Exercise 3

Vapor liquid equilibrium

The vapor-liquid coexistence point of a Lennard-Jones system at a certain temperature can be found by different simulation techniques. In this exercise we will locate the phase coexistence point using two different methods. In the first part, we will calculate the equation of state of the system using simulations in the canonical ensemble (NVT), and we will impose the conditions of phase equilibrium. In the second part, we will find the coexistence conditions by one single simulation in the Gibbs ensemble (μpT).

Questions:

- Modify the NVT Monte Carlo program from the last exercise to calculate the chemical potential. Use a truncated Lennard-Jones potential without tail corrections. The chemical potential can be calculated using the Widom's test particle method:

$$\mu = \mu_0 - \frac{\ln\left(\rho^{-1}\left\langle \exp[-\beta\Delta U^+]\right\rangle\right)}{\beta}$$

  where ρ is the density of the system, U^+ the energy of a test particle, and μ_0 a constant:

$$\mu_0 = -\frac{\ln(\Lambda^3)}{\beta} \qquad .$$

  Locate the vapor liquid coexistence densities at $T^* = 0.8$.
  Hint:What are the conditions for coexistence?

  Why is it more difficult to calculate the chemical potential at high densities than at low densities?

- Perform a Gibbs ensemble simulation of the system at $T^* = 0.8$ with the program provided. In the Gibbs ensemble, the chemical potential of box i is:

$$\mu = \mu_0 - \frac{\ln\left\langle \frac{V_i}{n_i+1}\exp\left[-\beta\Delta U_i^+\right]\right\rangle}{\beta}$$

  where n_i is the number of particles in box i and V_i the volume of box i. Do the vapor liquid density and chemical potential agree with the previous simulations in the NVT ensemble?