Introduction to Molecular Dynamics III

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18 MD simulation at constant temperature.

Notice that at equilibrium, the distribution of the velocity is,

$$(\mathbf{v}_1, \cdots, \mathbf{v}_N) \sim \frac{1}{Z} e^{-\beta \sum \frac{m_i \mathbf{v}_i^2}{2}}.$$

The Andersen's method.

1. Using the Verlet's method, integrate the system for one step.
2. Pick one atom randomly
3. Change its velocity to a random number drawn from the normal distribution.

19 Noŝe-Hoover thermostat

Extended Hamiltonian,

$$H_{\rm New}(\mathbf{q},\mathbf{p}) = \sum \frac{\mathbf{p}_i^2}{2s^2 m_i} + V(\mathbf{q}) + \frac{p_s^2}{Q} + g k_B T \ln s.$$

Virtual Variables:

1. $q' = q$
2. $p' = p/s$
3. $s' = s$
4. $p_s' = p_s/s$.

Canonical ensemble

The partition function,

$$
\begin{aligned}
Z &= \ln \int \delta(E - H_{New}) d\mathbf{q} d\mathbf{p} ds dp_s. \\
&= \ln \int s^{3N} \delta\Big(E - (\frac{\mathbf{p}_i'^2}{2m_i} + V(\mathbf{q}) + \frac{p_s^2}{Q} + g k_B T \ln s)\Big) d\mathbf{q}\mathbf{p}' ds dp_s. \\
&= \ln C \int e^{-\beta \frac{3N+1}{g} H(\mathbf{q}', \mathbf{p}')} d\mathbf{q}'\mathbf{p}'.
\end{aligned}
$$

For a quantity $A(\mathbf{q}, \mathbf{p})$,

$$
\Big\langle A(\mathbf{q}, \mathbf{p}/s) \Big\rangle_{NVE} = \Big\langle A(\mathbf{q}, \mathbf{p}) \Big\rangle_{NVT}.
$$

Time average

Average on the real time scale,

$$
\begin{aligned}
A &= \lim_{T'\to+\infty}\frac{1}{T'}\int_0^{T'} A(\mathbf{q}(t'),\mathbf{p}(t')/s(t'))dt' \\
&= \frac{\lim_{T\to+\infty}\frac{1}{T}\int_0^{T} A(\mathbf{q}(t),\mathbf{p}(t)/s(t))/s(t)dt}{\lim_{T\to+\infty}\frac{1}{T}\int_0^{T} 1/s(t)dt} \\
&= \frac{\langle A(\mathbf{q},\mathbf{p}/s)\rangle}{\langle 1/s\rangle} \\
&= \langle A(\mathbf{q},\mathbf{p}')\rangle_{NVT}
\end{aligned}
$$

provided that,

$$g = 3N.$$

20 Equation of motion for the virtual variables

$$
\begin{aligned}
\dot{\mathbf{q}}_i &= \mathbf{p}_i/(m_i s^2) \\
\dot{\mathbf{p}}_i &= -\nabla_{\mathbf{q}_i} V \\
\dot{s} &= p_s/Q \\
\dot{p}_s &= \frac{1}{s}\Big(\frac{\mathbf{p}_i^2}{2m_i s^2} - k_B T g\Big).
\end{aligned}
$$

Equation of motion for the real variables

$$\begin{cases} \dot{\mathbf{p}}_i & = & \mathbf{p}_i/m_i \\ \dot{\mathbf{q}}_i & = & -\nabla_{\mathbf{q}_i} V - \xi \mathbf{p}_i \\ \dot{\xi} & = & \frac{g}{Q}(T' - T) \end{cases}$$

1. $-\xi p_i$: damping term.
   - $\xi > 0$: takes away energy
   - $\xi < 0$: input energy
2. T' instantaneous temperature
3. T given temperature

21 Time integrator – Splitting method

Consider an ODE $\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x})$.. Define the Liouville operator,

$$L = \sum_i f_i \nabla_{x_i}.$$

For any function $\varphi(\mathbf{x})$, we have $\dot{\varphi} = L\varphi$. So we write $\varphi(t) = e^{Lt}\varphi(0)$.

For MD,

$$L = L_x + L_v.$$

Operator splitting,

$$e^{tL} \approx e^{L_v \Delta t/2} e^{L_x \Delta t} e^{L_v \Delta t/2}.$$

This is the same as the Verlet's method.

Splitting method for the NH model

For the NH model, we have,

$$L = L_x + L_v + L_{NH}, L_{NH} = \sum_i \xi \mathbf{v}_i \nabla_{\mathbf{v}_i} + \frac{g}{Q}(T' - T)\nabla_\xi.$$

Operator splitting,

$$e^{tL} \approx e^{tL_{NH}} e^{L_v \Delta t/2} e^{L_x \Delta t} e^{L_v \Delta t/2} e^{tL_{NH}}.$$

Further splitting,

$$e^{tL} \approx e^{tL_{NH}} \approx e^{L_1 \Delta t/2} e^{L_2 \Delta t} e^{L_1 \Delta t/2}.$$

where,

$$L_1 = \sum_i \xi \mathbf{v}_i \nabla_{\mathbf{v}_i}, L_2 = \frac{g}{Q}(T' - T)\nabla_\xi.$$