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

$$\Delta T = \frac{1}{2} \sum_{i=1}^{N} \frac{2}{3} \frac{m_i (\lambda v_i)^2}{Nk_B} - \frac{1}{2} \sum_{i=1}^{N} \frac{2}{3} \frac{m_i v_i^2}{Nk_B}$$
$$= \left(\lambda^2 - 1\right) T(t)$$
$$\lambda = \sqrt{T_{desired}} / T(t) \qquad \square "equations of the second second$$

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

$$\langle R_i(t)R_j(t+\tau)\rangle = 2m_i\gamma_ikT_0\delta(\tau)\delta_{ij}.$$

Time dependence of the total kinetic energy is given by $\frac{dE_k}{dt} = \lim_{\Delta t \to 0} \left[\left\{ \sum_{i=1}^{3N} \frac{1}{2} m_i v_i^2(t + \Delta t) - \sum_{i=1}^{3N} \frac{1}{2} m_i v_i^2(t) \right\} / \Delta t \right]$

N is the number of particles

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

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

Using the fact that $R_i(t')$ is uncorrelated with $v_i(t)$ and $R_i(t)$ for t' > t and using the relation [from Eq. (2)]

$$\sum_{i=1}^{3N}\int_{t}^{t+\Delta t}dt'\int_{t}^{t+\Delta t}dt'' R_{i}(t')R_{i}(t'')=6Nm\gamma kT_{0}\Delta t,$$

JCP, 81, 3684 (1984)

So we have

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

You can recognize the first term: it is just equal minus the time derivative of potential energy. Second term is 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

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

more general expression

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

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 $\delta t = 1$ 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

$$\int_{-\infty}^{\infty} dp_{\chi} e^{-\beta p_{\chi}^2/2m} = (2mkT)^{1/2} \int_{-\infty}^{\infty} e^{-s^2} ds = \sqrt{2\pi mkT}$$

So the partition function becomes

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

The Free energy can be written as

$$F = -k_B T \ln Q_N = -NkT \ln V - \frac{3NkT}{2} \ln \frac{2\pi mkT}{h^2} + N \ln N - N$$
$$-kT \ln \frac{1}{V^N} \frac{1}{V^N} \int d^{3N} r \prod_{pairs} (1+f_{ij})$$

Thermodynamically pressure is defined as

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

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

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

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

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

Taking derivative and keeping first order term we have

$$\frac{\partial \overline{F}}{\partial V} = -\left[\frac{N}{2V^2} \int f(r) d^3 r\right] \qquad \text{Virial equation} \qquad \frac{PV}{NkT} = 1 - \frac{N}{2V} \int f(r) d^3 r$$

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_i (the numerator only)

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

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.

$$W^{ext} = \left\langle \sum_{i} q_{i} F_{i} \right\rangle = -P \oint r.dS = -P \oint (div r) dV = -3PV$$

So we have virial equation

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

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

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

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

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

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

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

With μ given by

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/2Accelerations F/m on all atoms at time t Total kinetic energy and virial 1. Compute the scaling factors λ and μ 2. Update and scale velocities: $v' = \lambda(v+adt)$ 3. Compute new unconstrained coordinates: r'=r+v'dt4. 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 $\beta = 44.6 \times 10^{-6}$ /bar

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 d^2r , F, dr.

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

•*introduce a new degree of freedom, s, representing reservoir*

•associate kinetic and potential energy with s $U_{s} = -g$ $L_{Nose} = \sum_{i=1}^{N} \frac{m_{i}(s\dot{\mathbf{r}}_{i})^{2}}{2} - U(\mathbf{r}^{N}) + \frac{Q}{2}\dot{s}^{2} - gkT\ln s$ $K_{s} = \frac{1}{2}Q$

 $U_{s} = -gkT \ln s$ $K_{s} = \frac{1}{2}Q\dot{s}^{2}$ effective

mass

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

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

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.

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

m

$$\dot{\mathbf{p}}_{i} = \mathbf{F}_{i} - \frac{sp_{s}}{Q}\mathbf{p}_{i}$$
$$\frac{\dot{s}}{s} = \frac{sp_{s}}{Q}$$
$$\frac{\partial(sp_{s}/Q)}{\partial t} = \frac{1}{Q} \left(\sum_{i=1}^{N} \frac{p_{i}}{m_{i}} - gkT\right)$$

Nosé-Hoover Thermostat 2.

• Real-variable equations are of the form

 $\dot{\mathbf{r}}_{i} = \frac{\mathbf{p}_{i}}{m_{i}}$ $\dot{\mathbf{p}}_{i} = \mathbf{F}_{i} - \xi \mathbf{p}_{i}$ $\frac{\dot{s}}{s} = \xi \qquad (redundant; s \text{ is not present in other equations})$ $\dot{\xi} = \frac{1}{Q} \left(\sum_{i=1}^{N} \frac{p_{i}}{m_{i}} - gkT \right)$ Compare to isokinetic equations

$$\dot{\mathbf{r}}_{i} = \mathbf{p}_{i} / m \qquad \lambda = \frac{\sum \frac{1}{m_{i}} \mathbf{p}_{i} \cdot \mathbf{F}_{i}}{\sum \frac{1}{m_{i}} \mathbf{p}_{i} \cdot \mathbf{p}_{i}}$$

- 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

