Introduction to MC and MD methods

"Moving atoms around"

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IAS MOLECULAR AND MATERIALS MODELLING SCHOOL
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Why move atoms around?

- To *sample* the population of configurations accessible to an equilibrium system at non-zero temperature
  - More important for "soft matter" than hard materials.
  - Thermodynamic observables are averaged properties.
- To study *time evolution* of an out-of-equilibrium system toward equilibrium
  - E.g. crystal growth, molecular self-assembly
- To study driven non-equilibrium processes
  - E.g. active matter, crack propagation, radiation damage

Some notation

Concerned with systems of classical particles in three dimensions with Hamiltonian,

$$\mathcal{H}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3 \ldots \mathbf{r}_N) = \mathcal{H}(\mathbf{r}^N)$$

where we have some model *U* for the potential energy of the system.

$$\mathcal{H}(\mathbf{r}^N) = \mathcal{U}(\mathbf{r}^N) + \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} \qquad \beta = 1/k_B T$$

Today we're concerned only with the behaviour of the system in the canonical ensemble.

$$Q = \frac{1}{N! h^{3N}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \mathrm{d}\mathbf{r}^N \mathrm{d}\mathbf{p}^N \exp\left[-\beta \mathcal{H}(\mathbf{r}^N, \mathbf{p}^N)\right]$$

$$Q = \frac{1}{N! h^{3N}} \int_{-\infty}^{\infty} \mathrm{d}\mathbf{p}^N \exp\left[-\beta \sum_{i=1}^{N} \mathbf{p}_i^2 / 2m_i\right] \int_{-\infty}^{\infty} \mathrm{d}\mathbf{r}^N \exp\left[-\beta \mathcal{U}(\mathbf{r}^N)\right]$$

Monte Carlo simulation

Equilibrium and detailed balance

Global balance equation

$$\int P(\mathbf{r}_{new}^N) P(\mathbf{r}_{new}^N \to \mathbf{r}_{old}^N) \, \mathrm{d}\mathbf{r}_{new}^N = \int P(\mathbf{r}_{old}^N) P(\mathbf{r}_{old}^N \to \mathbf{r}_{new}^N) \, \mathrm{d}\mathbf{r}_{new}^N$$

Must be satisfied if *detailed* balance is imposed

$$P(\mathbf{r}_{new}^N) P(\mathbf{r}_{new}^N \to \mathbf{r}_{old}^N) = P(\mathbf{r}_{old}^N) P(\mathbf{r}_{old}^N \to \mathbf{r}_{new}^N)$$

Rearrange

$$P(\mathbf{r}_{old}^N \to \mathbf{r}_{new}^N) = \frac{P(\mathbf{r}_{new}^N)}{P(\mathbf{r}_{old}^N)} P(\mathbf{r}_{new}^N \to \mathbf{r}_{old}^N)$$

Monte Carlo moves

Split probability of moving from old to new coordinates into two parts

$$P(\mathbf{r}_{old}^N \to \mathbf{r}_{new}^N) = P_{att}(\mathbf{r}_{old}^N \to \mathbf{r}_{new}^N) P_{acc}(\mathbf{r}_{old}^N \to \mathbf{r}_{new}^N)$$

i.e. probability of *attempting* a move and the probability of *accepting* it

For *symmetric* moves, e.g. displacing a randomly selected atom by a random distance between 0 and Δr_{max} in a random direction

$$P_{att}(\mathbf{r}_{old}^N \to \mathbf{r}_{new}^N) = P_{att}(\mathbf{r}_{new}^N \to \mathbf{r}_{old}^N)$$

Which to satisfy detailed balance requires

$$\frac{P_{acc}(\mathbf{r}_{old}^N \to \mathbf{r}_{new}^N)}{P_{acc}(\mathbf{r}_{new}^N \to \mathbf{r}_{old}^N)} = \frac{P(\mathbf{r}_{new}^N)}{P(\mathbf{r}_{old}^N)}$$

Metropolis Monte Carlo

One choice for the acceptance probability which satisfies this is

$$P_{acc}\left(\mathbf{r}^N_{old} \rightarrow \mathbf{r}^N_{new}\right) = \min\left\{1, \frac{P\left(\mathbf{r}^N_{new}\right)}{P\left(\mathbf{r}^N_{old}\right)}\right\}$$

For the expected Boltzmann distribution

$$P\left(\mathbf{r}^N\right) = \exp\left[-\beta\mathcal{U}\left(\mathbf{r}^N\right)\right]$$

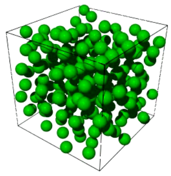
this reduces to

$$P_{acc}\left(\mathbf{r}^N_{old} \rightarrow \mathbf{r}^N_{new}\right) = \min\left\{1, \exp\left[\beta\mathcal{U}\left(\mathbf{r}^N_{old}\right) - \beta\mathcal{U}\left(\mathbf{r}^N_{new}\right)\right]\right\}$$

The resulting sequence of configurations is known as a *Markov Chain.*

The probability of generating configuration *n+1* from configuration n does not depend on any of the earlier configurations *n-1, n-2…*

Metropolis Monte Carlo

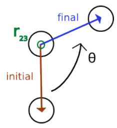


1. $\mathbf{r}^N_{new} = \mathbf{r}^N_{old} + \xi\Delta\mathbf{r}_N$
2. $P\left(\mathbf{r}^N_{old} \rightarrow \mathbf{r}^N_{new}\right) = \min\left\{1, \frac{\exp\left[-\beta\mathcal{U}\left(\mathbf{r}^N_{new}\right)\right]}{\exp\left[-\beta\mathcal{U}\left(\mathbf{r}^N_{old}\right)\right]}\right\}$
3. GOTO 1

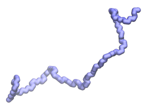
Generates samples according to:

$$P(U) = \frac{W(U)}{Z}\exp\left(-\beta\mathcal{U}\right)$$

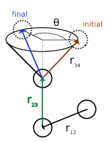
More complex moves



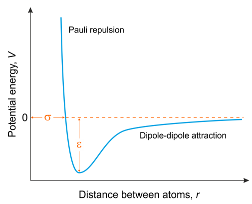
Change a bond angle by a random amount



Change a dihedral angle by a random amount



Example - Lennard-Jones fluid



Work in scaled units

k_B = 1, ε = 1, σ = 1

Energy measured in units of *ε*
Temperature measured in units of *ε*

Demo

- Equilibration
- Tuning move sizes for optimal efficiency
- Estimating uncertainties when working with correlated data

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Molecular Dynamics simulation

Microcanonical (NVE) dynamics

Equations of motion

$$\begin{aligned}\dot{\mathbf{r}}_i &= \mathbf{p}_i/m_i \\ \dot{\mathbf{p}}_i &= -\nabla_{\mathbf{r}_i}U\left(\mathbf{r}^N\right)\end{aligned}$$

Conserve the Hamiltonian (total energy)

$$\mathcal{H}\left(\mathbf{r}^N\right) = \mathcal{U}\left(\mathbf{r}^N\right) + \sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m_i}$$

Dynamics are exactly those realised by an isolated system

Numerical integration

Let *f* be some function of the positions and momenta of the atoms

$$\dot{f} = \sum_{j=1}^{N} \left(\dot{\mathbf{r}}_j \cdot \nabla_{\mathbf{r}_j} + \dot{\mathbf{p}}_j \cdot \nabla_{\mathbf{p}_j} \right) f = i\hat{L} f \qquad \text{defines } \textit{Liouville} \text{ operator}$$

This equation has a well-known solution

$$f(t) = \exp\left(i\hat{L}t\right) f(0)$$

Which defines the *time evolution operator*.

To rationally approximate this, we split the Liouville operator

$$i\hat{L} = \sum_{j=1}^{N} \left(i\hat{L}_r + i\hat{L}_p \right)$$

Numerical integration

Suggests an operator which evolves positions

$$\exp\left(i\hat{L}_r t\right) x = \left[1 + \frac{p}{m} t \frac{\partial}{\partial x} + \cancel{\frac{(pt)^2}{m^2 2!} \frac{\partial^2}{\partial x^2}} + \ldots \right] x = x + \frac{p}{m} t$$

i.e. expansion to first order captures the *exact* time evolution at fixed momentum *p*

Similarly $\exp\left(i\hat{L}_p t\right)$ evolves momenta at fixed forces

The two operators $i\hat{L}_r$ and $i\hat{L}_p$ do NOT commute, since updating positions changes forces (rate of change of momentum) and updating momenta changes rate of change of position

$$\exp(\mathcal{A} + \mathcal{B}) \neq \exp(\mathcal{A}) \exp(\mathcal{B}).$$

$$\exp\left(i\hat{L}t\right) \neq \exp\left(i\hat{L}_r t\right) \exp\left(i\hat{L}_p t\right).$$

Velocity Verlet Algorithm

Use Trotter factorisation

$$e^{(\mathcal{A}+\mathcal{B})} = \lim_{P\to\infty} \left(e^{\mathcal{B}/2P} e^{\mathcal{A}/P} e^{\mathcal{B}/2P} \right)^P$$

which leads to

$$\exp\left(i\hat{L}t\right) = \left[\exp\left(\frac{i\hat{L}_p \Delta t}{2}\right) \exp\left(i\hat{L}_r \Delta t\right) \exp\left(\frac{i\hat{L}_p \Delta t}{2}\right) \right]^P$$

being valid for small timesteps $\Delta t = t/P$.

i.e. we can approximate the action of the exact time evolution operator with

- $\mathbf{p}_j\left(t + \frac{1}{2}\Delta t\right) = \mathbf{p}_j(t) + \frac{\Delta t}{2} \dot{\mathbf{p}}_j(t)$
- $\mathbf{r}_j(t + \Delta t) = \mathbf{r}_j(t) + \frac{\Delta t}{m} \mathbf{p}_j\left(t + \frac{1}{2}\Delta t\right)$
- $\mathbf{p}(t + \Delta t) = \mathbf{p}_j\left(t + \frac{1}{2}\Delta t\right) + \frac{\Delta t}{2} \dot{\mathbf{p}}_j(t + \Delta t)$

Velocity Verlet Algorithm

- Algorithms derived in this way are *symplectic* – they preserve the configurations which are accessible from any other configuration – a necessary condition for obeying the global balance equation.
- The dynamics are exactly those of a *shadow Hamiltonian* which differs from the real Hamiltonian by a constant which depends on the timestep.
- It is better to simulate a slightly wrong system exactly, than to simulate the correct system with an error which grows with time.

Thermostats

- Rarely interested in isolated systems.
- Instead modify equations of motion to simulate coupling to the rest of the universe (i.e. a heat bath).
- Resulting system should generate samples distributed according to equilibrium statistics.
- How one simulates this coupling is a *modelling choice* – all choices lead to fictitious dynamics. Once can only achieve "correct" dynamics of a subsystem by explicitly simulating the atoms which couple it to its environment.

Nosé-Hoover equations

- Popular and sometimes correct method of coupling to heat bath

$$\begin{aligned}
\dot{\mathbf{r}}_i &= \mathbf{p}_i / m_i \\
\dot{\mathbf{p}}_i &= -\nabla_{\mathbf{r}_i} U\left(\mathbf{r}^{3N}\right) - \frac{p_s}{Q} \mathbf{p}_i \\
\dot{s} &= p_s / Q \\
\dot{p}_s &= \sum_{i=1}^{N} \mathbf{p}_i^2 / m_i - 3N k_B T
\end{aligned}$$

- Coupling parameter Q is a modelling choice

Langevin dynamics

- Uses stochastic equation mimicking the effect of many small collisions with light particles in some background medium.

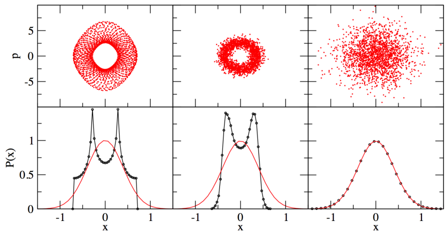
$$m_i \frac{\partial^2 \mathbf{r}_i(t)}{\partial t^2} = -\nabla_{\mathbf{r}_i} \mathcal{U}\left(\mathbf{r}^N(t)\right) - \gamma m_i \frac{\partial \mathbf{r}_i(t)}{\partial t} + \sqrt{2\gamma k_B T m_i} R_i(t)$$

$$\langle R_i(t) \rangle = 0$$
$$\langle R_i(t) R_i(t') \rangle = \delta(t - t')$$

- Coupling parameter γ is a modelling choice
- For large γ dynamics are *overdamped* – direction of motion random and biased toward direction of force, but not influenced by momentum.

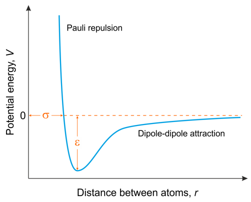
Ergodicity

- Beware of pathogenic cases!



Nosé-Hoover | Nosé-Hoover chain | Langevin

Example - Lennard-Jones fluid



Work in scaled units

$k_B = 1$, $\varepsilon = 1$, $\sigma = 1$

Energy measured in units of ε
Temperature measured in units of ε

Demo

- LAMMPS
- Repeat of earlier MC calculation