DFT for single component spheres in planar geometry

1 Hard sphere formalism

We start by setting out the formalism for hard spheres. This largely follows R. Roth, J. Phys.: Condens. Matter **22** 063102 (2010).

The intrinsic Helmholtz free energy functional $\mathcal{F}$ can be written

$$\mathcal{F}[\rho(z)] = \mathcal{F}_{id}[\rho(z)] + \mathcal{F}_{ex}[\rho(z)] \tag{1}$$

For hard spheres Rosenfeld suggests:

$$\beta\mathcal{F}_{ex}[\rho(z)] = \int dz \Phi(\{n_\alpha(z)\}) \tag{2}$$

with $\Phi(\{n_\alpha(z)\})$ the reduced excess free energy density for hard spheres. Let's consider two flavours of functionals for this: The White Bear (WB) functional:

$$\Phi^{WB} = -n_0 \ln(1-n_3) + \frac{(n_1 n_2 - \vec{n_1}\cdot\vec{n}_2)}{1-n_3} + (n_2^3 - 3n_2\vec{n_2}\cdot\vec{n}_2)\frac{n_3 + (1-n_3)^2\ln(1-n_3)}{36\pi n_3^2(1-n_3)^2},$$

and the Rosenfeld functional:

$$\Phi^{RF} = -n_0 \ln(1-n_3) + \frac{(n_1 n_2 - \vec{n_1}\cdot\vec{n}_2)}{1-n_3} + \frac{(n_2^3 - 3n_2\vec{n_2}\cdot\vec{n}_2)}{24\pi(1-n_3)^2}$$

The weighted densities are convolutions of the density profile with its weight function:

$$n_\alpha(z) = \int dz' \rho(z')\omega_\alpha(z-z')$$

with $\alpha = 0, 1, 2, 3$, and the weight functions are (for planar geometry)

$$\begin{aligned}
\omega_3(z) &= \pi(R^2 - z^2)\Theta(R-|z|) && (3)\\
\omega_2(z) &= 2\pi R\Theta(R-|z|) && (4)\\
\vec{\omega}_2(z) &= 2\pi z\vec{e_z}\Theta(R-|z|) && (5)\\
\omega_1(z) &= \omega_2(z)/(4\pi R) && (6)\\
\vec{\omega}_1(z) &= \vec{\omega}_2(z)/(4\pi R) && (7)\\
\omega_0(z) &= \omega_2(z)/(4\pi R^2) && (8)
\end{aligned}$$

The idea is to minimise the grand potential functional $\Omega[\rho(z)]$ w.r.t. variations in the density profile, i.e to solve the Euler-Lagrange equation:

$$\frac{\partial\Omega[\rho(z)]}{\partial\rho(z)} = \frac{\partial F_{ex}[\rho(z)]}{\partial\rho(z)} + \beta^{-1}\ln(\lambda^3\rho(z)) + V_{ext}(z) - \mu = 0 \tag{9}$$

Here

$$c^{(1)}(z) = -\beta \frac{\partial F_{ex}[\rho(z)]}{\partial \rho(z)} \tag{10}$$

$$= -\sum_{\alpha} \int dz' \frac{\partial \Phi}{\partial n_\alpha(z')} \frac{\partial n_\alpha(z')}{\partial \rho(z)} \tag{11}$$

We can rearrange (9) to write the condition for equilibrium:

$$\rho(z) = \rho_b \exp\left[-\beta V_{ext}(z) + c^{(1)}(z) + \beta \mu_{ex}\right] , \tag{12}$$

where we have used $\mu = \mu_{id} + \mu_{ex} = \beta^{-1} \ln(\rho_b) + \mu_{ex}$. Since $c^{(1)}(z)$ also depends on $\rho(z)$, this expression needs to be solved iteratively. Clearly to do this we need to calculate $c^{(1)}(z)$. The main problem in principle is to calculate the variation of the weighted densities $n_\alpha(z')$ wrt $\rho(z)$. However Roth shows that for planar geometry:

$$\frac{\partial n_\alpha(z')}{\partial \rho(z)} = \frac{\partial}{\partial \rho(z)} \int dz'' \rho(z'') \omega_\alpha(z' - z'') = \omega_\alpha(z' - z) \tag{13}$$

Thus

$$c^{(1)}(z) = -\sum_{\alpha} \int dz' \frac{\partial \Phi}{\partial n_\alpha(z')} \omega_\alpha(z' - z) \tag{14}$$

Also note that the functional derivatives can be performed analytically. Eg. for RF we find

$$\frac{\partial \Phi}{\partial n_0(z)} = -\ln(1 - n_3) \tag{15}$$

$$\frac{\partial \Phi}{\partial \vec{n}_1(z)} = -\frac{\vec{n}_2}{1 - n_3} \tag{16}$$

$$\frac{\partial \Phi}{\partial n_1(z)} = \frac{n_2}{1 - n_3} \tag{17}$$

$$\frac{\partial \Phi}{\partial n_2(z)} = \frac{n_1}{1 - n_3} + \frac{1}{24} \frac{(3n_2^2 - 3\vec{n}_2 \cdot \vec{n}_2)}{\pi(1 - n_3)^2} \tag{18}$$

$$\frac{\partial \Phi}{\partial \vec{n}_2(z)} = -\frac{\vec{n}_1}{1 - n_3} - \frac{1}{4} \frac{n_2 \vec{n}_2}{\pi(1 - n_3)^2} \tag{19}$$

$$\frac{\partial \Phi}{\partial n_3(z))} = \frac{\vec{n}_0}{1 - n_3} + \frac{n_1 n_2 - \vec{n}_{1v} \cdot \vec{n}_{2v}}{(1 - n_3)^2} + \frac{1}{12} \frac{n_2^3 - 3 n_2 \vec{n}_{2v} \cdot \vec{n}_{2v}}{\pi(1 - n_3)^3} \tag{20}$$

$$\tag{21}$$

For WB the corresponding results are

$$\frac{\partial \Phi}{\partial n_0(z)} = -\ln(1 - n_3) \tag{22}$$

$$\frac{\partial \Phi}{\partial \vec{n}_1(z)} = -\frac{\vec{n}_2}{1 - n_3} \tag{23}$$

$$\frac{\partial \Phi}{\partial n_1(z)} = \frac{n_2}{1 - n_3} \tag{24}$$

$$\frac{\partial\Phi}{\partial n_2(z)} = \frac{n_1}{1-n_3} + \frac{1}{36}\frac{(3n_2^2 - 3\vec{n}_2\cdot\vec{n}_2)(n_3 + (1-n_3)^2\ln(1-n_3))}{\pi n_3^2(1-n_3)^2} \quad (25)$$

$$\frac{\partial\Phi}{\partial \vec{n}_2(z)} = -\frac{\vec{n}_1}{1-n_3} - \frac{1}{6}\frac{(n_2\vec{n}_2(n_3 + (1-n_3)^2\ln(1-n_3))}{\pi n_3^2(1-n_3)^2} \quad (26)$$

etc...

2 Implementation

Evaluation of the weighted densities $n_\alpha(z)$ can be done in Fourier space via the convolution theorem $f \star g = \mathcal{F}^{-1}\{\mathcal{F}\{f\}\cdot\mathcal{F}\{g\}\}$ i.e

$$n_\alpha(z) = \int dz' \rho(z')\omega_\alpha(z-z') \quad (27)$$

$$= \rho(z') \star \omega_\alpha(z') \quad (28)$$

$$= \mathcal{F}^{-1}\{\mathcal{F}\{\rho(z')\}\cdot\mathcal{F}\{\omega_\alpha(z'\}\} \quad (29)$$

In practise this is done using FFTs, which apparently it is faster than quadrature in real space. However the numerical recipes convolution routines seem to lead to problems for me (plus they don't do double precision or C arrays properly), so I've found it more convenient to do the convolutions in real space instead.

For the direct correlation function we have

$$c^{(1)}(z) = -\sum_\alpha \int dz' \frac{\partial\Phi}{\partial n_\alpha}\omega_\alpha(z'-z) \quad (30)$$

$$= -\sum_\alpha \frac{\partial\Phi}{\partial n_\alpha(z')} \star \omega_\alpha(z') \quad (31)$$

Which is a sum of convolutions. We have to be careful though since the argument entering the calculation of $c^{(1)}(z)$ is negative, i.e. $z - z'$ becomes $z' - z$. For the scalar weight functions this is unimportant, since the scalar weight functions are even functions $\omega_\alpha(z' - z) = \omega_\alpha(z - z')$, but the vector-like weight functions are odd functions: $\vec{\omega}(z' - z) = -\vec{\omega}_\alpha(z - z')$, so we must use the negative of the function to get the right answer.

Operationally, the idea is to set up a 1D grid on which the density profile, weight functions, weighted densities etc are all defined. Note that Roth's equations assume that the wall is at $z = 0$. However, the weight functions are defined for negative z such that $|z| < R$. So I allow for the existence of negative z values 'inside' the wall. To do this, I start the grid at $z = -R + dz$ and set the external potential $V_{ext}(z) = \infty; z < 0$. We also make an initial assumption for the form of $\rho(z)$ on the grid $\rho(z) = \exp(-V_{ext}(z) + \mu)$.

The procedure is then as follows:

1. Using the initial $\rho(z)$, calculate the four scalar weighted densities $n_\alpha(z)$ and two vector weighted densities via real space convolution.

2. Use the weighted densities to calculate the functional derivatives via (22) etc, and then (via further convolution) the contributions to the direct correlation function $c^{(1)}(z)$ appearing in (31).

3. Together with V_{ext} and μ, this gives us an estimate for the new $\rho(z)$ via (12)

4. Mix this with the old profile to get a new profile according to

$$\rho_{new}^{(j+1)}(z) = (1-\alpha)\rho_{old}^{(j)}(z) + \alpha\rho^{(j)}(z).$$

I use $\alpha = 0.05 - 0.1$.

5. Return to 1 and iterate until $\rho(z)$ is converged.

2.1 Checks

A useful check for the hard wall is the sum rule:

$$p = k_B T \rho(0^+) \,. \tag{32}$$

For this we need the pressure. The WB functional satisfies the BMCSL equation of state,

$$\beta p^{CS} = \rho \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} \tag{33}$$

$$\beta\mu^{CS} = \ln(\rho) + \frac{8\eta-9\eta^2+3\eta^3}{(1-\eta)^3} \,, \tag{34}$$

while the RF case is described by PY theory for which

$$\beta p^{PY} = \rho \frac{1+\eta+\eta^2}{(1-\eta)^3} \tag{35}$$

$$\beta\mu^{PY} = \ln(\rho) + \frac{14\eta-13\eta^2+5\eta^3}{2(1-\eta)^3} - \ln(1-\eta) \,. \tag{36}$$

We shall consider the bulk densities listed in Tab. 2 for which Roland has sent WB solutions from his program. The table includes the corresponding values of the chemical potential and pressure for WB and RF and the measured contact density and bulk density from DFT.

ρ_b	$\beta\mu^{CS}$	βp^{CS}	$\rho(0^+)$	$\rho(\infty)$
0.304665	0.595694569	0.6059833770	0.606117	0.304665
0.700782	7.022223696	4.010885555	4.005861	0.700778
0.856918	12.07055385	7.975603899	7.964882	0.85685

Table 1: Some bulk parameters for hard spheres for which we compare to WB DFT.

ρ_b	$\beta\mu^{PY}$	βp^{PY}	$\rho(0^+)$	$\rho(\infty)$
0.304665	0.6045291013	0.6080664640	0.607574	0.304665
0.700782	7.262472818	4.147334295	4.142281	0.70079
0.856918	12.72234559	8.437500280	x	y

Table 2: Some bulk parameters for hard spheres for which we compare to RF DFT.

I find that the agreement with the sum rule improves as I reduce the grid spacing. However, it is not as good as the data Roland sent me. I think that this is because Roland uses a more sophisticated extended quadrature for the convolutions (see page 16 of his

review). I've used the simplest rectangular case and this means I can't get away with such a large gid spacing. Things are improved by using a simple trapezoidal rule, which also circumvents a numerical problem associated with the fact that $\omega_3(|R|) = 0$, which under the simple quadrature leads to $n_3(-R) = 0$ (ie at the first grid point) . However $n_3 = 0$ blows up the last term in Φ^{WB}, so has to be avoided.

Fig. 1 shows a comparison of $\rho(z)$ near the wall produced by Roland with his progam, with the output from my program.

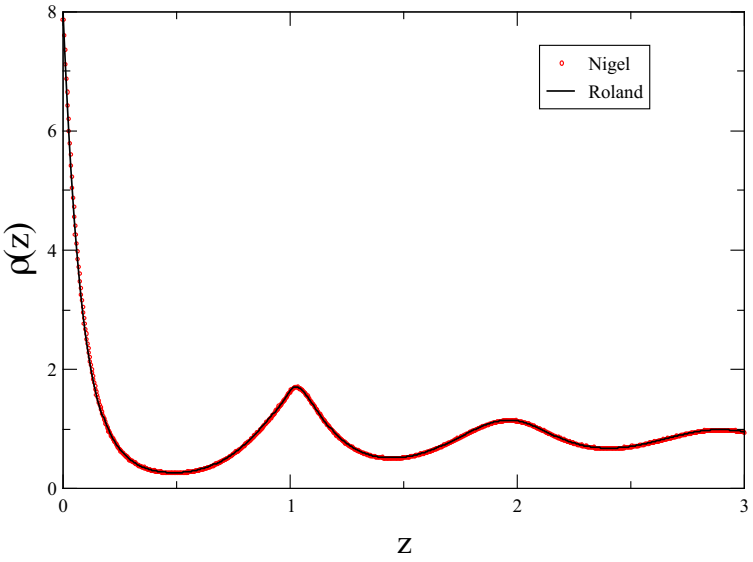

Figure 1: $\rho(z)$ DFT (White Bear functional) for hard spheres at a hard wall with $\rho_b = 0.856918$ Data is shown for my program and that of Roland published in Davidchack et al. The data overlap perfectly.

3 Extension to LJ-like ff interactions

Our approximate mean field (RPA) Helmholtz free energy functional is

$$\mathcal{F}[\rho(\mathbf{r})] = \mathcal{F}_{id}[\rho(\mathbf{r})] + \mathcal{F}_{ex}[\rho(\mathbf{r})] + \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\rho(\mathbf{r})\rho(\mathbf{r}')\phi_{\rm att}(|\mathbf{r}-\mathbf{r}'|) \tag{37}$$

where the last term on the RHS is a convolution.

In terms of the numerical procedure, this translates to solving

$$\rho_b(\mathbf{r}) = \exp\left[\beta\mu + c^{(1)}(\mathbf{r}) - \beta V_{ext}(\mathbf{r}) - \beta\int\ d\mathbf{r}'\rho(\mathbf{r}')\phi_{\rm att}(|\mathbf{r}-\mathbf{r}'|)\right]. \tag{38}$$

For a homogeneous system bulk phase behaviour can be found from the underlying equation of state as described in the next section. However we can also get this from DFT (which satisfies the underlying EOS). To do so we choose a periodic 1D grid and set the vector weighted densities to zero. We then have

$$\rho_b(z) = \exp\left[\beta\mu + c^{(1)}(z) - \beta\int\ 4\pi z'^2 dz'\rho(z')\phi_{\rm att}(|z-z'|)\right]\ , \tag{39}$$

where we have integrated over the volume of a sphere and assume $\rho(z')$ is constant. (Note that operationally we take the convolution with the wrap around version of ϕ_{att} so we need to multiple by 1/2 ie $\int_0^\infty 4\pi r^2\phi(r) \to \int_{-\infty}^{\infty} 2\pi r^2\phi(|r|)$.)

More generally for inhomogeneous systems, the integral in (38) will be more complicated. For planar geometry, we can do it by integrating over planes. Essentially we need to find the potential at some point a distance z from the wall due to an infinite plane of particles of density $\rho(z')$, a distance z' from the wall. The total potential energy at z is then obtained by integrating over all planes weighted by $\rho(z')$ of each plane.

The potential due to a single plane a distance $|z'-z|$ away is

$$u(|z-z'|) = 2\pi \int_0^\infty x\phi_{\rm att}(r)dx = 2\pi \int_{|z-z'|}^\infty r\phi_{\rm att}(r)dr \tag{40}$$

where $r = \sqrt{(z-z')^2+x^2}$ is the distance from the point at which we are calculating the potential to a point in the plane, and in the last equality we have changed the variable from x to r. This integral can be done analytically.

Hence we need to solve

$$\rho_b(z) = \exp\left[\beta\mu + c^{(1)}(z) - \beta\int_0^\infty dz'\rho(z')2\pi\int_{|z-z'|}^\infty r\phi_{\rm att}(r)dr\right]. \tag{41}$$

In this work we shall consider fluid-fluid interactions of the form:

$$\phi_{\rm att}(r) = \begin{cases} -\epsilon, & r < r_{\rm min} \\ 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], & r_{\rm min} < r < r_c\,, \\ 0, & r > r_c, \end{cases} \tag{42}$$

with $r_{min} = 2^{1/6}$. For this potential the form of the analytical integral depends on whether the distance to the plane is greater or less than $r_{\rm min}$. For $|z-z'| < r_{\rm min}$ one must consider the two parts of the potential seperately:

i.e

$$\int_{|z-z'|}^\infty r\phi_{\rm att}(r)dr = \int_{|z-z'|}^{r_{\rm min}} r\phi_{\rm att}(r)dr + \int_{r_{\rm min}}^{r_c} r\phi_{\rm att}(r)dr \tag{43}$$

Thus

$$\int_{|z-z'|}^\infty r\phi_{\rm att}(r)dr = \begin{cases} 0 & |z-z'| > r_c \\ \frac{2\epsilon}{5(|z-z'|)^{10}} - \frac{\epsilon}{(|z-z'|)^4} - \frac{2\epsilon}{5r_c^{10}} + \frac{\epsilon}{r_c^4}, & r_c > |z-z'| > r_{\rm min} \\ \frac{\epsilon}{2}((|z-z'|)^2 - r_{\rm min}^2) + \frac{2\epsilon}{5(r_{\rm min})^{10}} - \frac{\epsilon}{(|r_{\rm min})^4} - \frac{2\epsilon}{5r_c^{10}} + \frac{\epsilon}{r_c^4}, & |z-z'| < r_{\rm min}\,. \end{cases} \tag{44}$$

(Here one recognizes the similarity to the standard 10-4 planar wall potential which pertains to the full LJ potential.)

We consider the following wall-fluid potential

$$W_{\rm LR}(z) = \begin{cases} \infty, & z \le 0 \\ \epsilon_w\epsilon\left[\frac{2}{15}\left(\frac{\sigma}{z}\right)^9 - \left(\frac{\sigma}{z}\right)^3\right], & z > 0\,, \end{cases} \tag{45}$$

Incorporating this in (41) yields example results shown in Fig. 2. One sees the development of a drying layer at small attractive stengths.

3.1 Checks

The DFT seems to recover very accurately the exact PY bulk density far from the wall. If one moves off coexistence into the pure liquid phase then one can look at the approach to complete drying at a hard wall. The sum rule $k_BT\rho(0^+) = p$ should hold here. For

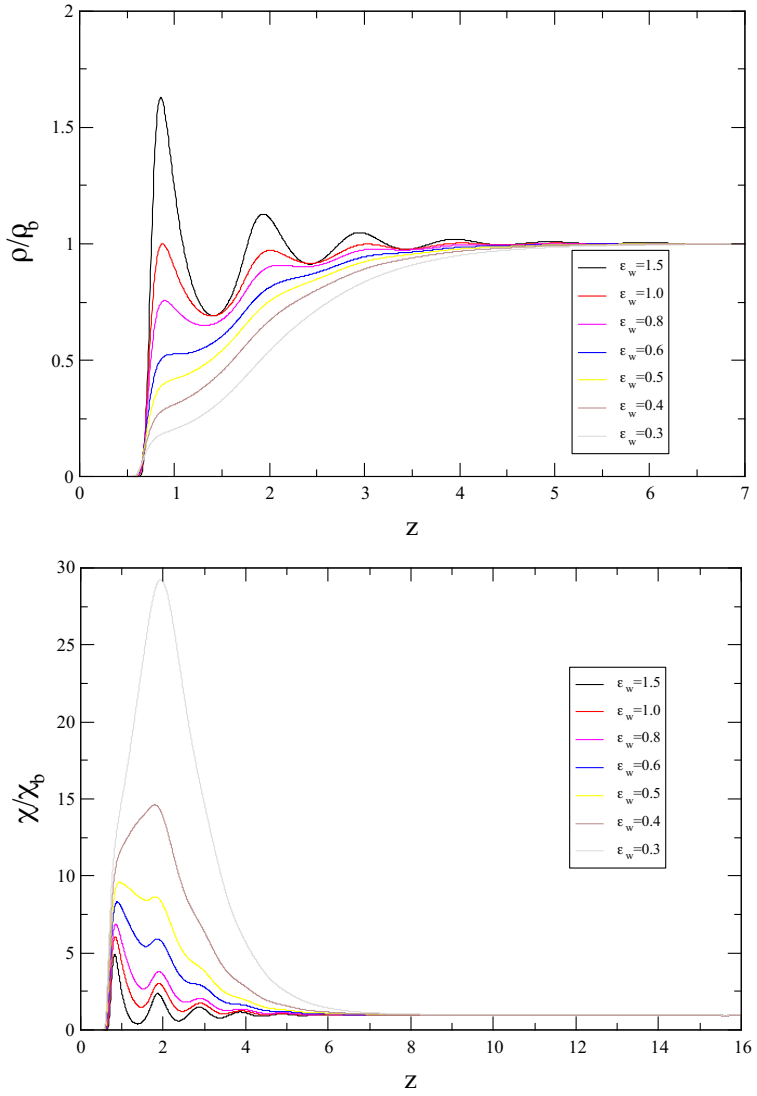

Figure 2: RF DFT results for the LJ model at a 9-3 attractive wall for various wall strengths ϵ_w. The coexistence state point is for $T = 0.775T_c$, see Sec. 4 for parameters.

$T = 1.022566 = 0.775T_c$, $\mu_{cx} = -3.8016747$ and one has $\rho_l = 0.597846$. I chose $\rho_b = 0.65$ (i.e. somewhat inside the liquid phase) for which, from (51) below, $\mu = -3.431279659$ and $p = 0.260866$. Setting a hard wall, I find $k_BT\rho(0^+) = 0.26107$ and $\rho(\infty) = 0.650004$. As another example closer to coexistence, consider $\rho_b = 0.61$. Here PY gives us that $\mu = -3.729785691$ and $p = 0.072476451$. Setting a hard wall, I find $k_BT\rho(0^+) = 0.07258$ and $\rho(\infty) = 0.610005$.

Another check valid beyond the hard wall case is the pressure sum rule for a continuous wall fluid potential:

$$p = -\int_0^\infty \frac{W_{\rm LR}(z)}{dz}\rho(z)dz = -\epsilon_w\epsilon\int_0^\infty \left(\frac{-6}{5}\left(\frac{\sigma^9}{z^{10}}\right) + 3\left(\frac{\sigma^3}{z^4}\right)\right)\rho(z)dz \qquad (46)$$

Here the idea is to measure the RHS and compare with the bulk pressure $p(\rho(\infty))$ given by the EOS. Let us work at coexistence where the bulk pressure is $p_{cx} = 0.029053$ for our temperature state point (see below). For $\epsilon_w = 0.15$ I measure the RHS of (46) to

be 0.029079, while for $\epsilon_w = 1.0$, I get 0.029077 and for $\epsilon_w = 2.0$ I get 0.029080. All this seems pretty good particularly when one notes that the PY pressure is very sensitive to the value of the liquid phase density. For instance the pressure discrepancy here in the 4th s.f. corresponds to a change of 10^{-5} in the density. One should also note that our quadrature is not very sophisticated either for the convolutions or the integral (46).

Yes another check is to see to what extent the Gibb's adsorption theorem is satisfied. This states that the adsorption:

$$\Gamma \equiv \int_0^\infty (\rho(z) - \rho_b) dz = -\left(\frac{d\gamma}{d\mu}\right) . \tag{47}$$

Here γ is the surface tension, which can be calculated from

$$\gamma = \frac{\Omega_{ex}}{A} = \frac{\Omega + pV}{A} \tag{48}$$

In DFT this is obtained as

$$\gamma = \beta^{-1} \int dz(\Phi_{id}(z) + \Phi_{ex}(\{n_\alpha\})) + \frac{1}{2} \int dz \rho(z) \int dz' \rho(z') \phi_{att}(z - z') + p \int dz \, , \tag{49}$$

where $\Phi_{id}(z) = \rho(z)(\ln \rho(z) - 1 + V_{ext}(z) - \mu)$. [1]

For $\epsilon_w = 1.5$, I get $\Gamma = -0.730711$, $-d\gamma/d\mu = -0.730706$; for $\epsilon_w = 1.0$, I get $\Gamma = -0.901037$, $-d\gamma/d\mu = -0.901046$; for $\epsilon_w = 0.15$, I get $\Gamma = -1.996297$, $-d\gamma/d\mu - 1.998021$.

4 Bulk behaviour

In the case of attractive interactions, one has a liquid-vapor phase transition. The properties of this are known exactly because the DFT satisfies the underlying PY or CS free energy and the RPA approximation leads to an extended van-der-Waals form for the pressure. Within PY one has

$$\mu = k_B T \left(\ln(\rho) + \frac{14\eta - 13\eta^2 + 5\eta^3}{2(1-\eta)^3} - \ln(1-\eta) \right) + 4\pi\rho \int dr r^2 \phi_{\rm att}(r) \tag{50}$$

$$p = k_B T \rho \frac{1 + \eta + \eta^2}{(1-\eta)^3} + 2\pi\rho^2 \int_0^\infty dr r^2 \phi_{att}(r) \tag{51}$$

For the truncated LJ-like potential eq. (42), the value of the integral is -1.171861897ϵ. We find coexistence densities by numerically solving $p(\rho_v) - p(\rho_l) = 0$ and $\mu(\rho_v) - \mu(\rho_l) = 0$ simultaneously. I do this using a Newton-Raphson approach for non-linear systems of equations (CH 9.6 of Numerical Recipes). This is convenient because the Jacobian can be calculated analytically. The results are shown in Fig. 3 ($\rho - T$ plane) and Fig. 4 ($T - p$ and $T - \mu$ planes).

As regards critical properties, Bob has calculated that for the full attractive potential $k_B T_c/\epsilon = 1.41539$, while for the version that is truncated at $r_c = 2.5\sigma$ one has $k_B T_c/\epsilon = 1.319440$. The critical density is $\sigma^3 \rho_c = 0.24913$ (WB) and $\sigma^3 \rho_c = 0.2457358$ (RF). Inserting ρ_c and T_c, in (51) gives the critical pressure in RF as $p_c = 0.11666$. μ_c is given by

[1] Note Φ_{ex} is a function of the weighted densities and therefore vanishes at $z = -R$, while Φ_{id} is proportional to the local density and vanishes at $z = 0$. So we have to shift Φ_{id} by $\delta z = -R$ before we add it to Φ_{ex} and the upper integration limit differs by one radius R.

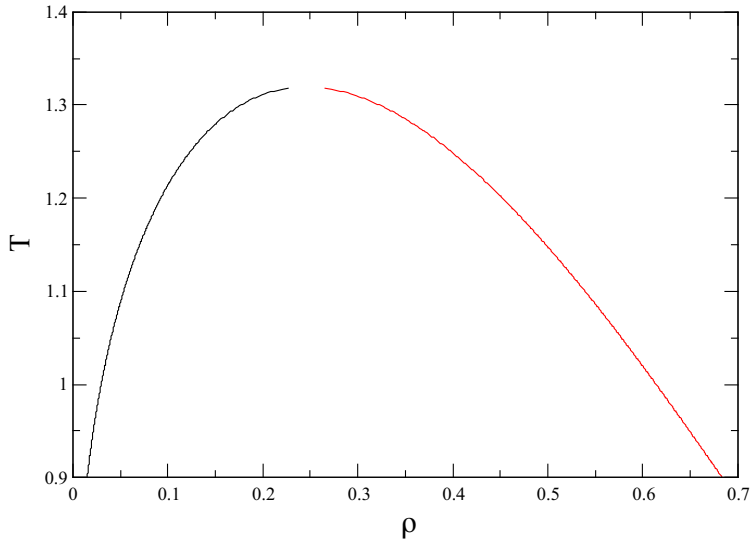

Figure 3: Mean field $\rho - T$ phase diagram of the PY system that underlies the RF DFT.

$$\beta\mu_c = \ln(\rho_c) + \frac{(14\eta - 13\eta^2 + 5\eta^3)}{2(1-\eta)^3} - \ln(1-\eta) - \frac{\partial}{\partial\rho}\left[\frac{\rho(1+\eta+\eta^2)}{(1-\eta)^3}\right] \tag{52}$$

evaluated at $\eta = \eta_c$. This gives $\mu_c = -3.6964267$. One coexistence state point of interest (see paper) is that for which $T = 0.775T_c = 1.022566$. For this I find $\mu_{cx} = -3.8016747, p_{cx} = 0.029053, \rho_v = 0.034306, \rho_l = 0.597846$.

One can also get the bulk properties from DFT using Eq. (39) and the results should be consistent with the above. Fig. 5 shows that they are.

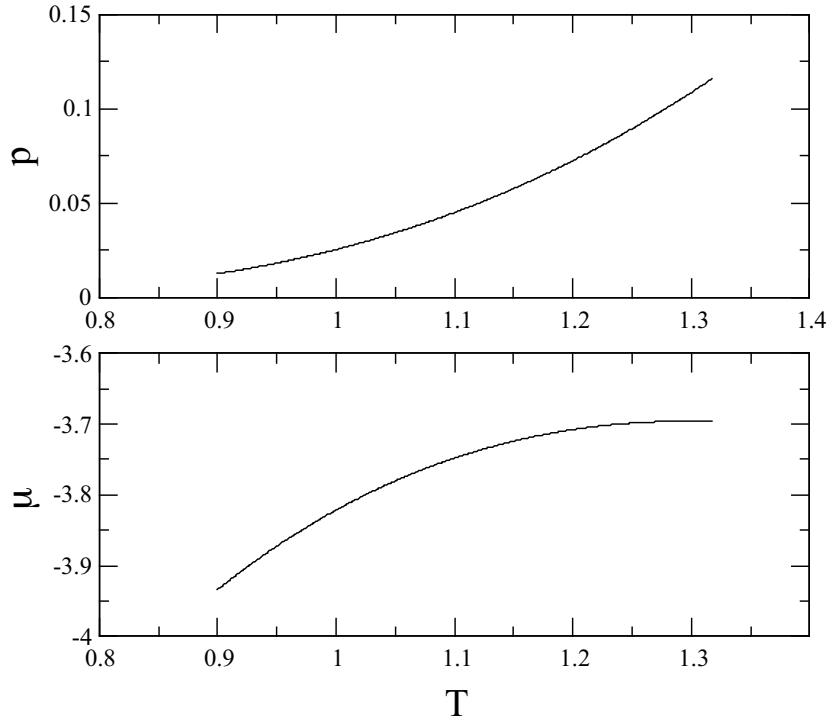

Figure 4: Mean field $T-p$ and $T-\mu$ phase diagrams of the PY system that underlies the RF DFT. Criticality is at $T = 1.3194$.

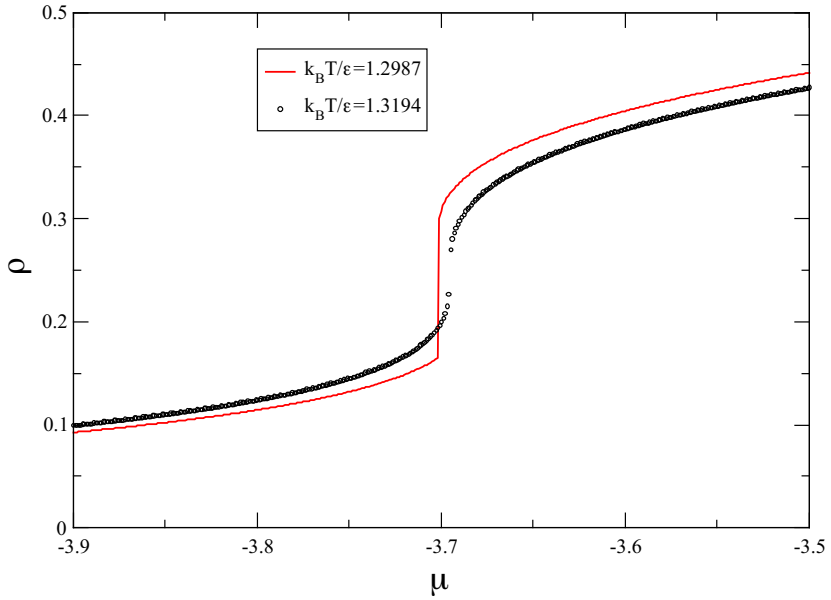

Figure 5: Plot of $\rho(\mu)$ in the bulk calculated from DFT using Φ^{RF}. The potential is truncated at $r_c = 2.5\sigma$. Data is shown for the critical temperature $T = 1.3194$ and a slightly subcritical temperature $T = 1.2987$