Computer Simulation of Condensed Matter

Monte Carlo simulations of Lennard-Jones system at constant N, P, T

Final Project

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Introduction

This document aims to answer some graded questions as part of the Final Project of *Computer Simulation of Condensed Matter*. Its objective is not to describe the implementation of the algorithm neither to show the results.

In particular, I will answer the questions:

> Q1. Summarize the Metropolis algorithm for (N,P,T) simulations. Describe the main hypothesis involved in its derivation.
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> Q2. Define the reduced units used in your simulations. Translate from reduced units to real units the values of T^*, ρ^*, U^* and P^*.
>
> Q3. Describe how did you fix the parameters involved in the trial changes of the volume.
>
> Q4. Derive the expressions for the tail corrections to the energy and pressure (U^*_{tail}, P^*_{tail})

Q1. Summarize the Metropolis algorithm for (N,P,T) simulations. Describe the main hypothesis involved in its derivation.

Monte Carlo simulations and the Metropolis method

In the context of statistical physics, Monte Carlo simulations are a broad class of algorithms that enable us to obtain statistical information about a system. They come in handy when the problem is too complex or costly to solve in a deterministic manner. In essence, these simulations use a random process to sample the system over its many possible states, aggregating the collection of samples to obtain statistical information that characterizes the system. Different ways of sampling the configuration space can be used, such as uniform random sampling, but we will focus on what is known as *importance sampling*.

Importance sampling exploits the fact that we know beforehand the probability distribution of the configuration space of our system. The idea is that the sampling gives more importance to the states which are more probable, in order to be more efficient with the sampling process. In particular, we will use the Metropolis method.

In a general manner, let $\mathcal{N}$ denote the probability distribution of the possible configurations of the system. Start from an old state $\mathcal{N}(o)$, and make a trial random step in configuration space to $\mathcal{N}(n)$. Note that we interpret $\mathcal{N}(o)$ and $\mathcal{N}(n)$ as being the probabilities of the system being in state *old* and *new* respectively. The key in the Metropolis method is that not all random steps will be accepted as valid, and we will develop a criteria for accepting this new state depending on the particular probability distribution. The end result is a random walk in configuration space, where some steps remain in the same "spot"(those of high probability).

First, we assume the system to be in thermodynamic equilibrium. In equilibrium, it is reasonable to argue that the average number of accepted trial moves that leave state o must be equal to the average number of accepted trial moves from any other state to state o. With n denoting *any other state*, we express this fact as:

$$\mathcal{N}(o)\pi(o \to n) = \mathcal{N}(n)\pi(n \to o) \tag{1}$$

This is known as the *detailed balance condition*. It can be interpreted as an equality of flow leaving state o and flow entering state o. Here $\pi(i \to j)$ denotes the transition probability $i \to j$, that is, the probability of changing from configuration i to j. We can further decompose this transition probability, considering that not all trial moves will be accepted as valid transitions:

$$\pi(i \to j) = \alpha(i \to j)\ \mathrm{acc}(i \to j) \tag{2}$$

Here, $\alpha(i \to j)$ denotes the transition matrix, that is, the probability of performing a trial move $i \to j$. The term $\mathrm{acc}(i \to j)$ denotes the probability of accepting the trial move. Next, we will assume that the transition matrix is symmetric, that is, that $\alpha(i \to j) = \alpha(j \to i)$. By doing so, we can easily rewrite the detailed balance condition (1) as:

$$\frac{\mathrm{acc}(o \to n)}{\mathrm{acc}(n \to o)} = \frac{\mathcal{N}(n)}{\mathcal{N}(o)} \tag{3}$$

Recall that our goal is to define an acceptance criterion to accept as valid a given random trial move. The previous equation lets us define $\alpha(o \to n)$ and $\alpha(n \to o)$ in an infinite number of ways. The choice fixed by the Metropolis method is the following:

$$\mathrm{acc}(o \to n) = \min\{1, \frac{\mathcal{N}(n)}{\mathcal{N}(o)}\} \tag{4}$$

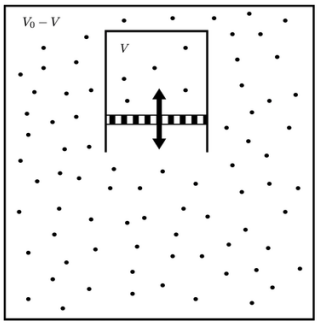
This way, we have developed a framework to sample the configuration space of our system. We perform random trial moves in this space, and for each trial move we apply criteria (4). If the trial move is accepted, we store it as the new configuration. If it is rejected, we leave the configuration as is (however, still storing it as a new sample). With enough steps, we will obtain a collection of configurations from which to extract the statistics.

Isobaric-Isothermal Ensemble (N,P,T)

What remains now is a statistical physics problem, finding the particular probability distribution of a system with a fixed number of particles, pressure and temperature.

We will take as a starting point the partition function for a Canonical Ensemble. That is, a system of N particles confined in a cubic box of volume V (with side lengths $L = V^{\frac{1}{3}}$) and with constant temperature T. By defining a scaled coordinate system for the positions of the particles, $\overrightarrow{r_i} = L\overrightarrow{s_i}$, we can write this partition function as:

$$Q(N,V,T) = \frac{V^N}{\lambda^{3N} N!} \int_0^1 \cdots \int_0^1 d\vec{s}^N e^{-\beta U(\vec{s}^N;L)} \tag{5}$$



Next, consider this canonical ensemble immersed in a bath of a much larger system consisting of an ideal gas of constant temperature and pressure, separated by a piston wall. In total, considering both systems, the volume is V_0 and the number of particles is M. However, when viewed independently, the inner system has volume V and constant number of particles N, while the outer system has volume $V_0 - V$ and constant number of particles $M - N$. The total partition function for a given configuration of $\{N, M, V, V_0, T\}$ can be written as the product of both sub-systems considered as canonical ensembles, recalling that for ideal gases $U_{\text{ideal gas}} = 0$, and that $\int d\vec{s'}^{M-N} = 1$ (we have implicitly assumed the ideal gas to have the same thermal wave-length as our system):

$$Q_{\text{sys + bath}}(N,M,V,V_0,T) = \frac{V^N (V_0 - V)^{M-N}}{\lambda^{3M} N!(M-N)!} \int d\vec{s}^N e^{-\beta U(\vec{s}^N;L)} \tag{6}$$

The key is that both sub-systems can exchange volume. Note that the previous equation should proportional to the probability to be in a configuration where the inner system will have a particular volume of V, out of the many volumes it could have. In particular, the probability density that the inner system has a volume V is simply the functional part from this partition function normalised (see [1]):

$$\mathcal{N}(V) = \frac{V^N (V_0 - V)^{M-N} \int d\vec{s}^N e^{-\beta U(\vec{s}^N;L)}}{\int_0^{V_0} dV' V'^N (V_0 - V')^{M-N} \int d\vec{s}^N e^{-\beta U(\vec{s}^N;L')}} \tag{7}$$

Next, assume that the size of the outer reservoir tends to infinity. The limit is:

$$V_0 \to \infty \ , \quad M \to \infty \ , \quad \frac{M-N}{V_0} \to \rho_{\text{ideal gas}} \ , \quad \frac{V}{V_0} \to 0$$

The key reasoning is that in this limit, a change in the volume of the inner system will not change the pressure of the larger system. P (and T) will be constant, making the inner system an Isobaric-Isothermal system. Substituting and taking such limit in (7), noting that $(V_0 - V)^{M-N} \to e^{-(M-N)V/V_0}$, and recalling that for ideal gases we have the relation $\rho = \beta P$, we have:

$$\mathcal{N}(V) = \frac{V^N e^{-\beta PV} \int d\vec{s}^N e^{-\beta U(\vec{s}^N;L)}}{\int_0^{V_0} dV' V'^N e^{-\beta PV'} \int d\vec{s}^N e^{-\beta U(\vec{s}^N;L')}} \tag{8}$$

From this expression, we can easily derive the probability density of the inner system having a volume V and a particular configuration of positions of the particles $\{\vec{s}^N\}$, which is simply the integrand of the previous integral over the positions:

$$\mathcal{N}(V;\vec{s}^N) \propto V^N e^{-\beta PV} e^{-\beta U(\vec{s}^N;L)} = V^N e^{-\beta\left[U(\vec{s}^N;L)+PV-\frac{NlnV}{\beta}\right]} \tag{9}$$

In parallel, we could also have found the partition function $Q_{tot}(N,P,T)$ by taking the limit in equation (9), integrating over all possible volumes of V and adding a factor βP to make it adimensional. From this total function one might simply divide by the partition function of the bath to recover the partition function of the subsystem $Q(N,P,T)$. An alternative to find this partition function is to simply take the denominator of equation (8) and add the necessary constants. Either way, one would obtain:

$$Q(N,P,T) = \frac{\beta P}{\lambda^{3N}N!}\int dV V^N e^{-\beta PV}\int d\vec{s}^N e^{-\beta U(\vec{s}^N;L)} = \beta P\int dV e^{-\beta PV} Q(N,V,T) \tag{10}$$

Metropolis sampling on (N,P,T) ensemble

Finally, we can particularise the Metropolis method to this ensemble.

Our configuration space consists of the variables $\{V,\vec{s}^N\}$. Thus, our trial moves could consist of small random changes on V and the positions of the particles $\vec{s}^N$. However, in this work we consider changes in the variable $\ln V$ [1]. This way we will move in a smoother fashion, avoiding drastic changes; but this means that the probability distribution function is slightly different, since we are performing changes to the new variable $\ln V$. We can rewrite equation (10) as:

$$Q(N,P,T) = \frac{\beta P}{\lambda^{3N}N!}\int d(\ln V) V^{N+1} e^{-\beta PV}\int d\vec{s}^N e^{-\beta U(\vec{s}^N;L)}$$

From which we easily deduce, as before, that the probability density of being in a state $\{V;\vec{s}^N\}$ when performing a random walk on $\ln V$ is:

$$\mathcal{N}_{\ln V}(V;\vec{s}^N) \propto V^{N+1} e^{-\beta PV} e^{-\beta U(\vec{s}^N;L)} = V^{N+1} e^{-\beta\left[U(\vec{s}^N;L)+PV-\frac{NlnV}{\beta}\right]} \tag{11}$$

The interpretation is that $P(V<x<V+dV) = \mathcal{N}(V)dV = \mathcal{N}_{lnV}(V)d(\ln V)$. By using the general Metropolis criterion (4) and this particular (N,P,T) distribution (9), we get the following acceptance probability:

$$\text{acc}(o\to n) = \min\{1,\exp\left[-\beta\left(U(\vec{s}_n^N;V_N) - U(\vec{s}_o^N;V_o) + P(V_n-V_o) - \frac{N+1}{\beta}\ln(\frac{V_n}{V_o})\right)\right]\} \tag{12}$$

Implementation

Regarding the implementation, we will not change $\ln V$ and $\vec{s_i}$ at the same time. For each trial move of volume, we will try to make of the order of N trial moves in the position of a random particle.

The Metropolis algorithm can be summarized as follows:

→ At each step, we evaluate a random variable $X \sim uniform(0, N_{particles}+1)$

(a) if $X < N_{particles}$ ⇒ trial move of a random's particle position$\{\vec{r_i}\}$

→ The acceptance probability of this move is given by (12) particularised for $V_o = V_n$, or simply the Canonical ensemble, that is:
$\text{acc}(o\to n) = min\{1,\exp\left[-\beta\left(U(\vec{r}_n^N;V_n) - U(\vec{r}_o^N;V_o)\right)\right]\}$

(b) else ⇒ trial move of the volume$\{V\}$

→ Acceptance probability of this move is simply given by (12)

→ If a trial move is accepted, it is stored. If it is rejected, the original state before the moves is stored. After sufficient steps, we may store a sample, and after sufficient samples we can analyze the statistics of the system.

Q2. Define the reduced units used in your simulations. Translate from reduced units to real units the values of T^*, ρ^*, U^* and P^*.

The reduced units used for the simulations are the following:

$$U^* = \frac{1}{\epsilon}U, \quad P* = \frac{\sigma^3}{\epsilon}P, \quad \rho* = \sigma^3\rho, \quad r* = \frac{1}{\sigma}r, \quad T* = \frac{k_B}{\epsilon}T \tag{13}$$

Recall that for our system:

atom	mass (uma)	ϵ/k_B (K)	σ (Å)
Ar	39.948	119.8	3.405

In our case, we are running all simulations at $T* = 2$, which means that $T = 239{,}6K$.

We performed a sweep of pressures. We can thus easily convert the results obtained from the simulations ($\rho*$ actually refers to $< \rho* >$, as well as $U*$ refers $< U* >$) at every value of $P*$ to physical units. The following table contains such results in reduced and real units:

P*	P [GPa]	U*	U [J]	$\rho*$	ρ $[nm^{-3}]$
0.15	0.00613	-270.3914	-4.470219e-19	0.08073	2.045
1.8	0.6768	-1827.498	-3.021294e-18	0.58396	14.792
3.45	0.13288	-2177.955	-3.60068e-18	0.70955	17.973
5.1	0.19901	-2343.060	-3.87364e-18	0.78161	19.798
6.75	0.26565	-2439.776	-4.03353e-18	0.83408	21.127
8.4	0.33267	-2498.984	-4.13142e-18	0.87608	22.192
10.05	0.40003	-2526.066	-4.17619e-18	0.90996	23.050
11.7	0.46799	-2535.754	-4.192210e-18	0.93945	23.797
13.35	0.53575	-2538.744	-4.197154e-18	0.96610	24.472
15	0.60387	-2527.107	-4.177915e-18	0.98949	25.064

Q3. Describe how did you fix the parameters involved in the trial changes of the volume.

Recall that we are performing two simultaneous random displacements along the configuration space. One, changing the position of a given particle with a random displacement in the spatial dimensions, and the other, performing small random changes to the logarithm of the volume of the system. This is because if we changed V directly, we risk making too big steps in configuration space. The following is the explicit formula for a trial step, where δ_V is a random variable uniformly distributed between $(-\delta_{V_{max}}, \delta_{V_{max}})$:

$$\ln V_{\text{trial}} = \ln V_0 + \delta_V \qquad \delta_V \sim \text{uniform}(-\delta_{V_{max}}, \delta_{V_{max}})$$

Thus, the only free parameter is $\delta_{V_{max}}$ and the question is how to fix it. The criterion followed is to choose $\delta_{V_{max}}$ such that about half of the trial changes of volume are accepted (for fixed conditions). This way, we ensure an equilibrium. We let enough freedom on the system to produce different configurations, without this freedom being too big to produce nonphysical configurations too often. In particular, we have established the following quotes:

$$\delta_{V_{max}} \quad \text{s.t.} \quad 0{,}39 < \frac{N_{\text{accepted}}}{N_{\text{trial}}} := a \ < 0{,}61$$

If for a given set of parameters we find a value of $\delta_{V_{max}}$ that produces an acceptance rate of volume trial changes inside this interval, we consider it optimal.

In our case, we have implemented an automatic algorithm to sample a range of different pressures (leaving N and T fixed). Thus, for every set of (N,P,T) we have to find an optimal $\delta_{V_{max}}$. The implementation has been the following: increasing or decreasing $\delta_{V_{max}}$ by 20 % in accordance to the acceptance rate a, until we are inside the previously defined interval.

$$\text{if} \quad a > 0{,}61 \quad \Rightarrow \quad \delta_{V_{max}} \to 1{,}2 \ \delta_{V_{max}}$$

$$\text{if} \quad a < 0{,}39 \quad \Rightarrow \quad \delta_{V_{max}} \to 0{,}8 \ \delta_{V_{max}}$$

Once we have found an appropriate value of $\delta_{V_{max}}$ for the given (N,P,T), we proceed with the statistical sampling. Note that exactly the same criterion has been used to fix $\delta_{r_{max}}$.

Q4. Derive the expressions for the tail corrections to the energy and pressure (U^*_{tail}, P^*_{tail})

The starting point are the following equations, derived in statistical physics for general systems (*D. A. McQuarrie, "Statistical Mechanics"*), which express the mean potential energy and total pressure as a function of the radial distribution function $g(r)$:

$$< U_N >= 2\pi\rho N \int_0^\infty U(r)g(r)r^2 dr \tag{14}$$

$$P = \rho k_B T - \frac{2\pi}{3}\rho^2 \int_0^\infty \frac{dU(r)}{dr} g(r) r^3 dr \tag{15}$$

Now, the problem is that numerically we only compute the mean energy and interactions up to a cutoff radius r_c. However, as the previous equations suggest, we should consider the interaction as $r \to \infty$ to obtain accurate results. The workaround is to correct is to simply add a constant correction term, corresponding to the mean interactions fro $r > r_c$. Thus, we actually compute the mean interaction energy and pressure as:

$$< U_N >= \left\langle \sum_{i=1}^{N} \sum_{\substack{j>i \\ r_{ij}<r_c}} U(r_{ij}) \right\rangle + U_{\text{tail}}$$

$$P = \rho k_B T - \frac{1}{3V} \left\langle \sum_{i=1}^{N} \sum_{\substack{j>i \\ r_{ij}<r_c}} \overrightarrow{r_{ij}} \cdot \overrightarrow{F_{ij}}) \right\rangle + P_{\text{tail}}$$

Where the correction terms are called P_{tail} and U_{tail}, and correspond to the definite integrals of (14) and (15) from $r = r_c$ to ∞:

$$U_{\text{tail}} = 2\pi\rho N \int_{rc}^\infty U(r)g(r)r^2 dr \qquad P_{\text{tail}} = -\frac{2\pi}{3}\rho^2 N \int_{rc}^\infty \frac{dU(r)}{dr} g(r) r^3 dr$$

Finally, we make the approximations that for $r > r_c$ the radial distribution function is constant, with value $g(r) \approx g_0$ corresponding to the mean density of the system. Thus, we get the following expressions for the tail terms, which only depend on the potential energy function of the system:

$$U_{\text{tail}} \approx 2\pi\rho N g_0 \int_{rc}^\infty U(r) r^2 dr \tag{16}$$

$$P_{\text{tail}} \approx -\frac{2\pi}{3}\rho^2 g_o \int_{rc}^\infty \frac{dU(r)}{dr} r^3 dr \tag{17}$$

Now, simply recalling that we are using a Lennard Jones interaction potential, we will carry out the integration of both expressions analytically:

$$U_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \tag{18}$$

Integration of U_{tail}

Using equations (16) and (18), we simply substitute the expression for U_{LJ} as the potential energy, and carry out the integration:

$$U_{\text{tail}} = 8\pi\rho N g_0 \epsilon \int_{rc}^{\infty} \left[\frac{\sigma^{12}}{r^{10}} - \frac{\sigma^6}{r^4}\right] dr = 8\pi\rho N g_0 \epsilon \left[\frac{-1}{9}\frac{\sigma^{12}}{r^9} + \frac{1}{3}\frac{\sigma^6}{r^3}\right]\Big|_{r_c}^{\infty} = \frac{8\pi}{3}\rho N g_0 \epsilon \left(\frac{1}{3}\frac{\sigma^{12}}{r_c^9} - \frac{\sigma^6}{r_c^3}\right)$$

Integration of P_{tail}

Similarly, we use equations (17) and (18), substituting the expression for U_{LJ} and integrating:

$$\begin{aligned} P_{\text{tail}} = & -\frac{8\pi}{3}\rho^2 g_o \epsilon \int_{rc}^{\infty} \frac{d}{dr}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] r^3 dr \quad = \quad -\frac{8\pi}{3}\rho^2 g_o \epsilon \int_{rc}^{\infty} \left[-12\frac{\sigma^{12}}{r^{13}} + 6\frac{\sigma^6}{r^7}\right] r^3 dr \\ = & -\frac{8\pi}{3}\rho^2 g_o \epsilon \int_{rc}^{\infty} \left[-12\frac{\sigma^{12}}{r^{10}} + 6\frac{\sigma^6}{r^4}\right] dr \quad = \quad -\frac{8\pi}{3}\rho^2 g_o \epsilon \left[\frac{12}{9}\frac{\sigma^{12}}{r^9} - \frac{6}{3}\frac{\sigma^6}{r^3}\right]\Big|_{rc}^{\infty} \\ = & -\frac{8\pi}{3}\rho^2 g_o \epsilon \left[\frac{-4}{3}\frac{\sigma^{12}}{r_c^9} + 2\frac{\sigma^6}{r_c^3}\right] \quad = \quad \frac{16\pi}{3}\rho^2 g_o \epsilon \left(\frac{2}{3}\frac{\sigma^{12}}{r_c^9} - \frac{\sigma^6}{r_c^3}\right) \end{aligned}$$

Reducing units

Now, we will change to reduced units. Recall the definitions of these units from Q2:

$$U^* = \frac{1}{\epsilon}U, \quad P* = \frac{\sigma^3}{\epsilon}P, \quad \rho* = \sigma^3\rho, \quad r* = \frac{1}{\sigma}r \tag{19}$$

Also, note that in reduced units $g_0 = 1$.
Thus, substituing (19) in the expressions for P_{tail} and U_{tail} we get the final expressions:

$$U^*_{\text{tail}} = \frac{1}{\epsilon}\frac{8\pi}{3}\frac{\rho^*}{\sigma^3}N1\epsilon\left(\frac{1}{3}\frac{\sigma^{12}}{\sigma^9 r_c^{*9}} - \frac{\sigma^6}{\sigma^3 r_c^{*3}}\right) = \frac{8\pi}{3}\rho^* N\left(\frac{1}{3}\frac{1}{r_c^{*9}} - \frac{1}{r_c^{*3}}\right) \tag{20}$$

$$P^*_{\text{tail}} = \frac{\sigma^3}{\epsilon}\frac{16\pi}{3}\left(\frac{\rho^*}{\sigma^3}\right)^2 g_o\epsilon\left(\frac{2}{3}\frac{\sigma^{12}}{\sigma^9 r_c^{*9}} - \frac{\sigma^6}{\sigma^3 r_c^{*3}}\right) = \frac{16\pi}{3}\rho^{*2}\left(\frac{2}{3}\frac{1}{r_c^{*9}} - \frac{1}{r_c^{*3}}\right) \tag{21}$$

References

[1] Daan Frenkel y Berend Smit. *Understanding molecular simulation: from algorithms to applications*. Elsevier, 2023.