Exercises

1) Calculate $g(r)$ for hard spheres and compare with simulation data. You can also plot $d(r) + 1 = y(r)$ (see notes), in the same figure. Or you can plot $h(r)$, $c(r)$ and $d(r)$ in the same figure. For $g(r)$ there is an analytical solution, you can plot this as well.

2) a) Calculate $g(r)$ for Lennard-Jones particles, use it to calculate the pressure and compare both with simulation results.

b) Explore the phase diagram and find out where there is no convergence.

3) a) Calculate $g(r)$ for cut-off Lennard-Jones particles and use it to calculate the pressure and compare with simulations.

b) In order to find out what the effect of the attractive part of the Lennard-Jones potential is, compare these results with the results from 2.

c) Explore the phase diagram.

Simulation Data

* Hard Spheres

- For the simulations of hard spheres I used a Markov-Chain Monte-Carlo algorithm.
- There is data for $\rho = 0.3$, 0.6 and 0.9, which is stored in rho03_g.dat, rho06_g.dat and rho09_g.dat. The corresponding r values are saved in r.dat.

* Lennard-Jones Particles

- The data for Lennard-Jones particles come from Brownian-Dynamics Simulations.
- There is data for $\rho = 0.05, 0.316, 0.85$
  $T = 0.9, 1.0, 1.1, 1.2, 1.3, 1.325, 1.35, 1.4$

The data files are called rho#_T#_g.dat
So the data for $\rho = 0.05$ $T = 0.9$ is saved in rho0_T0_g.dat
and the data for $\rho = 0.85$ $T = 1.0$ is saved in rho2_T1_g.dat
The r values for $\rho = 0.05$ are saved in r0.dat
$\rho = 0.316$ " r1.dat
$\rho = 0.85$ " r2.dat

The was calculated at different instances of time, and is saved in rho#_T#_p.dat. It is a list and you should take an average and the std. can be used as a measure for the error.

* Lennard-Jones Particles with cut off.

Everything is the same as for the case without cut off, but the potential is cut off at $2^{1/6}$ and shifted by $U_{ij}(2^{1/6})$.

The Algorithm

1) Guess $rd_0(r)$. $\lim_{r\to\infty} rd(r) = 0$

   or use a previous $rd(r)$

2) Get rc_n from rd_n and the PY approximation

3) Get kC_n by fourier transforming rc_n

4) Get kD_n by using the OZ equation and kC_n

5) Get m by inverse Fourier transforming kD_n

6) Check for convergence.

   If converged: go to 8

   else: go to 7

7) mix m with $rd_n(r)$

   $rd_{n+1}(r) = a\, rd_n(r) + (1-a)\, m(r)$

   and go back to 2

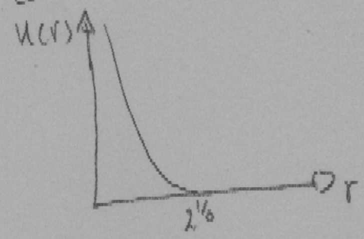
8) get $h(r)$ from rc and rd.

Potentials

Lennard Jones: $$u_{LJ}(r) = 4\left[\frac{1}{r^{12}} - \frac{1}{r^{6}}\right]$$

Lennard Jones with cut off: $$u(r) = \begin{cases} u_{LJ}(r) - u_{LJ}(r_{co}) & r < r_{co} \\ 0 & r > r_{co} \end{cases}$$

So if you only want the repulsive part of the Lennard Jones potential you should use $r_{co} = 2^{1/6}$. This will give you



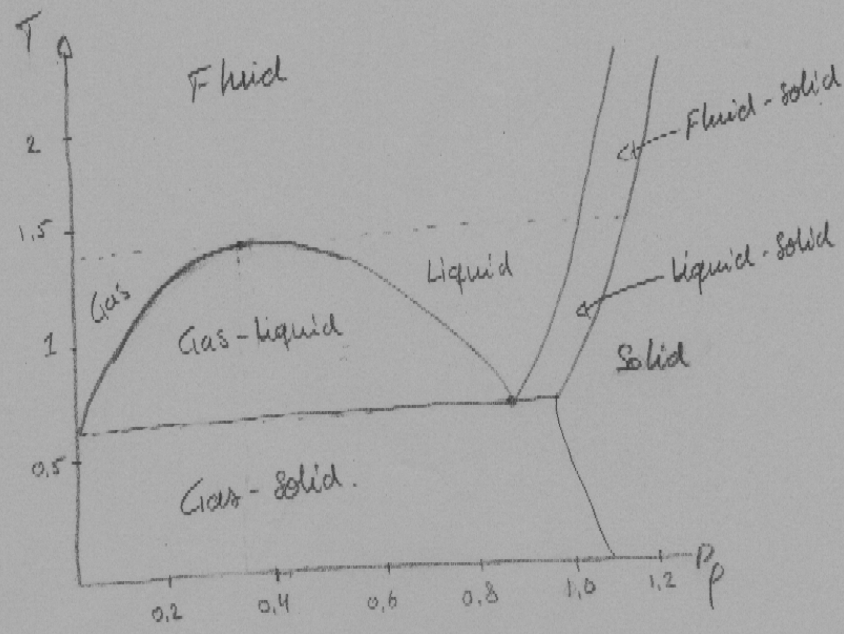
Hard spheres: $$u_{HS}(r) = \begin{cases} \infty & r < 1 \\ 0 & r > 1 \end{cases}$$

Units

The units for temperature are such that $k_b = 1$, $\varepsilon = 1$.

The units for length are such that $\sigma = 1$

A Sketch of the phase diagram of Lennard Jones particles



* Critical point $T \approx 1{,}325$ $\rho \approx 0{,}316$

* If you would calculate the phase diagram using the PY approximation it would be slightly different.

* A rule of thumb for where the PY eq. converges is that it converges in the gas, fluid and liquid regions.

* ## $y(r)$ for Hard Spheres

PY approximation: $c(r) = f(r)y(r)$

$$h(r) - c(r) = \left[e^{-\beta u(r)} - 1\right] y(r)$$

for hard spheres and $r<1$:

$$h(r) = -1$$

$$e^{-\beta u(r)} = 0$$

$$-1 - c(r) = -y(r) \qquad r<1$$

$$y(r) = c(r) + 1 \qquad r<1$$

* ## Solution to the PY equation for $g(\sigma^+)$:

$$g(1^+) = \frac{1 + \frac{1}{2}\eta}{(1-\eta)^2} \quad \text{with } \eta = \frac{1}{6}\pi\rho$$