Markov chain Monte Carlo Simulation
An Example with Argon

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Outline

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Brief introduction to Markov chain Monte Carlo

▶ For equilibrium distribution, the average of a physical quantity A in equilibrium is

$$\langle A \rangle = \int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{p}\, \rho(\mathbf{x}, \mathbf{p}) A(\mathbf{x}, \mathbf{p})$$

Here, $\rho(\mathbf{x}, \mathbf{p}) = e^{-\beta H(\mathbf{x},\mathbf{p})}/Z$ is the canonical ensemble distribution function, and $Z = \int d\mathbf{x}\mathrm{d}\mathbf{p}\, e^{-\beta H(\mathbf{x},\mathbf{p})}$ is the canonical partition function.

▶ Classically, momentum $\mathbf{p}$ and position $\mathbf{x}$ can be obtained simultaneously, which means $\langle e^{-\beta H(\mathbf{x},\mathbf{p})} \rangle = \langle e^{-\beta T(\mathbf{p})} \rangle \langle e^{-\beta U(\mathbf{x})} \rangle$, and if A only depends on $\mathbf{x}$, we have

$$\langle A \rangle = \int \mathrm{d}\mathbf{x}\, \rho(\mathbf{x}) A(\mathbf{x})$$

Here, $\rho(\mathbf{x}) = e^{-\beta U(\mathbf{x})}/Z$ and $Z = \int d\mathbf{x}\, e^{-\beta U(\mathbf{x})}$ only depends on $\mathbf{x}$.

Detailed balance

▶ When equilibrium, the probability of the system being in configuration $\mathbf{x}_a$ do not change with time. Therefore, we have

$$\frac{\mathrm{d}\rho_a}{\mathrm{d}t} = \sum_b \left[w_{b\rightarrow a}\rho_b - w_{a\rightarrow b}\rho_a \right] = 0$$

Here, $w_{b\rightarrow a}$ represents the transition probability from configuration $\mathbf{x}_b$ to $\mathbf{x}_a$.

▶ From the above relation, we can deduce that if **detailed balance** is satisfied, we can generate a sequence that follows the Boltzmann distribution

$$\frac{w_{a\rightarrow b}}{w_{b\rightarrow a}} = \frac{\rho_b}{\rho_a} = e^{-\beta(E_b - E_a)} = e^{\beta\Delta E_{ab}}$$

Metropolis–Hastings algorithm

▶ Metropolis transition probability

$$w_{a \to b} = \begin{cases} e^{\beta \Delta E_{ab}} & (E_b > E_a) \\ 1 & (E_b \le E_a) \end{cases}$$

▶ Metropolis–Hastings algorithm
  1. Initial configuration $\mathbf{x}_i$ with energy E_i;
  2. Random move to a new configuration $\mathbf{x}_{i'}$ with energy $E_{i'}$;
  3. If $E_{i'} \le E_i$ or $e^{\beta(E_{i'} - E_i)} < R$, R is random number in $[0, 1)$, accept the move.
  The next configuration will be $\mathbf{x}_{i+1} = \mathbf{x}_{i'}$;
  4. Return to step 2 and repeat until N configurations have been accumulated.

▶ Starting from any initial configuration, the system will eventually reach equilibrium
 and follow the Boltzmann distribution.

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Argon

▶ Argon is a chemical element; it has symbol Ar and atomic number 18. It is in group 18 of the periodic table and is a noble gas.

▶ Melting point: 83.81 K, boiling point: 87.302 K, triple point: 83.8058 K

▶ Liquid density (at b.p.): 0.02103 Å^{-3}

▶ Lattice: FCC (a=5.4691 Å), density: 0.02445 Å^{-3} (at triple point)
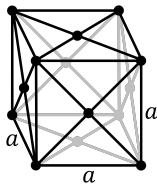
Mie potential

▶ Mie potential is an interaction potential describing the interactions between particles on the atomic level. It is mostly used for describing intermolecular interactions, but at times also for modeling intramolecular interaction.

$$U(r) = C\varepsilon \left[\left(\frac{\sigma}{r} \right)^n - \left(\frac{\sigma}{r} \right)^m \right]$$

with

$$C = \frac{n}{n-m} \left(\frac{n}{m} \right)^{\frac{m}{n-m}}$$

▶ The Lennard-Jones potential corresponds to the case where n=12 and m=6.

▶ For Ar, σ=3.404 Å, ε=117.84 k_B, n=12.085, m=6.0.

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Pair correlation function

▶ Pair correlation function $g(r)$ in a system of particles describes how density varies as a function of distance from a reference particle.

$$g(\mathbf{r}_1, \mathbf{r}_2) = \frac{\rho(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r})^2}$$

In fluid, $\rho(\mathbf{r}) = \rho$, $g(\mathbf{r}_1, \mathbf{r}_2) = g(|\mathbf{r}_1 - \mathbf{r}_2|) \equiv g(r)$. $g(r)$ can also be referred to as the radial distribution function. When $r \to +\infty$, $g(r) \to 1$.

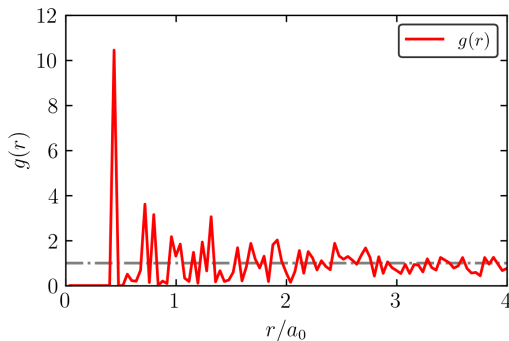▶ In practice, we choose a series of radius grids $\{r_i\}$, which have the same difference $\mathrm{d}r$, and the pair correlation function can be calculated using

$$g(r_i) = \frac{1}{\rho} \frac{n(r_i)}{4\pi r_i^2 \mathrm{d}r}$$
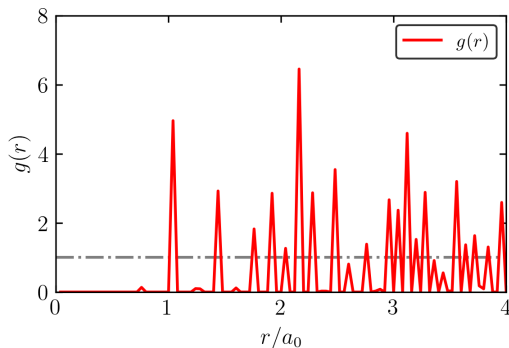
Liquid case

▶ Density : 0.02103 Å^{-3}, Tempreature: 84K

▶ nmol: 108, box: $3 \times 3 \times 3$ unit cell, a_0 is box size, ncycle: 1000, ngrid: 100.
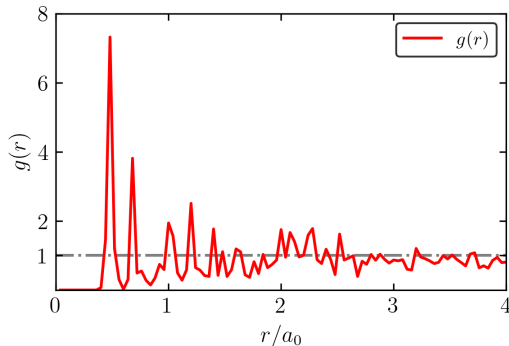
Solid case

▶ Density : 0.2103 $Å^{-3}$, Tempreature: 10K

▶ nmol: 108, box: $3 \times 3 \times 3$ unit cell, a_0 is box size, ncycle: 1000, ngrid: 100.

Why higher density

- ▶ Density : 0.02445 Å^{-3}, Tempreature: 10K

- ▶ nmol: 108, box: $3 \times 3 \times 3$ unit cell, a_0 is box size, ncycle: 1000, ngrid: 100.

▶ Mie potential is used to describe the potential of a fluid, and is not applicable for solids. In this case, only by applying sufficiently large pressure to the system can some solid-like properties be exhibited.

▶ The radius of the first peak in the three graphs, when converted to Å, is approximately the same (3.4506 Å, 3.2031 Å, 3.2814 Å) around the equilibrium position of the potential ($\sigma = 3.404$ Å).