Computational Statistical Mechanics

Monte-Carlo Simulation

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1 Introduction

In the following, the results of a simple Monte-Carlo simulation in the NVT ensemble will be presented.
The system under consideration consists of N monoatomic molecules in a cubic box of length L and volume $V = L^3$ that interact via the following potential:

$$V(r) = \begin{cases} \frac{A\sigma^3}{r^3} & \text{for } 0 < r < \sigma \\ \frac{A\sigma^2 e^{-\left(\frac{r}{\sigma}-1\right)}}{r^2} & \text{for } \sigma < r < r_c \\ 0 & \text{for } r > r_c \end{cases} \tag{1}$$

Periodic boundary conditions were applied. In the simulation, that was carried out in reduced units, $\frac{A}{k_B T}$ was set to 0.8. The reduced density of the system $\rho\sigma^3$ was set to 0.5, which is equivalent to choosing a reduced box length $\frac{L}{\sigma}$ of $(2N)^{\frac{1}{3}}$.
The simulations started from random initial configurations. Each Monte-Carlo cycle consisted of performing a trial move upon every particle, one after another. Such a move consisted of possibly changing every coordinate r_i of the considered atom:

$$r_{i,new} = r_{i,old} + \Delta(q_i - 0.5) \tag{2}$$

q_i are random numbers generated with uniform probability between 0 and 1. The choice of the value Δ is discussed in section 2. The decision upon the acceptance of a move was made according to the Metropolis rule.
The dimensionless pressure P^* was calculated from the virial:

$$P^* = \frac{P\sigma^3}{k_B T} = \rho\sigma^3 - \frac{1}{3k_B T \left(\frac{L}{\sigma}\right)^3} \sum_{i<j} r_{ij} \left.\frac{\partial V}{\partial r}\right|_{r=r_{ij}} \tag{3}$$

r_{ij} is the distance between the particles i and j that is obtained using the minimum-image convention. The derivative of the potential energy is given below.

$$\frac{\partial V}{\partial r} = \begin{cases} \frac{-3A\sigma^3}{r^4} & \text{for } 0 < r < \sigma \\ -Ae^{-\left(\frac{r}{\sigma}-1\right)} \left(\frac{2\sigma^2+\sigma r}{r^3}\right) & \text{for } \sigma < r < r_c \\ 0 & \text{for } r > r_c \end{cases} \tag{4}$$

Δ	N_{equi}	E^*/N	$\tau_{E^*/N}$	error(E^*/N)	P^*	τ_{P^*}	error(P^*)	acceptance ratio
$\frac{\sigma}{4}$	50	3.2172	7.3347	0.0048	2.5282	5.3020	0.0024	0.8766
$\frac{\sigma}{2}$	20	3.2282	2.4165	0.0027	2.5335	1.8219	0.0014	0.7616
σ	15	3.2241	1.5027	0.0022	2.5314	1.2030	0.0011	0.5674
2σ	10	3.2240	1.1573	0.0019	2.5315	0.9676	0.0010	0.3417
3σ	3	3.2230	1.1768	0.0019	2.5309	0.9741	0.0010	0.2592
L	3	3.2233	1.2443	0.0019	2.5312	0.9957	0.0010	0.2211

Table 1: For different values of Δ the number of necessary iterations for equilibration N_{equi} was estimated. Furthermore, the reduced energy per particle E^*/N and pressure P^* and the corresponding autocorrelation times τ and errors obtained with $N_{equi} = 100$ are given.

To correct for the fact that the potential was set to zero for distances beyond r_c tail corrections ΔE^*_{tail} and ΔP^*_{tail} were applied. The following expressions are derived under the assumption that r_c is chosen to be bigger than σ, which in general is recommendable and is also true for all the calculations carried out here:

$$\Delta E^*_{tail}/N = \frac{2\pi\rho}{k_B T}\int_{r_c}^{\infty} drr^2 V(r) = 2\pi\rho\sigma^3 \frac{A}{k_B T} e^{-\left(\frac{r_c}{\sigma}-1\right)} \tag{5}$$

$$\Delta P^*_{tail} = -\frac{2\pi\sigma^3}{3k_B T}\rho^2 \int_{r_c}^{\infty} drr^3 V'(r) = \frac{2\pi}{3}\frac{A}{k_B T}\left(\rho\sigma^3\right)^2 e^{-\left(\frac{r_c}{\sigma}-1\right)}(3+\frac{r_c}{\sigma}) \tag{6}$$

The effects of changing the cut-off radius and turning off tail corrections are discussed in section 3.

2 Role of Δ

To investigate the effect of different values of Δ simulations on a system of 60 particles each consisting of 5000 Monte-Carlo cycles and using a cut-off radius r_c of $\frac{L}{2}$ were carried out while using different Δ. By visual investigation of the potential energy per molecule plotted against the number of cycles the number of iterations necessary to reach equilibrium N_{equi} was estimated and is given in table 1. An exemplary plot of the change in energy during the first iteration cycles is given in graphic 1.
As expected N_{equi} decreases with rising Δ. In all future simulations it will be set to 100: Like this, it is considerably bigger than the rough estimates obtained here, so that one can safely consider the other data points in the analysis. There is no need to keep N_{equi} as low as possible since there are still many data points left to calculate the desired averages. Additionally, the computational cost for performing more iterations is very low here so that it could be easily afforded.
In addition to the average pressure and energy per particle the acceptance ratios of the moves performed after equilibration are given. As expected they monotonously decrease with rising Δ, from 88 % for $\Delta = \frac{\sigma}{4}$ to 22 % for $\Delta = L$. Furthermore, an autocorrelation analysis was performed on the data points received after equilibration. The error only slightly (i.e. in the 5th digit) changes for Δ between 2σ and L. Still, the lowest value is obtained for $\Delta = 3\sigma$ and thus this Δ will be used in the following calculations.

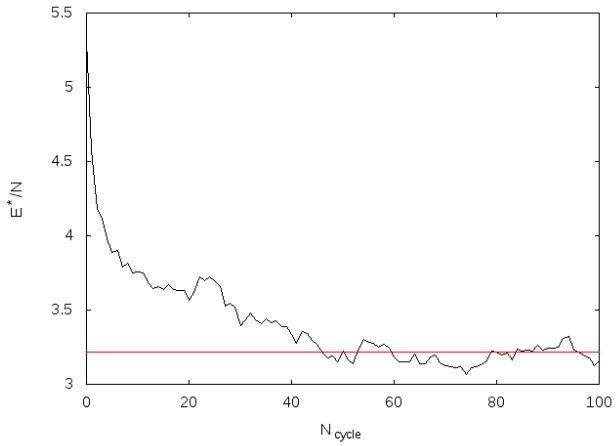

Figure 1: Evolution of the adimensional energy per particle over the first 100 iteration cycles for $\Delta = 0.25\,\sigma$. The horizontal line indicates the energy that was finally obtained.

3 Role of the cut-off radius r_c

To get an impression about the influence of the choice of the cutoff radius r_c the simulation was repeated for $r_c = 3L/8$ and $r_c = L/4$ with the optimal Δ obtained in paragraph 2. Both calculations were then repeated without employing tail corrections. The results are summarized in table 2.
As expected the tail corrections for both, the energy and the pressure, increase with a decreasing cutoff radius. It is worth to point out that while the final results including tail corrections are similar for r_c being $0.5L$ and $0.375L$, those for $r_c = 0.25L$ differ considerably. This indicates that a cutoff of $0.25L$ is too short for obtaining a reliable description of the system.

4 Size Effects

Finally, the influence of the size of the simulated box was investigated by changing the number of particles N. The optimal Δ obtained in section 1 and a cutoff radius of $0.5L$ were applied. The results are given in table 3. The influence of the number of particles on the final results including tail corrections is sufficiently small to consider the system size large enough to obtain reliable results. The decreasing contribution of the tail corrections with rising N is due to the fact that if a larger box with equal density is chosen, within a cutoff radius given in terms of the box length more interactions are considered explicitly. For $N = 200$ also the pair distribution function $g(R)$ was calculated by using $g_\epsilon(R)$, the average of $g(R)$ over a spherical shell with a width of 2ϵ around radius R, as an estimate. The value of ϵ was chosen to be the smallest one for which fluctuations due

r_c	E^*/N	$E^*_{without}/N$	$\Delta E^*_{tail}/N$	P^*	$P^*_{without}$	ΔP^*_{tail}
0.5 L	3.2258	2.6447	0.5812	2.5323	2.0033	0.5290
0.375 L	3.2217	2.1439	1.0777	2.5294	1.6594	0.8700
0.25 L	3.1056	1.1180	1.9877	2.4707	1.0677	1.4029

Table 2: Results for the dimensionless average energy per particle and pressure for different cutoff radii. The index "without" labels values that were obtained without tail corrections.

N	E^*/N	$E^*_{without}/N$	$\Delta E^*_{tail}/N$	P^*	$P^*_{without}$	ΔP^*_{tail}
60	3.2258	2.6447	0.5812	2.5323	2.0033	0.5289
100	3.2274	2.8604	0.3669	2.5334	2.1711	0.3623
200	3.2314	3.0584	0.1730	2.5356	2.3438	0.1918

Table 3: Results for the dimensionless average energy per particle and pressure for different N. The index "without" labels values that were obtained without tail corrections.

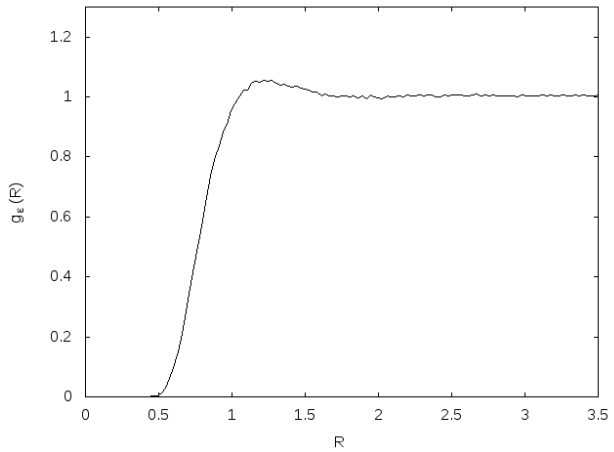

Figure 2: Pair distribution function $g(r)$ for $N = 200$

to statistical errors seemed acceptably small. The resulting pair distribution function is displayed in graph 2.
Due to the fact that the system is very dilute there is only one peak and no higher order shells visible. As expected $g(R)$ is zero for low R and approaches 1 for big distances.