \langle A(p'^N, r^N)\rangle_{\text{NVT}}$$

$g = 3N$

The sampling at integer multiples of real time gives the correct canonical sampling provided one sets $g = 3N$!

Equations of motion

Nosé Hamiltonian

$$\mathcal{H}_{\text{Nosé}} = \sum_{i=1}^{N} \frac{p_i^{\,2}}{2m_i\, s^2} + U(r^N) + \frac{p_s^{\,2}}{2Q} + \frac{g}{\beta} \ln s$$

Hamilton equations in virtual Nosé variables

(1.) $$\frac{d\vec{r}_i}{dt} = \frac{\partial \mathcal{H}_{\text{Nosé}}}{\partial \vec{p}_i} = \frac{\vec{p}_i}{m_i\, s^2}$$

(2.) $$\frac{d\vec{p}_i}{dt} = -\frac{\partial \mathcal{H}_{\text{Nosé}}}{\partial \vec{r}_i} = -\frac{dU(r^N)}{d\vec{r}_i}$$

(3.) $$\frac{ds}{dt} = \frac{\partial \mathcal{H}_{\text{Nosé}}}{\partial p_s} = \frac{p_s}{Q}$$

(4.) $$\frac{dp_s}{dt} = -\frac{\partial \mathcal{H}_{\text{Nosé}}}{\partial p_s} = \left(\sum_{i=1}^{N} \frac{p_i^{\,2}}{m_i\, s^2} - \frac{g}{\beta} \right) \frac{1}{s}$$

Change of variables

$dt \rightarrow dt' = dt/s$ (virtual → real)

$r \rightarrow r' = r$ (virtual → real)

$p \rightarrow p' = p/s$ (virtual → real)

$p_s \rightarrow p'_s = p_s/s$ (virtual → real)

Transformation of the equations of motions

(1'.) $$\frac{d\vec{r}_i'}{dt'} = s\,\frac{d\vec{r}_i}{dt} \overset{(1.)}{=} \frac{\vec{p}_i}{m_i s} = \frac{\vec{p}_i'}{m_i}$$

(2'.) $$\frac{d\vec{p}_i'}{dt'} = s\,\frac{d\vec{p}_i/s}{dt} = \frac{d\vec{p}_i}{dt} - \frac{1}{s}\,\vec{p}_i\,\frac{ds}{dt}$$

(2.) ↓ (3.) ↓

$$= -\frac{dU(r^N)}{d\vec{r}_i} - \vec{p}_i'\,\frac{p_s}{Q} = -\frac{dU(r^N)}{d\vec{r}_i} - \vec{p}_i'\,\frac{s\,p_s'}{Q}$$

(3'.)

… and so on

(4'.)

Equations of motion in real variables

$$
\left\{
\begin{aligned}
&\frac{d\vec{r}_i{}'}{dt'} = \frac{\vec{p}_i{}'}{m_i} \\
&\frac{d\vec{p}_i{}'}{dt'} = -\frac{dU(r'^N)}{d\vec{r}_i{}'} - \vec{p}_i{}' \frac{s\,p_s{}'}{Q} \\
&\frac{1}{s}\frac{ds}{dt'} = \frac{s\,p_s{}'}{Q} \\
&\frac{d}{dt'}\left(\frac{s\,ps'}{Q}\right) = \frac{1}{Q}\left(\sum_{i=1}^{N}\frac{p_i{}'^2}{m_i} - \frac{g}{\beta}\right)
\end{aligned}
\right.
$$

Constant of motion

$$E_{NH}{}^{const} = \sum_{i=1}^{N}\frac{p_i{}'^2}{2m_i} + U(r_i{}'^N) + \frac{s^2 p_s{}'^2}{2Q} + \frac{g}{\beta}\ln s$$

More convenient set of variables

We define $\quad \dot{x}_{NH} = \dfrac{s\, p_s'}{Q}$

Equations of motion

$$
\left.
\begin{aligned}
\dot{\vec{r}}_i &= \frac{\vec{p}_i}{m_i} \\
\dot{\vec{p}}_i &= -\frac{dU(r'^{\,N})}{d\vec{r}_i} - \dot{x}_{NH}\,\vec{p}_i \\
\ddot{x}_{NH} &= \frac{1}{Q}\left(\sum_{i=1}^{N} \frac{p_i^{\,2}}{m_i} - \frac{g}{\beta} \right)
\end{aligned}
\right\} \text{closed system}
$$

$$
\frac{\dot{s}}{s} = \frac{d \ln s}{dt} = \dot{x}_{NH}
$$

Constant of motion

$$
E_{NH}^{\;const} = \sum_{i=1}^{N} \frac{p_i^{\,2}}{2m_i} + U\left(r_i^{\,N}\right) + \frac{Q\,\dot{x}_{NH}^2}{2} + \frac{g}{\beta}\,x_{NH}
$$

Setting of inertia parameter Q

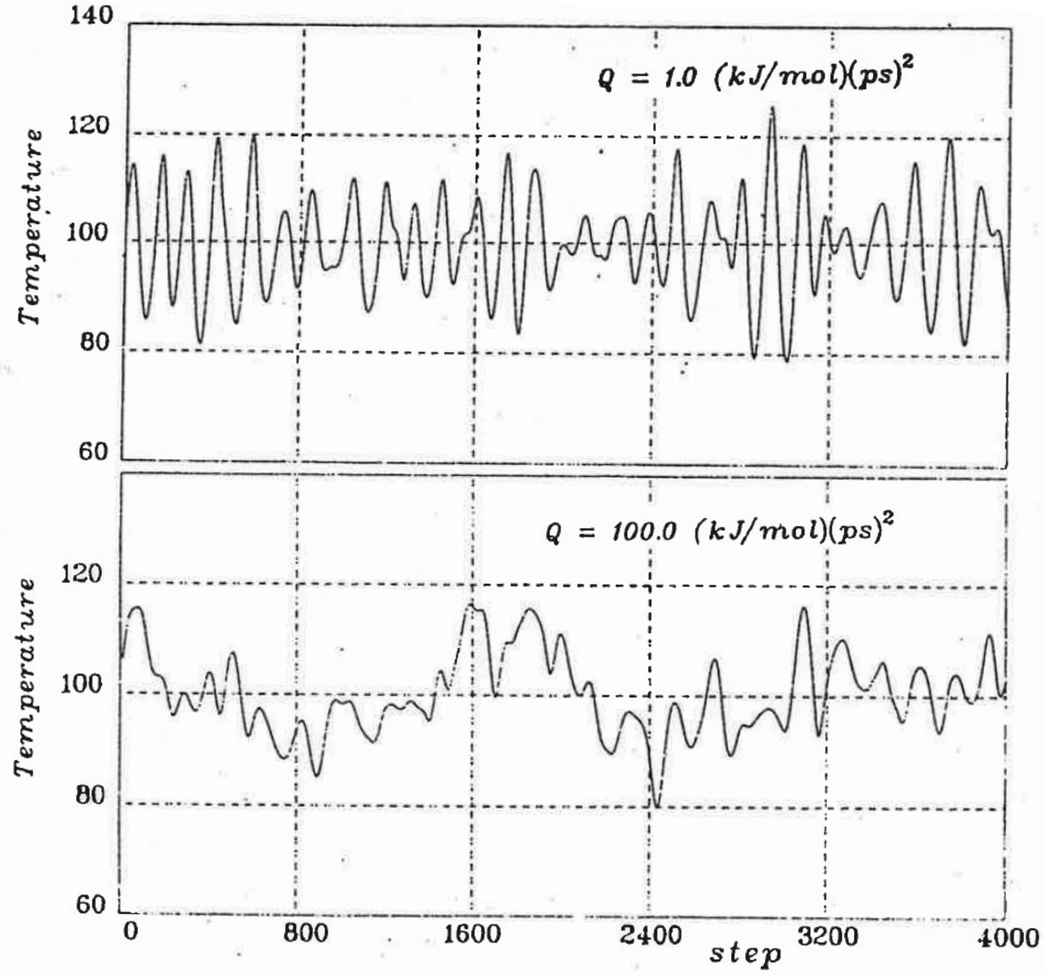
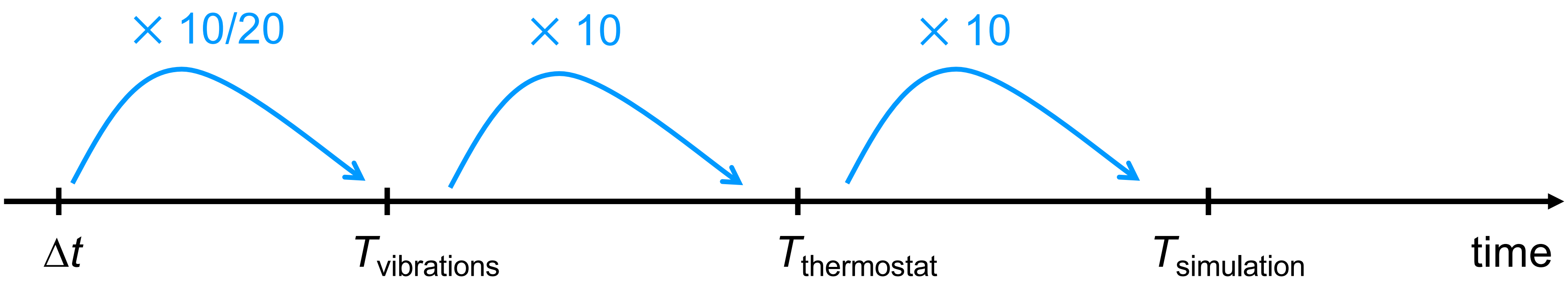


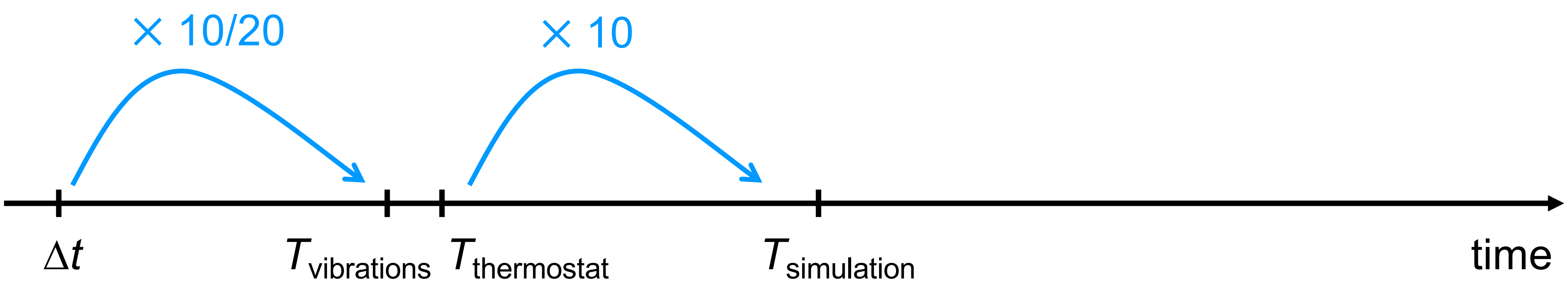
Figure 2. Comparison of the temperature fluctuations in runs with different Q values at 100 K. Above: $Q=1$ (kJ mol^{-1})(ps)^2, Below: $Q=100$ (kJ mol^{-1})(ps)^2. The total real time is about 7 ps.

Setting of inertia parameter Q : choice of time-scales

Ideally

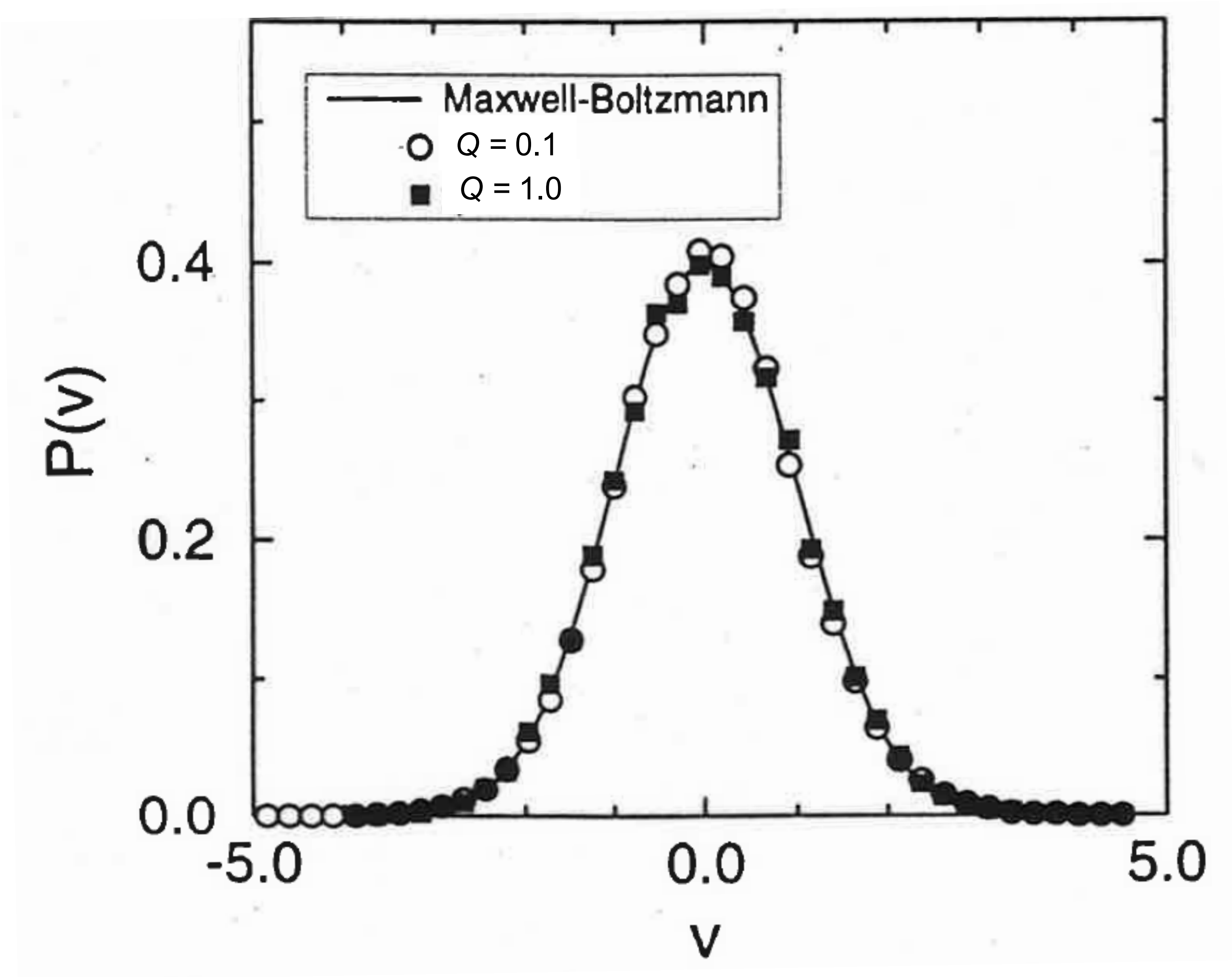


In practice



The trajectories are poorly affected because there is only one auxiliary variable s for $3N$ particles: $3N \gg 1$.

Distribution of velocities for various *Q*



Mean square displacement for various Q

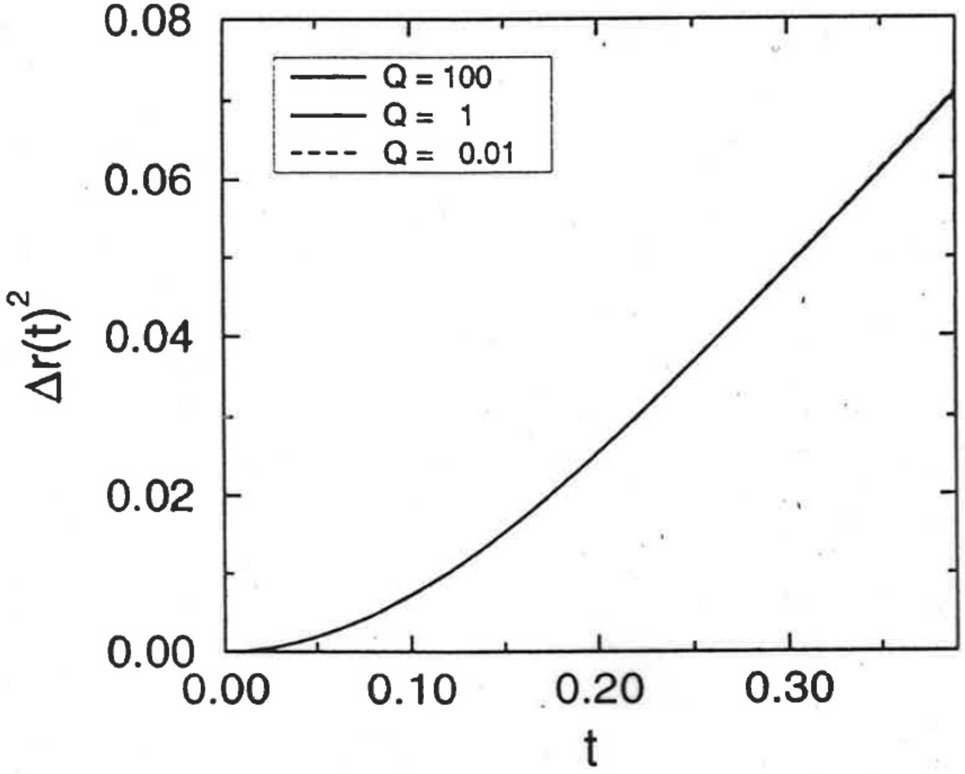


Figure 6.6: Effect of the coupling constant Q on the mean square displacement for a Lennard-Jones fluid ($T = 1.0$, $\rho = 0.75$, and $N = 256$).

Conclusive remarks

- Uniform sampling in real time: $g = 3N$.

- Only static properties like $A(\{p\}, \{r\})$ are correctly sampled.
  This method does not allow one to obtain time-correlations.

- However, when the inertial mass Q is chosen suitably (time-scales),
  the trajectories are poorly affected because there is only one auxiliary variable
  s for $3N$ particles: $3N \gg 1$.

- Caveat: do not use this method to thermalize starting from a fully
  relaxed structure.

Course 06/2

Nosé-Hoover thermostats.

- Real variables vs virtual variables (scaling of time)
- Equations of Nosé-Hoover thermostat
- Setting of inertia parameter Q