Advanced methods in Simulation

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Molecular dynamics: Symplectic algorithms

Liouville formalism

- In the Gibbs formalism, the phase space distribution is given by an N-particle probability distribution $f^{(N)}(\mathrm{r}^N, \mathrm{p}^N, t)$ (N is the particle number)

  By writing the local conservation of the probability distribution, one obtains

$$\frac{\partial f^{(N)}(\mathrm{r}^N, \mathrm{p}^N, t)}{\partial t} + \sum_{i=1}^{N} \left(\frac{\partial}{\partial \mathrm{r}_i} \left(\frac{d\mathrm{r}_i}{dt} f^{(N)}(\mathrm{r}^N, \mathrm{p}^N, t) \right) + \frac{\partial}{\partial \mathrm{p}_i} \left(\frac{d\mathrm{p}_i}{dt} f^{(N)}(\mathrm{r}^N, \mathrm{p}^N, t) \right) \right) = 0,$$

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- If the dynamics is Hamiltonian

$$\left(\frac{\partial \mathcal{H}_N}{\partial \mathrm{p}_i} \right) = \mathrm{v}_i = \frac{d\mathrm{r}_i}{dt}$$
$$\left(\frac{\partial \mathcal{H}_N}{\partial \mathrm{r}_i} \right) = -\mathrm{f}_i = -\frac{d\mathrm{p}_i}{dt}.$$

Liouville formalism (2)

- $$\frac{\partial}{\partial \mathrm{r}_i}\left(\frac{d\mathrm{r}_i}{dt}\right) = -\frac{\partial}{\partial \mathrm{p}_i}\left(\frac{d\mathrm{p}_i}{dt}\right)$$

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- $$\frac{\partial f^{(N)}(\mathrm{r}^N, \mathrm{p}^N, t)}{\partial t} + \sum_{i=1}^{N}\left(\frac{d\mathrm{r}_i}{dt}\frac{\partial f^{(N)}}{\partial \mathrm{r}_i} + \frac{d\mathrm{p}_i}{dt}\frac{\partial f^{(N)}}{\partial \mathrm{p}_i}\right) = 0,$$

Hamiltonian dynamics

- The time evolution of the distribution probability can be expressed as

$$\frac{\partial f^{(N)}(\mathrm{r}^N, \mathrm{p}^N, t)}{\partial t} - \{\mathcal{H}_N, f^{(N)}\} = 0,$$

where $\mathcal{H}_N$ denotes the Hamiltonian of the system of N particles, and the bracket $\{A, B\}$ corresponds the Poisson bracket.

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- $$\{A, B\} = \sum_{i=1}^{N} \left(\frac{\partial A}{\partial \mathrm{r}_i} \frac{\partial B}{\partial \mathrm{p}_i} - \frac{\partial B}{\partial \mathrm{r}_i} \frac{\partial A}{\partial \mathrm{p}_i} \right)$$

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- $$\mathcal{L} = i\{H_N, \ \} = \sum_{i=1}^{N} \left(\left(\frac{\partial \mathcal{H}_N}{\partial \mathrm{r}_i} \right) \frac{\partial}{\partial \mathrm{p}_i} - \left(\frac{\partial \mathcal{H}_N}{\partial \mathrm{p}_i} \right) \frac{\partial}{\partial \mathrm{r}_i} \right)$$

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$$f^{(N)}(\mathrm{r}^N, \mathrm{p}^N, t) = \exp(-i\mathcal{L}t) f^{(N)}(\mathrm{r}^N, \mathrm{p}^N, 0).$$

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- Similarly, if A is a function of r^N, and p^N, obeys

$$\frac{dA}{dt} = \sum_{i=1}^{N} \left(\frac{\partial A}{\partial \mathrm{r}_i} \frac{d\mathrm{r}_i}{dt} + \frac{\partial A}{\partial \mathrm{p}_i} \frac{d\mathrm{p}_i}{dt} \right).$$

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- $\frac{dA}{dt} = i\mathcal{L}A$, which gives formally

$$A(\mathrm{r}^N(t), \mathrm{p}^N(t)) = \exp(i\mathcal{L}t) A(\mathrm{r}^N(0), \mathrm{p}^N(0))$$

Hamiltonian dynamics

- $$\mathcal{L} = \mathcal{L}_r + \mathcal{L}_p$$

  where

  $$i\mathcal{L}_r = \sum_i \frac{d\mathrm{r}_i}{dt} \frac{\partial}{\partial \mathrm{r}_i}$$

  and

  $$i\mathcal{L}_p = \sum_i \frac{d\mathrm{p}_i}{dt} \frac{\partial}{\partial \mathrm{p}_i}$$

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- Time evolution of $A(t)$ is given by

  $$A(\mathrm{r}(t), \mathrm{p}(t)) = \exp(i\mathcal{L}_r^0 t)A(\mathrm{r}(0), \mathrm{p}(0))$$

Hamiltonian dynamics

- Expanding the exponential, one obtains

$$
\begin{aligned}
A(\mathrm{r}^N(t), \mathrm{p}^N(t)) &= A(\mathrm{r}^N(0), \mathrm{p}^N(0)) + i\mathcal{L}_r^0 A(\mathrm{r}^N(0), \mathrm{p}^N(0)) \\
&\quad + \frac{(i\mathcal{L}_r^0)^2}{2!} A(\mathrm{r}^N(0), \mathrm{p}^N(0)) + \dots \\
&= \sum_{n=0}^{\infty} \sum_i \frac{\left(\frac{d\mathrm{r}_i}{dt}(0)t\right)^n}{n!} \left(\frac{\partial^n}{\partial \mathrm{r}_i^n}\right) A(\mathrm{r}(0), \mathrm{p}(0)) \\
&= A(\mathrm{r}(0) + \frac{d\mathrm{r}_i}{dt}(0)t, \mathrm{p}(0))
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- The solution is a simple translation of spatial coordinates, which corresponds to a galilean motion of particles without interaction, as expected.

Hamiltonian dynamics

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Discretization of the Liouville equation

- $$\exp(\mathcal{L}t) \neq \exp(\mathcal{L}_r t)\exp(\mathcal{L}_p t)$$

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Discretization of the Liouville equation

- $$\exp(\mathcal{L}t) \neq \exp(\mathcal{L}_r t)\exp(\mathcal{L}_p t)$$
- The Trotter identity

$$\exp(B+C) = \left(\exp\left(\frac{B}{2P}\right)\exp\left(\frac{C}{P}\right)\exp\left(\frac{B}{2P}\right)\right)^P \exp\left(\mathcal{O}\left(\frac{1}{P^2}\right)\right)$$

Hamiltonian dynamics

- By introducing $\frac{B}{P} = \frac{i\mathcal{L}_p t}{P}$ and $\frac{C}{P} = \frac{i\mathcal{L}_r t}{P}$, one obtains for a timestep

$$e^{i\mathcal{L}_p \Delta t/2} e^{i\mathcal{L}_r \Delta t} e^{i\mathcal{L}_p \Delta t/2}.$$

- or

$$e^{i\mathcal{L}_r \Delta t/2} e^{i\mathcal{L}_p \Delta t} e^{i\mathcal{L}_r \Delta t/2}.$$

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- Because the operators $\mathcal{L}_r$ and $\mathcal{L}_p$ are hermitian, the exponential operator is unitary, we may derive symplectic algorithms namely algorithms preserving the volume of the phase space.

Hamiltonian dynamics

- $$e^{i\mathcal{L}_p \Delta t/2} A\left(\mathrm{r}^N(0), \mathrm{p}^N(0)\right) = A\left(\mathrm{r}^N(0), \left(\mathrm{p}(0) + \frac{\Delta t}{2}\frac{d\mathrm{p}(0)}{dt}\right)^N\right)$$

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- and lastly, applying $e^{i\mathcal{L}_p \Delta t/2}$, we have

$$A\left(\left(\mathrm{r}(0) + \Delta t \frac{d\mathrm{r}(\frac{\Delta t}{2})}{dt}\right)^N, \left(\mathrm{p}(0) + \frac{\Delta t}{2}\frac{d\mathrm{p}(0)}{dt} + \frac{\Delta t}{2}\frac{d\mathrm{p}(\Delta t)}{dt}\right)^N\right)$$

Hamiltonian dynamics

- In summary, one obtains the global transformations

$$\mathrm{r}(\Delta t) = \mathrm{r}(0) + \Delta t \frac{d\mathrm{r}(\Delta t/2)}{dt}$$

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- By expanding the velocity of half-time at the second order one obtains

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- this is the Velocity-Verlet algorithm.
- The Position-Verlet algorithm is obtained by inverting the operators.

Molecular Dynamics in other ensembles

Andersen algorithm

- The Andersen algorithm: stochastic process which modifies velocities of particles by the presence of instantaneous forces. Between these stochastic "collisions", the system evolves with the usual Newtonian dynamics. The coupling strength is controlled by the collision frequency denoted by ν. In addition, one assumes that the stochastic "collisions" are totally uncorrelated, which leads to a Poissonian distribution of collisions, $P(\nu, t)$

$$P(\nu, t) = e^{-\nu t} \tag{1}$$

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- 1. The system follows Newtonian dynamics over one or several time steps, denoted Δt.
  2. On chooses randomly a number of particles for stochastic collisions. The probability of choosing a particle in a time interval Δt is $\nu \Delta t$.
  3. When a particle is selected, its velocity is chosen randomly in a Maxwellian distribution with a temperature T. Other velocities are not updated.

Molecular Dynamics in other ensembles

Nosé-Hoover algorithm

- One considers the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \frac{(\mathrm{p}_i)^2}{2m_i s^2} + U(\mathrm{r}^N) + \frac{p_s^2}{2Q} + \frac{L}{\beta} \ln(s)$$

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- Let us reexpress the microcanonical partition function of this system made of N interacting particles and of this additional degree of freedom interacting with N particles.

$$Z = \frac{1}{N!} \int dp_s ds d\mathrm{p}^N d\mathrm{r}^N \delta(\mathcal{H} - E)$$

Molecular Dynamics in other ensembles

Nosé-Hoover algorithm (2)

- Let us introduce $\mathrm{p}' = \mathrm{p}/s$.

$$Z = \frac{1}{N!}\int dp_s ds\, s^{3N} d\mathrm{p}'^N d\mathrm{r}^N \delta\left(\sum_{i=1}^{N}\frac{(\mathrm{p}'_i)^2}{2m_i} + U(\mathrm{r}^N) + \frac{p_s^2}{2Q} + \frac{L}{\beta}\ln(s) - E\right)$$

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Nosé-Hoover algorithm (3)

- By using the property

$$\delta(h(s)) = \frac{\delta(s - s_0)}{h'(s_0)}$$

where $h(s)$ is a function crossing only once the x-axis at the value $s = s_0$.

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- Integrating over s

$$\delta(\mathcal{H}' + \frac{p_s^2}{2Q} + \frac{L}{\beta}\ln(s) - E) = \frac{\beta s}{L}\delta(s - \exp(-\frac{\beta}{L}(\mathcal{H}' + \frac{p_s^2}{2Q} - E)))$$

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-

$$Z = \frac{\beta \exp(E(3N+1)/L)}{LN!}\int dp_s d\mathrm{p}'^N d\mathrm{r}^N \exp\left(\frac{-\beta(3N+1)}{L}(\mathcal{H}' + \frac{p_s^2}{2Q})\right)$$

Molecular Dynamics in other ensembles

Nosé-Hoover algorithm (4)

- Setting $L = 3N + 1$, and integrating over p_s, one obtains

$$Z \propto \int d\mathrm{p}'^N d\mathrm{r}^N \exp\left(-\beta \mathcal{H}'\right)$$

Molecular Dynamics in other ensembles

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- It is worth noting that variables used are r, p' and t'. Discretizing the equations of motion would give a variable time step which is not easy to control in Molecular Dynamics. It is possible to return to a constant time step by using additional changes of variable. This work was done by Hoover.

Molecular Dynamics in other ensembles

Nosé-Hoover algorithm (5)

- the equations of motion are

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

$$\dot{\mathrm{p}}_i = -\frac{\partial U(\mathrm{r}^N)}{\partial \mathrm{r}_i} - \xi \mathrm{p}_i$$

$$\dot{\xi} = \left(\sum_{i=1}^{N} \frac{\mathrm{p}_i^2}{2m_i} - \frac{L}{\beta} \right) \frac{1}{Q}$$

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