

# Exercise sheet 1

Units and the Lennard-Jones potential  
PUE Advanced Computational Physics  
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## Metropolis Monte Carlo simulations of the Lennard-Jones fluid

The Lennard-Jones (LJ) potential,

$$u(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right], \quad (1)$$

has proven to be a good model for the effective pair interaction between pairs of noble gas atoms or molecules with a spherical symmetry. The prime example is argon, which is often simulated using the (not necessarily optimal) parameters  $\epsilon/k_B = 119.8 \text{ K}$  and  $\sigma = 3.405 \text{ \AA}$ .

In this exercise sheet, we will do some basic calculations and start doing some simulations using the Metropolis Monte Carlo algorithm, the details of which will be discussed later. For now, you only need to know that each MC step consists of selecting a random particle and proposing a random displacement that is then either accepted or rejected.

### 1 Reduced units

Often when dealing with simple model systems one uses a system of reduced or \* - units. This means that every observable is multiplied with a combination of parameters to make the observable dimensionless. In the case of the LJ potential the parameters are the mass  $m$ , the particle radius  $\sigma$ , and the potential depth  $\epsilon$ .

- Write down formulas for the reduced units of energy ( $E^*$ ), pressure ( $p^*$ ), time ( $t^*$ ), viscosity ( $\eta^*$ ), action ( $S^*$ ), and charge ( $q^*$ ).
- Using the LJ parameters of argon, which pressure corresponds to  $p^* = 1$ ? A typical timestep used in molecular dynamics simulations is  $t^* = 0.005$ . Which timestep does this correspond to?

For other systems more realistic units are used. Answer the following questions based on the “real” unit system that *LAMMPS* (a popular molecular dynamics simulation package—<http://lammmps.sandia.gov/doc/units.html>) uses.

- c. Based on the “real”-units of length, time, and mass, what are the expected units of force and energy? Compare this to the unit of energy that is used by LAMMPS; what is the conversion factor between the two units?
- d. What is the numerical value that corresponds to a pressure of 1 atm in these units?
- e. What is the value of  $\hbar$  in these units?

## 2 A basic LJ MC Simulation

Use the program package *lj-canonical* to perform a simulation of liquid argon at the triple point ( $T = 83.80\text{ K}$ ,  $V = 28.24\text{ cm}^3\text{ mol}^{-1}$ ) using  $n = 256$  particles. Record the instantaneous values of the potential energy,  $U_i$ , and the pressure,  $p_i$ .

- a. Calculate the ensemble averages  $\langle U \rangle$  and  $\langle p \rangle$ .
- b. Calculate the heat capacity at constant volume,  $C_V$ .

For comparison, the experimental values for pressure and potential energy of the liquid phase of argon at the triple point is  $p = 0.689\text{ bar}$  and  $U = -5.97\text{ kJ mol}^{-1}$ . The configurational part of the specific heat (i. e. excluding the contributions from kinetic energy) is  $C_V' = 6.9\text{ J K}^{-1}\text{ mol}$ .

## 3 Statistics of correlated variables

A downside of the Metropolis algorithm is that the sample that it generates is not uncorrelated, i. e. the particle positions of the next timestep depend on the particle positions at the current timestep. How far “apart” the samples are from each other (i. e. how strongly the samples are correlated), depends on the displacement  $\Delta$  chosen for the simulation. As this displacement becomes larger, fewer moves are accepted, but a larger accepted move decorrelates the sample faster. A common rule of thumb says that acceptance rates around 40% give the best convergence of the simulation. We can deal with correlated samples by formally introducing a correlation time  $\tau_A$  like so:

$$\text{Var}(\bar{A}) = \frac{1}{M/2\tau_A} \text{Var}(A). \quad (2)$$

$\tau_A$  describes the fact, that each correlated sample is effectively less useful to calculate the average, because it is not independent of the previous value. A practical way to calculate  $\tau_A$  is to use a so-called block mean method in which the sample of size  $M$  is split into blocks of size  $n$ :

$$\underbrace{A_1, A_2, \dots, A_n}_{A_1^{(n)}}, \underbrace{A_{n+1}, A_{n+2}, \dots, A_{2n}, \dots}_{A_2^{(n)}} \quad (3)$$

Over each of these blocks we can then calculate a mean value  $A_i^{(n)}$ . For an uncorrelated sample, one would expect the variance of the block means to scale as

$$\text{Var}(A^{(n)}) = \frac{1}{n} \text{Var}(A). \quad (4)$$

However, since our sample is correlated, the length of each block is effectively reduced by a factor  $s$ , the statistical inefficiency:

$$\text{Var}(A^{(n)}) = \frac{1}{n/s} \text{Var}(A). \quad (5)$$

To calculate  $s$  we have to be sure that our blocks are longer than the correlation length, so we formally write

$$s = \lim_{n \rightarrow \infty} n \frac{\text{Var}(A^{(n)})}{\text{Var}(A)}. \quad (6)$$

In practice, one calculates  $s$  for increasing block sizes and takes the plateau value observed for big  $n$ . The effective variance of the sample is then calculated by setting  $2\tau_A = s$ .

- Demonstrate equation (4) numerically using a random process of your choice.
- Implement this procedure and provide error bars for your calculations of  $\langle U \rangle$  and  $\langle p \rangle$ .
- Study the effect of the trial displacement  $\Delta$  on the statistics of  $\langle U \rangle$ . How would you choose your optimal  $\Delta$ ?

## 4 Background corrections

- Calculate the background corrections to the potential energy,

$$\Delta U_c/N = 2\pi\rho \int_{r_c}^{\infty} dr r^2 u(r), \quad (7)$$

and to the virial,

$$\Delta W_c/N = 2\pi\rho \int_{r_c}^{\infty} dr r^2 [ru'(r)], \quad (8)$$

for the LJ potential.

- These terms approximately correct for the contributions that are neglected by using a cutoff in molecular simulations. How large are these corrections to the potential energy, the virial and the pressure in the liquid phase of the Lennard-Jones system at the triple point?

## 5 Pair correlation and nearest neighbors

The mean number of neighbors that are found within a radius  $R$  around a reference particle,

$$n(R) = 4\pi\rho \int_0^R dr r^2 g(r), \quad (9)$$

is referred to as the *running coordination number*. If the integral is carried out up to the distance of the first minimum in the pair correlation function  $g(r)$ ,  $R_{\min}$ , then the resulting number is often referred to as the *coordination number* or the *number of nearest neighbors* (*note*: this definition is not the only possible definition for these terms).

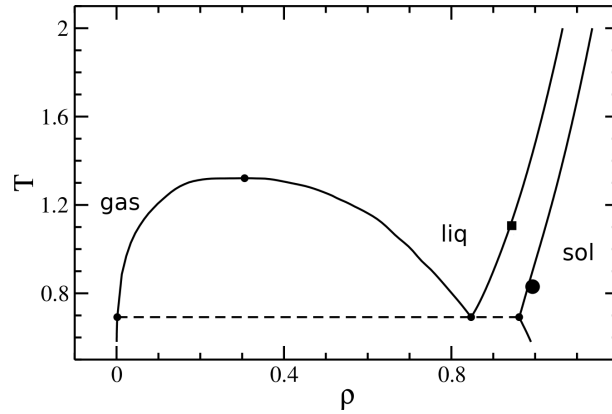


Figure 1:  $\rho$ - $T$  phase diagram of the Lennard-Jones system. Figure modified from Daniele Moroni, *Efficient Sampling of Rare Event Pathways*, Ph.D. thesis, Universiteit van Amsterdam, 2005.

- Calculate  $g(r)$  for an LJ system in the gas, liquid, and solid phase at the triple point ( $T^* = 0.694$  and  $\rho_g^* = 0.0020$ ,  $\rho_l^* = 0.84$ ,  $\rho_s^* = 0.96$ ).
- Calculate  $n(R)$  and the coordination number for all three phases.
- The table below compiles the temperatures and densities of a couple of points on the various coexistence lines of the LJ system. Pick a few of them and redo the calculations. Discuss your findings.

$T^*$	$\rho_g^*$	$\rho_l^*$	$\rho_l^*$	$\rho_s^*$
2.74	-	-	1.167	1.230
1.35	-	-	0.982	1.056
1.15	0.073	0.605	0.947	1.028
0.75	0.0035	0.822	0.856	0.967
0.694	0.0020	0.84	0.84	0.96