Exercise 7 Properties of a liquid

a) Start with a box with randomly oriented particles and let this equilibrate (point 1 ensemble averaging). After equilibration determine the RDF by binning within a certain distance interval how many other particles are available. This needs to be done for many distance points within the minimum image convention (half the smallest cell length, point 1 RDF) and is averaged for all particles in the simulation box. This is then again averaged over during the simulation after N accepted cycles to ensure independent measures (point 2 ensemble averaging). For distance determination extra care needs to be taken to account for the periodic boundaries (point 2 RDF).

b) For a free energy, one needs to have access to the partition function which is not possible with an ensemble average.

c) Free energies can be determined by reversibly changing the system from a system with known free energy to the system of interest by changing order parameter λ.

$$F(\lambda = 1) - F(\lambda = 0) = \int_0^1 \mathrm{d}\lambda \left\langle \frac{\partial E(\mathbf{r}^N, \lambda)}{\partial \lambda} \right\rangle_\lambda$$

Since we are interested in a liquid, a good reference system would be a Lennard-Jones fluid.

Exercise 8 Self-diffusion constant

a) One would either need to determine the mean square displacement or the velocity autocorrelation.

b) In both cases, these properties need to be determined as a function of time and hence we will need to chop up one simulation into short segments that will then need to be averaged in time intervals. You will need to store either the displacement as a function of time on during each time segment or you will need to store the x, y, z components of the velocity during a segment. There are clearly two ways.

c) You will need a simulation method with time defined: Molecular Dynamics or Kinetic Monte Carlo.

d) Molecular Dynamics follows the dynamics from the potential energy surface in a rather straightforward way, without the need for a Table of Events (kMC does) which is computationally demanding to determine, since we would like to work off-lattice here. Otherwise a RDF would not give much added value. MD is however limited to rather short timescales.

Exercise 9 Rate of a torsion rotation

We consider the rotation of the methyl groups around the C-C bond (torsion angle ϕ) of the molecule ethane, C_2H_6. The molecules torsion energy, ϵ_t around the minimum can be approximated by $\epsilon_t = k(\phi - \pi/3)^2$ with $k = 30$ kJ/mol. At the saddle point (eclipsed at $\phi = 0$ rad), the potential energy can be approximated by $\epsilon_t = 12\text{kJ/mol} - k(\phi)^2$ with the same value for k.

a) 12 kJ/mol.

b) It assumes that the potential energy has a harmonic shape in all coordinates around the minimum and at the saddle point. Since the PES is only determined by ϕ and in both cases quadratically this assumption applies here.

c) The reduce moment of inertia depends on the moving atoms during the torsion which in this case are the 6 hydrogen atoms.

d)
$$k_{\text{HTST}} = \frac{\Pi_{i=1}^{3N} \nu_{A,i}}{\Pi_{i=1}^{3N-1} \nu_{\ddagger,i}} \exp(-(V_{\text{SP}} - V_{\text{min}})/k_B T) = \frac{1}{2\pi}\sqrt{\frac{\kappa}{\mu}} \exp(-E_{\text{act}}/k_B T)$$

$$= \frac{1}{2\pi}\sqrt{\frac{30000/6.63 \times 10^{23}}{1 \times 10^{-46}}} \exp(-12000/(8.3145 \cdot 300)) = 2.76 \times 10^{10}\text{Hz}$$

e) It would be lower, since the TST is always higher since it ignores recrossings where the system goes over the saddle point and then back without leading to rotation.