Thermostat and Barostat

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Velocity rescaling method

Temperature of the system during the simulation is calculated from the kinetic energy $KE=3/2Nk_BT$

Simplest way to maintain a constant T is to rescale the velocities consistent with the desired temperature

Suppose at time t temperature is T(t) and the velocities are multiplied by a factor λ. Then the change in temperature is

$$\Delta T = \frac{1}{2}\sum_{i=1}^{N}\frac{2}{3}\frac{m_i(\lambda v_i)^2}{Nk_B} - \frac{1}{2}\sum_{i=1}^{N}\frac{2}{3}\frac{m_i v_i^2}{Nk_B}$$

$$= \left(\lambda^2 - 1\right)T(t)$$

$$\lambda = \sqrt{T_{desired}/T(t)}$$

At each time step multiply the velocities by λ. T(t) is calculated from the KE at time t

- ❑ *"equations of motion" are irreversible*
  - ❑"transition probabilities" cannot satisfy detailed balance
- ❑ *does not sample any well-defined ensemble*

Berendsen Temperature coupling

JCP, 81, 3684 (1984)

Berendsen algorithm mimics weak coupling to a an external heat bath at constant temperature T_0 . Such a coupling can be accomplished by inserting a stochastic and friction term in equation of motion

$$m_i \dot{v}_i = F_i - m_i \gamma_i v_i + R(t)$$

Where γ_i is damping constant which determine the strength of the coupling with the heat bath. For time being consider $\gamma_i = \gamma$ (friction constant equal for all particles). R(t) is a Gaussian stochastic variable satisfying following relation

$$< R_i(t) R_j(t+\tau) >= 2 m_i \gamma_i k T \delta(\tau) \delta_{ij}$$

Time dependence of the total kinetic energy is given by

$$\frac{dE_k}{dt} = \lim_{\Delta t \to 0} [\{ \sum_{i=1}^{3N} \frac{1}{2} m_i v^2{}_i (t + \Delta t) - \sum_{i=1}^{3N} \frac{1}{2} m_i v^2{}_i (t) \} / \Delta t]$$

N is the number of particles

$$\Delta v_i = v_i(t+\Delta t) - v_i(t)$$

$$= \frac{1}{m_i} \int_t^{t+\Delta t} [F_i(t') - m_i \gamma v_i(t') + R_i(t')] dt$$

Since R is Gaussian noise

$$\sum_{i=1}^{3N} \int_t^{t+\Delta t} dt' \int_t^{t+\Delta t} dt'' R_i(t') R_i(t'') = 6 N m \gamma k T_0 \Delta t$$

Also note that $R_i(t)$ is uncorrelated with velocities and systematic force F_i

JCP, 81, 3684 (1984)

So we have

$$\frac{dE_k}{dt} = \sum_{i=1}^{3N} v_i F_i + 2\gamma\left(\frac{3N}{2}kT_0 - E_k\right)$$

Home work

You can recognize the first term: it is just equal minus the time derivative of potential energy and so would be unaltered in the absence of thermostat. Second term can be identified with the temperature change due to the coupling to the heat bath and we can associate this with time dependence of the system temperature

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

Time constant for the coupling τ_T is equal to $(2\gamma)^{-1}$

So the temperature deviation decays exponentially with time with time constant τ_T and the equation of motion can be written as

$$m_i \dot{v}_i = F_i - m_i \gamma \left(\frac{T_0}{T} - 1 \right) v_i$$

From the above equation we have

$$\frac{dE_k}{dt} = \sum_i m_i v_i \dot{v}_i = \sum_{i=1}^{3N} v_i F_i + 3N\gamma k \left(T_0 - T \right)$$

This is equivalent to the original stochastic equation

So the temperature is controlled by scaling the velocities of the particle as each time step with a time dependent constant given by

$$\lambda = 1 + \frac{\Delta t}{2\tau_T}\left(\frac{T_0}{T} - 1\right)$$

Remember the leap-frog integrator $\mathbf{v}(t+\tfrac{1}{2}\delta t) = \mathbf{v}(t-\tfrac{1}{2}\delta t) + \tfrac{1}{m}\mathbf{F}(t)\delta t$

We can impose similar condition on temperature

$$T(t+\tfrac{1}{2}\delta t) = T(t-\tfrac{1}{2}\delta t) + 2\gamma\delta t[T_0 - T(t-\tfrac{1}{2}\delta t)]$$

more general expression

$$\lambda = \left[1 + \frac{\Delta t}{\tau_T}\left(\frac{T_0}{T} - 1\right)\right]^{1/2}$$

Home work

If τ_T is large, then the coupling will be weak. If τ_T is small, the coupling will be strong and when the coupling parameter equal to integration time step ($\tau_T = \delta t$) then this algorithm is equivalent to simple velocity rescaling method. A good value is 0.5 –1 ps when δt = 1 fs.

Advantage:

- Strength of the coupling can be varied and adapted to the use requirement
- Very easy to code
- Very efficient to bring the system to a desired temperature.

Disadvantage:

Does not represent a true canonical ensemble. Velocity rescaling artificially prolongs any temperature difference among components of the system, which can lead to the phenomena of ‘hot solvent’ and ‘cold solute’, even though the temperature of the system is at its desired value. This can be avoided by having separate temperature coupling to the solute and solvent, but this leads to the unequal distribution of energy among various components.

Solution: Extended system method, like Nose-Hoover thermostat

For pair wise interaction the energy of the system of N particles is given by

$$E = \sum \frac{p^2}{2m} + \sum_{ij} v(r_{ij})$$

Partition function is given by

$$Q_N = \frac{1}{N!}\left[\frac{1}{h^{3N}}\int d^{3N}r \int d^{3N}p \exp\left(-\beta \sum \frac{p_i^2}{2m}\right) \exp\left[-\beta \sum v(r_{ij})\right]\right]$$

The momentum integral can easily be carried out

$$\int_{-\infty}^{\infty} dp_x e^{-\beta p_x^2/2m} = \left(2mkT\right)^{1/2} \int_{-\infty}^{\infty} e^{-s^2} ds = \sqrt{2\pi mkT}$$

So the partition function becomes

$$Q_N = \frac{1}{N!}\left[V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]^N \frac{1}{V^N}\int d^{3N}r \exp\left[-\beta\sum v(r_{ij})\right]$$

$$= \frac{1}{N!}\left[V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]^N \frac{1}{V^N}\int d^{3N}r \prod_{pairs}(1+f(r_{ij})) \qquad f(r) = e^{-\beta v(r)} - 1$$

Also called Mayer function

The Free energy can be written as

$$F = -k_B T \ln Q_N = -NkT \ln V - \frac{3NkT}{2}\ln\frac{2\pi mkT}{h^2} + N\ln N - N$$

$$-kT\ln\frac{1}{V^N}\int d^{3N}r \prod_{pairs}(1+f_{ij})$$

Thermodynamically pressure is defined as

$$P = kT\left(\frac{\partial \ln Q_N}{\partial V}\right)_T = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$\begin{aligned} P &= -\left(\frac{\partial F}{\partial V}\right)_T = \frac{NkT}{V} + kT\,\frac{\partial}{\partial V}\ln\frac{1}{V^N}\int d^{3N}r \prod_{pairs}(1+f_{ij}) \\ &= \frac{NkT}{V}\left[1+\frac{V}{N}\frac{\partial}{\partial V}\ln\frac{1}{V^N}\int d^{3N}r \prod_{pairs}(1+f_{ij})\right] \\ &= \frac{NkT}{V}\left[1+V\,\frac{\partial \overline{F}}{\partial V}\right] \end{aligned}$$

where

$$\overline{F} = \frac{1}{N}\ln\frac{1}{V^N}\int d^{3N}r \prod_{pairs}(1+f_{ij})$$

In general we can not evaluate the above expression exactly for any $v(r_{ij})$. If we assume $v(r_{ij})$ is small and so is $f(r_{ij})$. Then we can simply the above equation keeping only first order terms

$$\overline{F} = \frac{1}{N}\ln\frac{1}{V^N}\int d^{3N}r \prod_{pairs}(1+f_{ij})$$

$$= \frac{1}{N}\ln\frac{1}{V^N}\left[V^N + \frac{N(N-1)V^{N-1}}{2}\int f(r)d^3r\right]$$

$$= \frac{1}{N}\ln\left[1+\frac{N^2}{2V}\int f(r)d^3r\right] \qquad N(N-1)/2 = N^2/2$$

Taking derivative and keeping first order term we have

$$\frac{\partial\overline{F}}{\partial V} = -\left[\frac{N}{2V^2}\int f(r)d^3r\right]$$

Virial equation

$$\frac{PV}{NkT} = 1 - \frac{N}{2V}\int f(r)d^3r$$

Equipartition and virial theorem

We want to compute the expectation value of $x_i \frac{\partial H}{\partial x_j}$ In the canonical ensemble it is given by

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{\int \left(x_i \frac{\partial H}{\partial x_j} \right) e^{-\beta H} dw}{\int e^{-\beta H} dw}$$

Integrate by parts over x_j (the numerator only)

$$\int \left[-\frac{1}{\beta} x_i e^{-\beta H} \; | + \frac{1}{\beta} \int \left(\frac{\partial x_i}{\partial x_j} \right) e^{-\beta H} dx_j \right] dw_{(j)}$$

First part vanishes because whenever any of the coordinates takes an extreme value the Hamiltonian of the system becomes infinite.

Second term becomes

$$\frac{1}{\beta}\delta_{ij}\int e^{-\beta H}\,dw$$

So the expectation value becomes

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \delta_{ij} kT$$

This gives

$$\left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle \equiv \left\langle p_i \dot{q}_i \right\rangle = kT$$

$$\left\langle q_i \frac{\partial H}{\partial q_i} \right\rangle \equiv -\left\langle q_i \dot{p}_i \right\rangle = kT$$

Summing over all i from i=1.. 3N

$$\left\langle \sum_i p_i \frac{\partial H}{\partial p_i} \right\rangle \equiv \left\langle \sum_i p_i \dot{q}_i \right\rangle = 3NkT$$

$$\left\langle \sum_i q_i \frac{\partial H}{\partial q_i} \right\rangle \equiv -\left\langle \sum_i q_i \dot{p}_i \right\rangle = 3NkT$$

Virial theorem states that

$$W = \left\langle \sum_i q_i \dot{p}_i \right\rangle = -3NkT$$

Virial has two component: one from the external forces W^{ext} (like the pressure exerted by the wall of the container) and W^{int} arising from the forces between the particles.

$$W^{ext} = \left\langle \sum_i q_i F_i \right\rangle = -P \oint_s r.dS = -P \int_V (div\, r) dV = -3PV$$

So we have virial equation

$$\begin{aligned} PV &= NkT + \frac{1}{3}\left\langle W^{\text{int}} \right\rangle \\ &= NkT - \frac{1}{3}\left\langle \sum_{i=1}^{N} r_i \cdot \nabla_i U(r^N) \right\rangle \end{aligned}$$

More details Allen and Tildesley , section 2.4

Computation of the pressure for the rigid molecules

The thermodynamic definition of the pressure

$$P = k_B T \left(\frac{\partial \ln Q_N}{\partial V} \right)_T$$

In order to derive the molecular expression for the pressure we explicit the volume dependence of the configurational integral by introducing dimensionless positional variable s_i, defined as

$$\mathbf{r}_i = V^{\frac{1}{3}} \mathbf{s}_i \qquad \text{for i = 1, … N}$$

In terms of this new variable the partition function becomes

$$Q_N = \frac{V^N}{N!} \int d\mathbf{s}^N d\omega^N \exp(-U(\{\mathbf{s}, \omega\}^N)/k_B T)$$

We have the pressure expression given by

$$\begin{aligned} P &= \frac{Nk_BT}{V} - \frac{V^N}{Z_N}\int d\mathbf{s}^N d\omega^N \frac{\partial U(\{\mathbf{s},\omega\}^N)}{\partial V} \exp -U(\{\mathbf{s},\omega\}^N)/k_BT \\ &= \frac{Nk_BT}{V} - \left\langle \frac{\partial U(\{\mathbf{r},\omega\}^N)}{\partial V} \right\rangle \end{aligned}$$

Constant pressure simulation (NPT ensemble)

Pressure during the simulation can be computed from the virial. For a pairwise additive interactions

$$P = \rho k_B T + \frac{1}{dV}\left\langle \sum_{i<j} f(r_{ij}).r_{ij} \right\rangle$$

Constant pressure simulation (NPT ensemble)

Easiest way to maintain constant pressure is by changing the volume of the simulation cell. The volume fluctuation is related to the isothermal compressibility

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

In the same way as the temperature coupling, the system can be coupled to pressure path to control the pressure of the system: at each time step both the coordinates and box size will be rescaled. To achieve this an extra term is added to the equation of motion

$$\frac{dP}{dt} = \frac{P_0 - P}{\tau_P}$$

Pressure can be computed as

$$P = \frac{2}{3V}\left(E_k - \Xi\right)$$ where $\Xi = -\frac{1}{2}\sum_{i<j} r_{ij} . F_{ij}$ is the internal virial

The pressure change is related to the isothermal compressibility β as follows:

$$\frac{dP}{dt}=-\frac{1}{\beta V}\frac{dV}{dt}=-\frac{3\alpha}{\beta}$$

With α given by

$$\alpha=-\beta\left(P_0-P\right)/3\tau_P$$

So the modified equation of motion is given by

$$\dot{x}=v-\frac{\beta\left(P_0-P\right)}{3\tau_P}x=\mu x$$

With μ given by

$$\mu=1-\frac{\beta\Delta t}{3\tau_P}\left(P_0-P\right)$$

So at each time step x is scaled by μx and length of the simulation box is scaled by μl

The Update algorithm

Given

Positions *r* of all the atoms at time *t*

Velocities v of all atoms at time t-dt/2

Accelerations F/m on all atoms at time t

Total kinetic energy and virial

⇓

1. Compute the scaling factors $\lambda$and μ

⇓

2. Update and scale velocities: $v' = \lambda(v+adt)$

⇓

3. Compute new unconstrained coordinates: $r'=r+v'dt$

⇓

4. Scale coordinates and box: $r = \mu r'$ and $b = \mu b$

Pressure fluctuations

$$< \Delta P^2 > = -kT \frac{\partial P}{\partial V} = kT/(\beta V)$$

So $$< \Delta P > = \sqrt{1/\beta}$$

For water β= 44.6x10^{-6}/bar

Andersen Thermostat

Frenkel and Smit
Chapter 6

- Each molecule undergoes impulsive "collisions" with a heat bath at random intervals
- Between collisions the system evloves at constant energy
- Collision frequency ν describes strength of coupling
  - Probability of collision over time dt is ν dt
  - Poisson process governs collisions $P(t;\nu) = \nu e^{-\nu t}$

➢Start with an initial set of *{r,p}* and integrate the equations of motion.

➢A number of particles are selected to undergo a collision with heat bath. The probability that a particle is selected in a time step of length δt is $\nu\delta t$

➢ If particle *i* has been selected to undergo a collision, its new velocity will be drawn from MB distribution corresponding to desired T. All other particles are unaffected.

Algorithm 15 (Equations of Motion: Andersen Thermostat)

```
   subroutine integrate(switch,f            integrate equations of motion:
+                      ,en,temp)            with Andersen thermostat
   if (switch.eq.1) then                    first step velocity Verlet
      do i=1,npart
         x(i)=x(i)+dt*v(i)+                 update positions current time
+           dt*dt*f(i)/2
         v(i)=v(i)+dt*f(i)/2                first update velocity
      enddo
   else if (switch.eq.2) then               second step velocity Verlet
      tempa=0
      do i=1,npart
         v(i)=v(i)+dt*f(i)/2                second update velocity
         tempa=tempa+v(i)**2
      enddo
      tempa=tempa/(s*npart)                 instantaneous temperature
      sigma=sqrt(temp)                      Andersen heat bath
      do i=1,npart
        if (ranf().lt.nu*dt) then           test for collision with bath
           v(i)=gauss(sigma)                give particle Gaussian velocity
        endif
      enddo
   endif
   return
   end
```

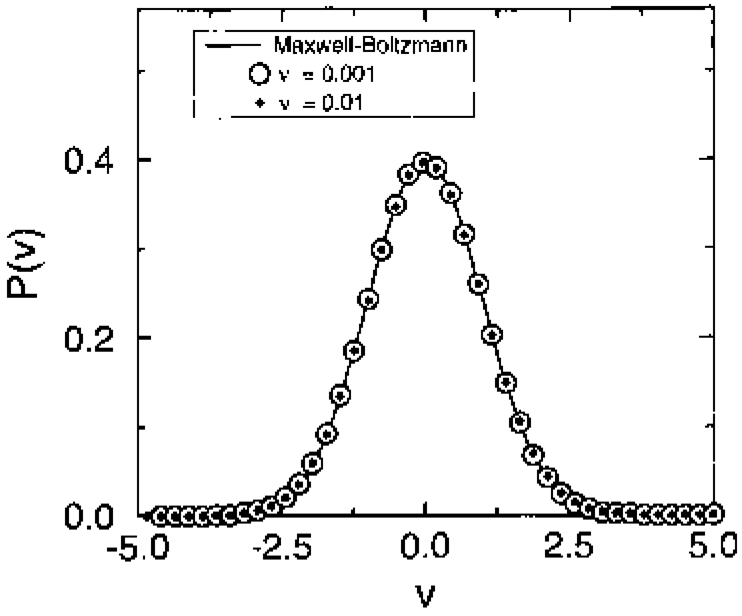


Figure 6.1: Velocity distribution in a Lennard-Jones fluid ($T = 2.0$, $\rho = 0.8442$, and $N = 108$). The solid line is the Maxwell-Boltzmann distribution (6.1.1), and the symbols are from a simulation using $\nu = 0.01$ and $\nu = 0.001$ as collision rates.

Nose-Hoover thermostat

In the extended ensemble approach the system Hamiltonian is extended by introducing a thermal reservoir and a friction term in the equation of motion. The friction force is proportional to the product of each particle velocity and a friction parameter ξ. The friction parameter is a fully dynamic quantity with its own equation of motion; the time derivative is calculated from the difference between the current and reference temperature

$$\frac{d^2 r_i}{dt^2} = \frac{F_i}{m_i} - \xi \frac{dr_i}{dt}$$

- *introduce a new degree of freedom,* s, *representing reservoir*
- *associate kinetic and potential energy with* s

$$U_s = -gkT \ln s$$

$$K_s = \tfrac{1}{2} Q \dot{s}^2$$

effective mass

$$L_{Nose} = \sum_{i=1}^{N} \frac{m_i (s \dot{\mathbf{r}}_i)^2}{2} - U(\mathbf{r}^N) + \frac{Q}{2} \dot{s}^2 - gkT \ln s$$

- *Momenta*

$$\mathbf{p}_i \equiv \frac{\partial L}{\partial \dot{\mathbf{r}}_i} = m_i s^2 \dot{\mathbf{r}}_i$$

$$p_s \equiv \frac{\partial L}{\partial s} = Q \dot{s}$$

Frenkel and Smit
Chapter 6

Extended-Lagrangian Formulation

To construct isothermal Molecular Dynamics, Nosé introduced an additional coordinate s in the Lagrangian of a classical N-body system:

$$\mathcal{L}_{\text{Nose}} = \sum_{i=1}^{N} \frac{m_i}{2} s^2 \dot{\mathbf{r}}_i^2 - \mathcal{U}(\mathbf{r}^N) + \frac{Q}{2}\dot{s}^2 - \frac{L}{\beta}\ln s, \tag{6.1.3}$$

where L is a parameter that will be fixed later. Q is an effective "mass" associated to s. The momenta conjugate to $\mathbf{r}_i$ and s follow directly from equation (6.1.3):

$$\mathbf{p}_i \equiv \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_i} = m_i s^2 \dot{\mathbf{r}}_i \tag{6.1.4}$$

$$p_s \equiv \frac{\partial \mathcal{L}}{\partial \dot{s}} = Q\dot{s}. \tag{6.1.5}$$

This gives for the Hamiltonian of the extended system of the N particles plus additional coordinate s:

$$\mathcal{H}_{\text{Nose}} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i s^2} + \mathcal{U}(\mathbf{r}^N) + \frac{p_s^2}{2Q} + L\frac{\ln s}{\beta}. \tag{6.1.6}$$

We consider a system containing N atoms. The extended system generates a microcanonical ensemble of $6N + 2$ degrees of freedom. The partition function of this ensemble[1] is

$$\begin{aligned} Q_{\mathrm{Nose}} &= \frac{1}{N!}\int dp_s\, ds\, d\mathbf{p}^N d\mathbf{r}^N \delta\left(E - \mathcal{H}_{\mathrm{Nose}}\right) \\ &= \frac{1}{N!}\int dp_s\, ds\, d\mathbf{p}'^N d\mathbf{r}^N s^{3N} \\ &\quad \times \delta\left[\sum_{i=1}^{N} \frac{\mathbf{p}'^2_i}{2m_i} + \mathcal{U}(\mathbf{r}^N) + \frac{p_s^2}{2Q} + \frac{L}{\beta}\ln s - E\right], \end{aligned} \tag{6.1.7}$$

in which we have introduced

$$\mathbf{p}' = p/s.$$

Let us define

$$\mathcal{H}(\mathbf{p}', \mathbf{r}) = \sum_{i=1}^{N} \frac{\mathbf{p}'^2_i}{2m_i} + \mathcal{U}(\mathbf{r}^N). \tag{6.1.8}$$

$$
\begin{aligned}
Q_{\text{Nose}} &= \frac{1}{N!}\int dp_s\, d\mathbf{p}'^N d\mathbf{r}^N ds\ \frac{\beta s^{3N+1}}{L} \\
&\quad \times\delta\left\{s-\exp\left[-\beta\frac{\mathcal{H}(\mathbf{p}',\mathbf{r})+p_s^2/(2Q)-E}{L}\right]\right\} \\
&= \frac{1}{N!}\frac{\beta\exp[E(3N+1)/L]}{L}\int dp_s\ \exp\left[-\beta\frac{3N+1}{L}p_s^2/(2Q)\right] \\
&\quad \times\int d\mathbf{p}'^N d\mathbf{r}^N\ \exp\left[-\beta\frac{3N+1}{L}\mathcal{H}(\mathbf{p}',\mathbf{r})\right] \\
&= C\frac{1}{N!}\int d\mathbf{p}'^N d\mathbf{r}^N\ \exp\left[-\beta\frac{3N+1}{L}\mathcal{H}(\mathbf{p}',\mathbf{r})\right]. \qquad (6.1.9)
\end{aligned}
$$

If we perform a simulation in this extended ensemble, the average of a quantity that depends on $\mathbf{p}', \mathbf{r}$ is given by

$$
\bar{A} = \lim_{\tau\to\infty}\frac{1}{\tau}\int_0^\tau dt\ A(\mathbf{p}(t)/s(t), \mathbf{r}(t)) \equiv \langle A(\mathbf{p}/s, \mathbf{r})\rangle_{\text{Nose}}. \qquad (6.1.10)
$$

From the Hamiltonian (6.1.6), we can derive the equations of motion for the virtual variables **p**, **r**, and t:

$$\begin{aligned}
\frac{d\mathbf{r}_i}{dt} &= \frac{\partial \mathcal{H}_{\text{Nose}}}{\partial \mathbf{p}_i} = \mathbf{p}_i/(m_i s^2) \\
\frac{d\mathbf{p}_i}{dt} &= -\frac{\partial \mathcal{H}_{\text{Nose}}}{\partial \mathbf{r}_i} = -\frac{\partial \mathcal{U}(\mathbf{r}^N)}{\partial \mathbf{r}_i} \\
\frac{ds}{dt} &= \frac{\partial \mathcal{H}_{\text{Nose}}}{\partial p_s} = p_s/Q \\
\frac{dp_s}{dt} &= -\frac{\partial \mathcal{H}_{\text{Nose}}}{\partial s} = \left(\sum_i p_i^2/(m_i s^2) - \frac{L}{\beta}\right)/s.
\end{aligned}$$

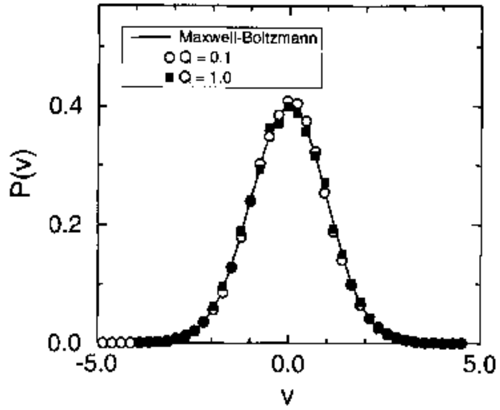


Figure 6.4: Velocity distribution in a Lennard-Jones fluid (T = 1.0, ρ = 0.75, and N = 256). The solid line is the Maxwell-Boltzmann distribution (6.1.1) the symbols were obtained in a simulation using the Nosé-Hoover thermostat.

Nosé Thermostat 2.

- Extended-system Hamiltonian is conserved

$$H_{Nose} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i s^2} - U(\mathbf{r}^N) + \frac{p_s^2}{2Q} - gkT \ln s$$

- Thus the probability distribution can be written

$$\pi(\mathbf{r}^N, \mathbf{p}^N, s, p_s) = \frac{\delta(H_{Nose} - E_{Nose})}{Q_{Nose}}$$

  - it can be shown that the molecular positions and momenta follow a canonical (NVT) distribution if g = 3N+1
- s can be interpreted as a time-scaling factor
  - $t_{true} = t_{sim}/s$
  - since *s* varies during the simulation, each “true” time step is of varying length

Nosé-Hoover Thermostat 1.

○ Advantageous to work with non-fluctuating time step

- Scaled-variables equations of motion
  - constant simulation Δt
  - fluctuating real Δt

$$\dot{\mathbf{r}}_i = \frac{\partial H}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m_i s^2}$$

$$\dot{\mathbf{p}}_i = -\frac{\partial H}{\partial \mathbf{r}_i} = \mathbf{F}_i$$

$$\dot{s} = \frac{\partial H}{\partial p_s} = \frac{p_s}{Q}$$

$$\dot{p}_s = -\frac{\partial H}{\partial s} = \frac{1}{s}\left(\sum_{i=1}^{N} \frac{p_i}{m_i s^2} - gkT\right)$$

- Real-variables equation of motion

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

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \frac{s p_s}{Q}\mathbf{p}_i$$

$$\frac{\dot{s}}{s} = \frac{s p_s}{Q}$$

$$\frac{\partial (s p_s / Q)}{\partial t} = \frac{1}{Q}\left(\sum_{i=1}^{N} \frac{p_i}{m_i} - gkT\right)$$

Nosé-Hoover Thermostat 2.

- Real-variable equations are of the form

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

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \xi \mathbf{p}_i$$

$$\frac{\dot{s}}{s} = \xi$$

(redundant; s is not present in other equations)

$$\dot{\xi} = \frac{1}{Q}\left(\sum_{i=1}^{N} \frac{p_i}{m_i} - gkT\right)$$

- Compare to isokinetic equations

$$\dot{\mathbf{r}}_i = \mathbf{p}_i / m$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \lambda \mathbf{p}$$

$$\lambda = \frac{\sum \frac{1}{m_i} \mathbf{p}_i \cdot \mathbf{F}_i}{\sum \frac{1}{m_i} \mathbf{p}_i \cdot \mathbf{p}_i}$$

- Difference is in the treatment of the friction coefficient
  - Nosé-Hoover correctly samples NVT ensemble for both momentum and configurations; isokinetic does NVT properly only for configurations

Nosé-Hoover Thermostat 3.

- Equations of motion

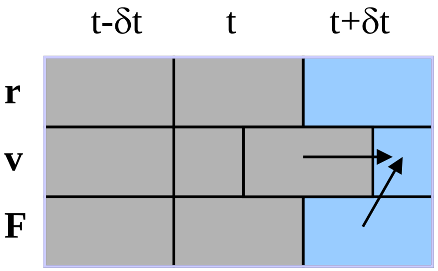
$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \xi \mathbf{p}_i$$

$$\frac{\dot{s}}{s} = \xi$$

$$\dot{\xi} = \frac{1}{Q}\left(\sum_{i=1}^{N} \frac{p_i}{m_i} - gkT\right)$$

- Integration schemes
  - Verlet algorithm is feasible, but tricky to implement



At this step, update of ξ depends on p; update of p depends on ξ

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \xi \mathbf{p}_i$$

$$\dot{\xi} = \frac{1}{Q}\left(\sum_{i=1}^{N} \frac{p_i}{m_i} - gkT\right)$$