

M6 Computer Simulation Methods: Problem Sheet for Part I

NST Chemistry Part III — Michaelmas 2018

December 3, 2021

1 Integrators Relevant, may show up in exams

1.1 Momentum conservation without Noether

The total linear momentum of an N -particle system is $\mathbf{P} = \sum_{i=1}^N \mathbf{p}_i$, where \mathbf{p}_i is the momentum of particle i . The particles interact only through pairwise potentials of the form $u_{ij}(\mathbf{r}_i - \mathbf{r}_j)$. Show that \mathbf{P} is a constant of motion.

1.2 Leap-Frog algorithm

The Leap-Frog algorithm makes explicit use of velocity as an iteration variable. Here, the position and velocity are out of phase by a half time step. The velocities are given by

$$\begin{aligned} \mathbf{v}_i(t + \delta t/2) &= \frac{\mathbf{r}_i(t + \delta t) - \mathbf{r}_i(t)}{\delta t}, \\ \mathbf{v}_i(t - \delta t/2) &= \frac{\mathbf{r}_i(t) - \mathbf{r}_i(t - \delta t)}{\delta t}. \end{aligned}$$

The integration step thus consists of

$$\begin{aligned} \mathbf{v}_i(t + \delta t/2) &= \mathbf{v}_i(t - \delta t/2) + \frac{\delta t}{m_i} \mathbf{f}_i(t), \\ \mathbf{r}_i(t + \delta t) &= \mathbf{r}_i(t) + \mathbf{v}_i(t + \delta t/2) \delta t. \end{aligned}$$

For the evaluation of the total energy, the velocity at time t is obtained as

$$\mathbf{v}_i(t) = \frac{1}{2} [\mathbf{v}_i(t + \delta t/2) + \mathbf{v}_i(t - \delta t/2)].$$

Show that the leap-frog algorithm is equivalent to the Verlet algorithm.

1.3 Harmonic motion

- a) Using the definition of the time correlation function as an average over reference times, show that the time autocorrelation of $A(t) = \cos(\omega t)$ averaged over a period $\Delta t \gg 2\pi/\omega$ is given by

$$C_{AA}(\tau) = \frac{1}{2} \cos(\omega \tau).$$

- b) Similarly, find the autocorrelation function of a superposition of two harmonic modes,

$$A(t) = a_1 \cos(\omega_1 t) + a_2 \cos(\omega_2 t).$$

2 Structural descriptors: Radial distribution function (RDF)

2.1 RDF of an ideal gas Irrelevant for Tripos, takes too long

A trajectory composed by 50 independent configurations of an ideal gas system is provided ('ideal.xyz'). Compute its radial distribution function (averaged over all the different configurations) and check that independently of the distance from a given particle, the value of $g(r)$ should be always (roughly) 1.

2.2 RDF of bulk liquid water

For the provided trajectory 'water.xyz' containing 50 independent configurations, compute the Oxygen-Oxygen and Oxygen-Hydrogen radial distribution function. Please note that in the employed water model (Tip4p/2005), Oxygen is defined as atom type 1, and the two Hydrogens as atom type 2. The coordinates of all the positions are given in Å. Please be aware of the periodic boundary conditions when computing the radial distribution function. For the meaning of the different columns in the trajectory, please see the annotations included in the first frame.

2.3 Characterising different crystal and liquid phases through their RDFs

By computing the radial distribution function for 3 different set of trajectories of colloidal particles ('set1.xyz', 'set2.xyz' and 'set3.xyz'), identify which ones belong to a crystal phase and which one to a liquid phase. Furthermore, identify the nature of each crystal solid phase by computing the coordination number of the particles at consecutive crystal shells. For all these calculations, do not consider the identity of the different colloidal particles (column 3). The meaning of the different columns is the same as in the different provided configurations.

3 Potential energy, kinetic energy and total energy of a given configuration

By using the provided set of initial positions for a given snapshot ('conf.xyz'):

3.1 Potential energy

1) Compute the potential energy assuming a Lennard Jones intermolecular potential:

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

being $\sigma=3.405$ Å and $\epsilon/k_B=119.87$ K. The cut-off for the potential needs to be set at 3σ .

2) Compute the potential energy assuming a Pseudo-Hard-Sphere intermolecular potential:

$$E_{PHS} = \begin{cases} \lambda_r \left(\frac{\lambda_r}{\lambda_a} \right)^{\lambda_a} \epsilon_R \left[\left(\frac{\sigma}{r} \right)^{\lambda_r} - \left(\frac{\sigma}{r} \right)^{\lambda_a} \right] + \epsilon_R; & \text{if } r < \left(\frac{\lambda_r}{\lambda_a} \right) \sigma \\ 0; & \text{if } r \geq \left(\frac{\lambda_r}{\lambda_a} \right) \sigma \end{cases} \quad (2)$$

being $\lambda_a=49$, $\lambda_r=50$, $\sigma=3.405$ Å, $\epsilon_R/k_B=119.87$ K. The cut-off for the potential needs to be set at 1.5σ .

3) Compute the potential energy assuming a pure Hard-Sphere potential in combination with a Yukawa-Debye Huckel potential:

$$E_{HS} = \begin{cases} \infty & \text{if } r < \sigma \\ 0 & \text{if } r \geq \sigma \end{cases} \quad (3)$$

$$E_{Yukawa} = \pm \epsilon \frac{\sigma}{r} e^{-\kappa(r-\sigma)} \quad (4)$$

being $\sigma=3.05$ Å, $\epsilon/k_B=119.87$ K and $\kappa=5$ Å. The cut-off for the Yukawa-Debye potential needs to be set at 3.5σ .

The description of the different columns in trajectory file is included in the heading (Please note that for the LJ and PHS potentials, the identity of the particles does not need to be considered (column 3), while for the oppositely charged colloidal mixture, the interactions between particles of the same type is with $+\epsilon$ and the interactions between particles of opposite sign (1 with 2 or vice versa) requires $-\epsilon$).

3.2 Kinetic energy

By using a Maxwell-Boltzmann velocity distribution:

$$f(p) = \left(\frac{\beta}{2\pi m} \right)^{3/2} \exp \left(\frac{-\beta p^2}{2m} \right) \quad (5)$$

assign a velocity for every given particle in the 'conf.xyz' file and plot an histogram of the velocity distribution for the initial configuration. Please use a given T of 179.81K and a particle mass of $m = 6.63 \times 10^{-26}$ kg.

3.3 Total energy

Provide the total energy of the initial configuration for the three different potentials described in part 3.1. For the generated velocities computed in point 3.2, please check that the average kinetic energy corresponds to that of the assigned temperature to the Maxwell-Boltzmann velocity distribution.

4 Calculation of the isotropic instantaneous pressure

4.1 Pressure through the virial expression

By means of the virial expression for the isotropic instantaneous pressure in absence of a potential term explicitly volume-dependent:

$$P = \frac{1}{3V} \left\langle \sum_{i=1}^N \frac{p_i^2}{m} + r_i \cdot f_i \right\rangle \quad (6)$$

compute the instantaneous pressure over time for the following trajectory ('press.xyz'). Please note that for every frame in the trajectory you will need to consider the total volume of the simulation box (V), the velocities of the particles (v_x, v_y, v_z in Å/fs), their positions (x, y, z in Å), and the forces $f_i = -\frac{dU}{dr}$.

For this calculation, assume two different potentials:

1) A Lennard-Jones potential:

$$E_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (7)$$

being $\sigma=3.405$ Å and $\epsilon=0.24$ kcal/mol. The cut-off for the potential needs to be set at 3σ .

2) A Pseudo-Hard-Sphere intermolecular potential:

$$E_{PHS} = \begin{cases} \lambda_r \left(\frac{\lambda_r}{\lambda_a} \right)^{\lambda_a} \epsilon_R \left[\left(\frac{\sigma}{r} \right)^{\lambda_r} - \left(\frac{\sigma}{r} \right)^{\lambda_a} \right] + \epsilon_R; & \text{if } r < \left(\frac{\lambda_r}{\lambda_a} \right) \sigma \\ 0; & \text{if } r \geq \left(\frac{\lambda_r}{\lambda_a} \right) \sigma \end{cases} \quad (8)$$

being $\lambda_a=49$, $\lambda_r=50$, $\sigma=3.305$ Å, $\epsilon_R=0.24$ kcal/mol. The cut-off for the potential needs to be set at 1.5σ .

4.2 Time evolution of enthalpy

Combining the instantaneous pressure evaluated in the previous part of the exercise with the code for the calculation of the potential energy developed in Exercise 3.1, compute the enthalpy time-evolution for the trajectory provided using the two provided potentials in 4.1

4.3 Statistical analysis of pressure and enthalpy

Perform a block average analysis of the time evolution of both pressure and enthalpy assuming blocks of 5 and 10 configurations, and provide an average value of both magnitudes with their corresponding associated standard deviation. Discuss the uncertainty and the fluctuations of each magnitude.

5 Dynamic properties: Diffusion coefficient

1) Compute the mean square displacement ($MSD = \frac{1}{N} \sum_{i=1}^N |r_i(t) - r_i(0)|^2$) of the systems A and B using the following trajectories: ('diffusionA.xyz') and ('diffusionB.xyz'). The timestep between every simulation step is 2 fs. Do not consider different identities between atom types 1 and 2 (column 3). The positions are given in Å (not in box units).

Once evaluated the mean square displacement as function of time, compute the diffusion coefficient of each system. Please refer the diffusion coefficient (D) in reduced units, using $\sigma = 3.405$ Å as a unit of distance, and $\tau = \sqrt{m\sigma^2/\epsilon}$ (being $m=6.63 \times 10^{-26}$ kg and $\epsilon=0.24$ kcal/mol) as a unit of time. Discuss the obtained MSDs and diffusion coefficients for both systems. Please note that when computing the mean square displacement of a given system, a correction for the center-of-mass drift needs to be applied.

2) How can we modify our code to optimise the sampling in the evaluation of the MSD?

6 Local order parameters and phase diagram

For a polymer model system of 40-bead chains, we simulate different temperatures in the NVT ensemble. The system contains $N=90$ polymers in a volume $V= 5.74 \times 10^5 \text{\AA}^3$ at $T=264, 276, 288$ and 300K . We aim to identify under which temperatures the system undergoes a phase transition leading to a liquid-vapour coexistence, and at which temperatures the system is unable to phase-separate (i.e., is above the critical temperature).

6.1 Number of contacts through a local order parameter

For every temperature, evaluate the average number of polymer contacts (both inter and intramolecular) along the provided trajectory ($\langle Nc \rangle = \frac{1}{M} \sum_{j=1}^M \frac{1}{N} \sum_{i=1}^N n_i(r < r_c)$ being M the number of frames in the trajectory, N the total number of polymers in the system, and $r_c = 4.1 \text{\AA}$ the cut-off distance to consider a particle to be in contact with a given neighbour particle n_i). Do not consider molecular contacts those between directly bonded beads along the same polymer chain.

Plot the number of contacts $\langle Nc \rangle$ as a function of temperature (T).

6.2 Computing the phase diagram

Using the same trajectories, estimate the density along the z axis of the simulation box. To do that, you need to define a given number of bins along the z coordinate and evaluate the number of polymer beads in each bin (of width Δz). Number density (ρ), needs to be provided in reduced units ($\rho = N/V$; being V of each bin $L_x \cdot L_y \cdot \Delta z$; and the reduced unit of length $\sigma=3.4 \text{\AA}$). Please be aware that very small number of bins will lead to very smooth and inaccurate density profiles, while a too large number of bins, to very noisy profiles.

A) Plot the density profiles as a function of z for each temperature, and identify the density of the liquid and the vapour phase in the coexistence simulation box.

B) Plot a phase diagram in the T - ρ plane (Fig. 1 (Right)).

C) By using the law of rectilinear diameters and critical exponents, estimate the location of the critical temperature and the critical density in our system.

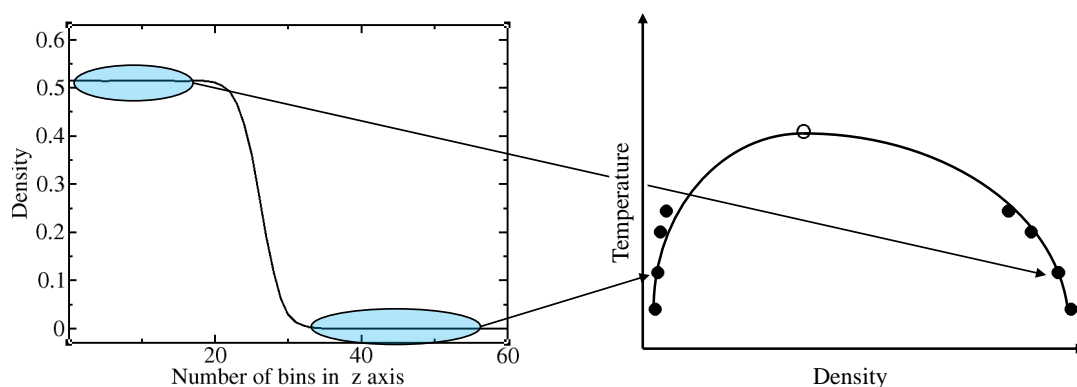


Figure 1: Sketch of how to extract the coexistence densities from a NVT simulation density profile to evaluate the phase diagram