

Computing Excess Chemical Potential using Thermodynamic Integration

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Abstract

In this work, we calculate the change in excess chemical potential using Thermodynamic Integration between two states having same temperature and number of particles but with different densities. We apply the method to Lennard-Jones liquid and use results of hard-sphere liquid to validate the method. The thermodynamic properties eg. pressure are calculated using HALMD package [1]

1 Introduction

Chemical potential is a central concept in thermodynamics as all of the thermodynamic properties of a substance at a given pressure and temperature can be obtained by knowledge of its chemical potential. The chemical potential determines stability of substances and their tendency of transition from one physical state to another. The chemical potential of any species is defined as a change in Gibbs free energy on inclusion of single particle to the system under constant pressure and temperature. So, for calculation of chemical potential, we need to compute free energy. But free energy depends on phase space volume and not directly measurable in simulations or experiments except few cases e.g. ideal gas phase, low temperature harmonic crystal. Therefore, free energy is always calculated as a difference or relative to a particular state. It is usually taken as Helmholtz(N,V,T) or Gibbs(N,P,T) free energy. Free energy helps us to understand about a process and its probability to adapt to a particular state. Moreover, it also helps in studying phase transitions, critical phenomena or other transformations. In this section, we read brief definitions and explanations of the key terms which are used in this work.

1.1 Definitions:

1.1.1 Thermodynamic Equations:

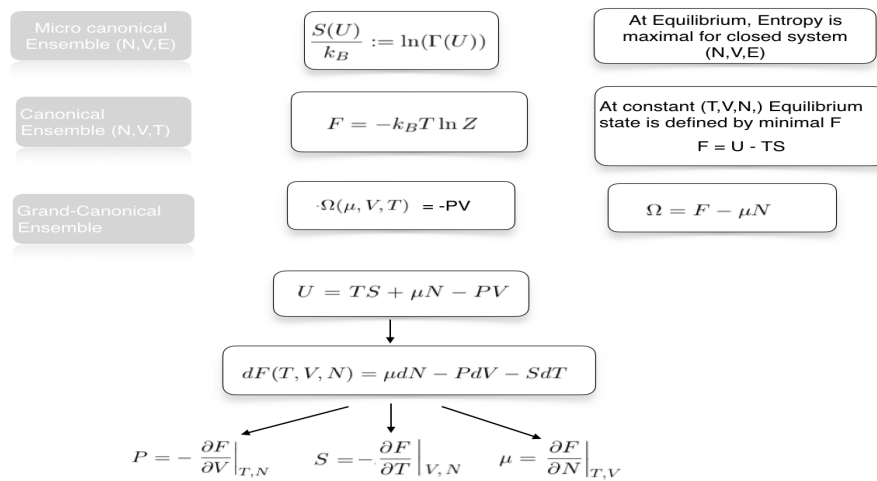


Figure 1.1: Thermodynamic equations

In figure 1.1, U, F, S represent internal energy, Helmholtz free energy and entropy of the system respectively at given thermodynamic conditions temperature T, pressure P, volume V and number of particles N. Chemical potential is represented by μ .

1.1.2 Helmholtz Free Energy:

For a system with fixed temperature T, volume V, and number of particles N, the Helmholtz free energy is written as

$$F = U - TS \quad (1.1)$$

where U, T, S are internal energy, temperature and entropy of the system respectively. Helmholtz free energy of a system in canonical ensemble depends on partition function Q and is defined as

$$F = -K_B T \ln Q(N, V, T) = -K_B T \ln \left(\frac{\int e^{-\beta U(p^N, r^N)} dp^N dr^N}{\Lambda^{dN} N!} \right) \quad (1.2)$$

where $\beta = \frac{1}{k_B T}$ and $\Lambda = \frac{h}{\sqrt{2\pi m K_B T}}$ is the thermal wavelength.

The partition function for a system of N particles in a cubic volume with diameter L and volume $V = L^d$ at constant temperature T is given by[2]

$$Q(N, V, T) = \frac{V^N}{\Lambda^{dN} N!} \int_0^1 \dots \int_0^1 ds^N e^{-\beta U(s^N, L)} \quad (1.3)$$

where $s^N = r^N/L$ are scaled coordinates.

So, the expression for the Helmholtz Free energy of the system is

$$\begin{aligned} F(N, V, T) &= -K_B T \ln Q(N, V, T) = -K_B T \ln \left(\frac{V^N}{\Lambda^{dN} N!} \right) - K_B T \ln \int ds^N e^{-\beta U(s^N, L)} \\ &= F_{id}(N, V, T) + F_{ex}(N, V, T) \end{aligned} \quad (1.4)$$

Thus, the Helmholtz free energy is expressed as combination of ideal gas and an excess part.

1.1.3 Gibbs Free Energy:

For a system of N particles at constant pressure P and temperature T, the Gibbs free energy is defined as

$$G = F + PV = \mu N \quad (1.5)$$

and G is at a minimum for a system at equilibrium.

1.1.4 Chemical Potential:

For a system of more than one particle species(e.g. α, β), chemical potential μ of a particular species α is defined as the derivative of the free energy with respect to the respective particle number N_α [2].

$$\begin{aligned} \mu_\alpha &= \left(\frac{\partial F}{\partial N_\alpha} \right)_{V, T, N_{\beta \neq \alpha}} \\ &= \left(\frac{\partial G}{\partial N_\alpha} \right)_{P, T, N_{\beta \neq \alpha}} \end{aligned} \quad (1.6)$$

For a single species system, we drop the subscript and chemical potential is given as

$$\mu_\alpha = \left(\frac{\partial F}{\partial N} \right)_{V,T,N} \quad (1.7)$$

In other words, for sufficiently large N, chemical potential can be defined as the change of free energy when one particle is being inserted into the system under fixed temperature T and volume V. Therefore, for single species system with sufficiently large N, chemical potential can be defined as

$$\mu = F_{N+1} - F_N$$

Using the definition of free energy,

$$\begin{aligned} \mu &= -k_B T \ln (Q_{N+1}/Q_N) = -k_B T \ln \left(\frac{V/\Lambda^d}{N+1} \right) - k_B T \ln \left(\frac{\int ds^{N+1} e^{-\beta U(s^{N+1})}}{\int ds^N e^{-\beta U(s^N)}} \right) \\ &\equiv \mu_{id}(\rho) + \mu_{ex} \end{aligned} \quad (1.8)$$

Now, the chemical potential has been separated into ideal gas contribution and the excess part.

1.1.5 Excess Chemical Potential:

The excess chemical potential μ_{ex} is defined as the difference of chemical potential of a given species and an ideal gas under the same thermodynamic conditions. We separate the potential energy of (N+1) particle system into two parts.

1. Potential energy $U(s^N)$ of the N-particle system
2. Interaction potential energy of the $(N+1)^{th}$ particle with other particles.

Thus, $\Delta U = U(s^{N+1}) - U(s^N)$ and using equation (1.12), we can write μ_{ex} as

$$\mu_{ex} = -k_B T \ln \int ds_{N+1} \langle e^{-\beta \Delta U} \rangle_N$$

where $\langle \dots \rangle_N$ denotes canonical ensemble averaging over the configuration space of N-particle system. We can also derive a general expression of excess chemical potential as follows:

Using figure 1.1,

$$P(V, T, N) = - \frac{\partial F(V, T, N)}{\partial V} \quad (1.9)$$

Or,

$$\Delta F = - \int_i^f P dV = N \int_{\rho_i}^{\rho_f} \frac{P}{\rho^2} d\rho \quad (1.10)$$

Or, we can write

$$\frac{\beta \Delta F}{N} = \int_{\rho_i}^{\rho_f} \frac{\beta P}{\rho} \frac{d\rho}{\rho}$$

For ideal gas, $\frac{\beta P}{\rho} = 1$ and $\Delta F_{ex} = \Delta F - \Delta F_{id}$, so

$$\frac{\beta \Delta F_{ex}}{N} = \int_{\rho_i}^{\rho_f} \left(\frac{\beta P}{\rho} - 1 \right) \frac{d\rho}{\rho} \quad (1.11)$$

when $\rho_i = 0$, $\Delta F_{ex} = F_{ex}$, Therefore,

$$\frac{\beta F_{ex}}{N} = \int_0^{\rho_f} \left(\frac{\beta P}{\rho} - 1 \right) \frac{d\rho}{\rho} \quad (1.12)$$

Furthermore, by definition of excess chemical potential,

$$\mu_{ex} = \frac{\partial F_{ex}}{\partial N}$$

or,

$$\begin{aligned}\beta\mu_{ex} &= \frac{\partial \beta F_{ex}}{\partial N} = \frac{\partial}{\partial \rho} \left[\rho \int_0^{\rho_f} \left(\frac{\beta P}{\rho} - 1 \right) \frac{d\rho}{\rho} \right] \\ &= \int_0^{\rho_f} \left(\frac{\beta P}{\rho} - 1 \right) \frac{d\rho}{\rho} + \frac{\beta P}{\rho} - 1 \\ &= \beta \frac{F_{ex}}{N} + \frac{\beta P}{\rho} - 1\end{aligned}$$

So,

$$N\mu_{ex} = F_{ex} + PV - NK_B T \quad (1.13)$$

In the expression(1.13), $NK_B T$, PV corresponds to ideal and real parts respectively. Therefore expression(1.13) gives us total excess Gibbs free energy for a given P , V , N , T .

At constant T , N we can write,

$$\Delta\mu_{ex} = \frac{\Delta F_{ex}}{N} + \Delta\left(\frac{P}{\rho}\right) \quad (1.14)$$

using equation (1.11) and (1.14), we can write

$$\Delta\mu_{ex} = \frac{1}{\beta} \int_{\rho_i}^{\rho_f} \left(\frac{\beta P}{\rho} - 1 \right) \frac{d\rho}{\rho} + \Delta\left(\frac{P}{\rho}\right)$$

or,

$$\Delta\mu_{ex} = \int_{\rho_i}^{\rho_f} \frac{P}{\rho^2} d\rho - K_B T \ln\left(\frac{\rho_f}{\rho_i}\right) + \left(\frac{P_f}{\rho_f} - \frac{P_i}{\rho_i}\right) \quad (1.15)$$

Here, $\int_{\rho_i}^{\rho_f} \frac{P}{\rho^2} d\rho - K_B T \ln\left(\frac{\rho_f}{\rho_i}\right)$ corresponds to change in excess Helmholtz free energy $\frac{\Delta F_{ex}}{N}$ and $\left(\frac{P_f}{\rho_f} - \frac{P_i}{\rho_i}\right)$ is additional change in excess part because of change in P and ρ at constant T , N between two states.

2 Method used for calculation of change in Excess chemical potential:

The change in excess chemical potential $\Delta\mu_{ex}$ is calculated for desired density range under given temperature and number of particles.

2.1 Calculation of change in Helmholtz free energy :

As in section 1.1.2, we see the free energy is not simply average of functions of the phase space coordinates of the system. It is rather directly related to the volume in phase space that is accessible to a system. However, we can determine pressure in experiments or simulations which is expressed as the derivative of the free energy. So using (1.10)

$$\Delta F = - \int_i^f P dV = N \int_{\rho_i}^{\rho_f} \frac{P}{\rho^2} d\rho \quad (2.1)$$

Therefore, free energy difference between two desired states can be calculated by numerical Integration techniques. This method is called as Thermodynamic Integration.

2.2 Calculation of change in Gibbs free energy:

As we know, Gibbs free energy is written as:

$$G = F + PV = \mu N \quad (2.2)$$

so, we calculate the ΔG between the two states as

$$\Delta G = \Delta F + \Delta(PV) = \Delta F + P_f V_f - P_i V_i = N \int_{\rho_i}^{\rho_f} \frac{P}{\rho^2} d\rho + N \left(\frac{P_f}{\rho_f} - \frac{P_i}{\rho_i} \right) \quad (2.3)$$

2.3 Calculation of change in Chemical potential :

For constant N,

$$\Delta G = \Delta \mu N \quad (2.4)$$

using equation 2.3,

$$\Delta \mu = \frac{\Delta F}{N} + \left(\frac{P_f}{\rho_f} - \frac{P_i}{\rho_i} \right) \quad (2.5)$$

Or,

$$\Delta \mu = \int_{\rho_i}^{\rho_f} \frac{P}{\rho^2} d\rho + \left(\frac{P_f}{\rho_f} - \frac{P_i}{\rho_i} \right) \quad (2.6)$$

2.4 Calculation of change in Ideal chemical potential:

Using equation (1.8),

$$\mu_{id} = -k_B T \ln \left(\frac{V/\Lambda^d}{N+1} \right) = k_B T \ln (\Lambda^d \rho)$$

Therefore,

$$\Delta \mu_{id} = k_B T_i \ln (\Lambda^d \rho_f) - k_B T_f \ln (\Lambda^d \rho_i)$$

if $T_f = T_i = T$

$$\Delta \mu_{id} = k_B T \ln \left(\frac{\rho_f}{\rho_i} \right) \quad (2.7)$$

2.5 Calculation of change in Excess chemical potential:

Using equation (1.8),

$$\Delta \mu_{ex} = \Delta \mu - \Delta \mu_{id} \quad (2.8)$$

Using equation (2.6) and (2.7),

$$\Delta \mu_{ex} = \int_{\rho_i}^{\rho_f} \frac{P}{\rho^2} d\rho - K_B T \ln \left(\frac{\rho_f}{\rho_i} \right) + \left(\frac{P_f}{\rho_f} - \frac{P_i}{\rho_i} \right) \quad (2.9)$$

We see the resultant expression of method is same as general expression of $\Delta \mu_{ex}$ in equation (1.15).

3 Method used in reference papers for Chemical potential

In one of the reference paper[3] used in this work, the chemical potential is determined using Integral OZ equation theory. The chemical potential is calculated within the framework of exact series of bridge functionals under certain assumptions. The excess chemical potential is defined as

$$\beta\mu = -4\pi n \int C^{(1)}(r)r^2 dr \quad (3.1)$$

where $C^{(1)}(r)$: one particle direct correlation function has the form

$$C^{(1)}(r) = [h(r) - \omega(r)] - 0.5h(r)[\omega(r) + B^{(1)}[r]] \quad (3.2)$$

where $h(r)$ is correlation function, ω is thermal potential and $B^{(1)}[r]$ is bridge functional.

To evaluate the expression (3.2), non local bridge functional $B^{(1)}[r]$ is approximated with help of local bridge functions $B^{(1)}(r)$ and $B^{(2)}(r)$ and certain assumptions like linear dependence of potential with coupling parameter are used.

The other paper which is used as reference is work by J. Karl Johnson et.al [7]. The paper presents an equation of state for cut and shifted LJ liquids and compares it to simulation results. The equation of state is mentioned in section 5.2.2.

4 Excess chemical potential for Hard sphere liquid

The Hard sphere(HS) system is defined as a system composed of impenetrable spheres which interact with the following inter-molecular pair potential,

$$\Phi(r) = \begin{cases} \infty & r < \sigma \\ 0 & r \geq \sigma \end{cases}$$

where r is the separation of a pair of spheres and σ is their diameter.

In this work, we will follow the Carnahan-Starling approximation which gives a simple but very accurate equation of state for hard sphere liquids. Other formulations have been devised but the simple form of the Carnahan-Starling equation makes it very convenient for use in thermodynamic calculations. This formulation is used to validate the numerical approach mentioned in section 2. The equation of state as per Carnahan-Starling approximation[4]:

$$\frac{\beta P}{\rho} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad (4.1)$$

where $\eta = \pi\rho\sigma^3/6$ is termed as volume fraction or packing fraction of fluid which is the volume occupied by the spheres divided by the volume available.

Using result of equation(4.1), we can write

$$\int_{\rho_i}^{\rho_f} \frac{P}{\rho^2} d\rho = \frac{1}{\beta} \int_{\eta_i}^{\eta_f} \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \frac{d\eta}{\eta} \quad (4.2)$$

Furthermore, analytical expression for excess Helmholtz free energy for HS liquid[4]:

$$\frac{\beta F_{ex}}{N} = \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} \quad (4.3)$$

The results of HS liquid are used to test the numerical approach.

5 Parameters and Results:

5.1 Parameters:

The change in excess chemical potential ($\Delta\mu_{ex}$) for LJ liquid is calculated with following parameters. All quantities are in reduced LJ units.

1. Temperature $T^* = 2.74$
2. Number of particles : 10000
3. Density ranges : (0.1 - 0.2) , (0.2 - 0.3),, (0.9 - 1.0)
4. For calculation of Lennard-jones potentials, smooth truncation[5] and cut-off radius $r_c = 4\sigma$ is used.
5. The simulation time is calculated as per below formula to ensure that lower density values have longer simulation time.

$$simulation\ time = \frac{1000}{(1 + 0.2\rho)}$$

The time of simulation step is taken as 0.005.

5.2 Results:

5.2.1 Testing for calculated pressure :

For test check for pressure calculated using simulation in step 2.1, the values are compared with the paper published by J. Karl Johnson et. al [7]. The pressure values are calculated for one parameter set $T^* = 1.3$ and $N = 864$ and cut-off = 4. The results are shown in figure 5.1.

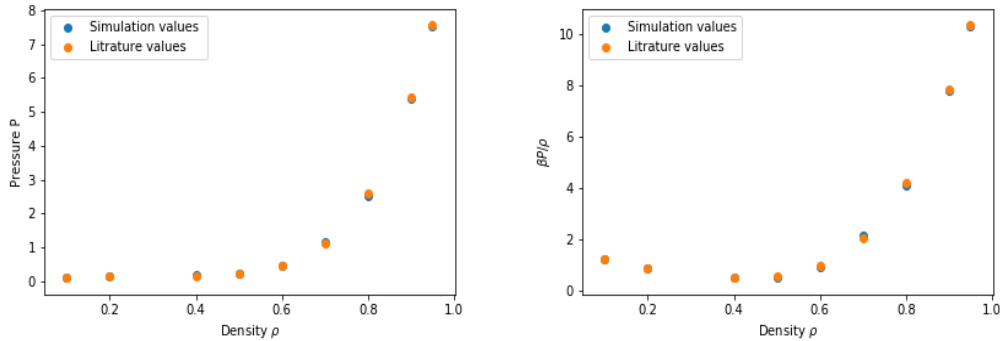


Figure 5.1: Comparison of pressure and compressibility factor between simulation and literature values

Figure 5.1 shows simulation results are quite similar to literature values. Furthermore, the values of $\frac{\beta P}{\rho}$ also show the desired pattern [8] which shows simulation outputs are close to correct values.

5.2.2 Testing for calculated Free energy difference $\frac{\Delta F}{N}$:

To test the values of calculated free energy difference, analytical solution for $\frac{\Delta F}{N}$ is calculated using the equation of state given in the paper published by J. Karl Johnson et.all [7]. According to paper, the equation of state for LJ liquid is expressed as:

$$P = \rho T + \sum_{i=1}^8 a_i \rho^{i+1} + F \sum_{i=1}^6 b_i \rho^{2i+1} \quad (5.1)$$

where $F = \exp(-\gamma\rho^2)$ and $\gamma = 3$ and quantities are in LJ reduced units.

The table 5.1 and 5.2 lists the values of coefficients a_i and b_i and parameters x_j as mentioned in paper.

i	a_i	b_i
1	$x_1T + x_2\sqrt{T} + x_3 + x_4/T + x_5/T^2$	$x_{20}/T^2 + x_{21}/T^4$
2	$x_6T + x_7 + x_8/T + x_9/T^2$	$x_{22}/T^2 + x_{23}/T^4$
3	$x_{10}T + x_{11} + x_{12}/T$	$x_{24}/T^2 + x_{25}/T^3$
4	x_{13}	$x_{26}/T^2 + x_{27}/T^4$
5	$x_{14}/T + x_{15}/T^2$	$x_{28}/T^2 + x_{29}/T^3$
6	x_{16}/T	$x_{30}/T^2 + x_{31}/T^3 + x_{32}/T^4$
7	$x_{17}/T + x_{18}/T^2$	
8	x_{19}/T^2	

Table 5.1: a_i and b_i coefficients values

j	x_j	j	x_j
1	0.8623085097507421	17	6.398607852471505e1
2	2.976218765822098	18	1.603993673294834e1
3	-8.402230115796038	19	6.805916615864377e1
4	0.1054136629203555	20	-2.791293578795945e3
5	-0.8564583828174598	21	-6.245128304568454
6	1.582759470107601	22	-8.116836104958410e3
7	0.7639421948305453	23	1.488735559561229e1
8	1.753173414312048	24	-1.059346754655084e4
9	2.798291772190376e3	25	-1.131607632802822e2
10	-4.8394220260857657e-2	26	-8.867771540418822e3
11	0.9963265197721935	27	-3.986982844450543e1
12	-3.698000291272493e1	28	-4.689270299917261e3
13	2.084012299434647e1	29	2.593535277438717e2
14	8.305402124717285e1	30	-2.694523589434903e3
15	-9.574799715203068e2	31	-7.218487631550215e2
16	-1.477746229234994e2	32	1.721802063863269e2

Table 5.2: x_j values

$\rho_f - \rho_i$	$\frac{\Delta F}{N}$ using analytical results	$\frac{\Delta F}{N}$ using project method
0.1 - 0.2	1.863	1.881
0.2 - 0.3	1.133	1.153
0.3 - 0.4	0.884	0.909
0.4 - 0.5	0.807	0.834
0.5 - 0.6	0.833	0.859
0.6 - 0.7	0.944	0.967
0.7 - 0.8	1.133	1.155
0.8 - 0.9	1.407	1.432
0.9 - 1.0	1.778	1.806

Table 5.3: Comparison of $\frac{\Delta F}{N}$ for LJ liquids at $T^* = 2.74$

For parameter set given in section 5.1, free energy difference $\frac{\Delta F}{N}$ is calculated using equation of state(5.1) and compared with corresponding numerical results by the method of this work. Table 5.3 includes the comparison. The values are close to literature values which validates that the method used to calculate free energy difference using simulation pressure values is correct.

For each density range, values of $\Delta\mu_{ex}$ is calculated using the analytical results of table 5.3, calculating ΔF_{ex} by subtracting ΔF_{id} and putting them into equation (1.14). The values are expressed as $\Delta\mu_{ex}^{(jk)}$ and listed in table 5.5.

5.2.3 Testing for calculation of $\Delta\mu_{ex}$:

A test check of numerical method for $\Delta\mu_{ex}$ (section 2.2 - 2.5) is carried out with the help of analytical results of HS liquids. The results of equation (4.1) and equation (4.2) are used in equation (1.14) to get analytical results of $\Delta\mu_{ex}$. The numerical results are obtained by numerical integration of equation (4.2) and putting them into equation (2.9). Table 5.4 shows the step-wise results.

T*	Numerical results					Analytical results	
	$\rho_f - \rho_i$	$\frac{\Delta F}{N}$	$\frac{P_f}{\rho_f} - \frac{P_i}{\rho_i}$	$\Delta\mu$	$\Delta\mu_{id}$	$\Delta\mu_{ex}$	$\Delta\mu_{ex}$
2.74	0.1 - 0.2	2.6048	0.5912	3.1959	1.8992	1.2967	1.2967
	0.2 - 0.3	1.9291	0.7323	2.6614	1.1109	1.5504	1.5504
	0.3 - 0.4	1.7466	0.912	2.6586	0.7882	1.8703	1.8703
	0.4 - 0.5	1.7471	1.1445	2.8915	0.6114	2.2801	2.2801
	0.5 - 0.6	1.8633	1.4506	3.3139	0.4996	2.8144	2.8144

Table 5.4. Test check of Numerical method with help of HS liquid results

We get numerical results same as analytical results. The numerical integration is calculated using `scipy.quad()` function [6] with parameters `epsabs`(absolute error tolerance) and `epsrel`(relative error tolerance) as 1% . This validates the correctness of the steps (2.2) - (2.5) of numerical method.

5.2.4 Application of the method to LJ liquids:

The step-wise results of application of the method to LJ liquids are listed in Table 5.5. The table compares the calculated change in excess chemical potential($\Delta\mu_{ex}$) with reference values for each density range. For each range, the average relative unbiased estimate of variance of pressure ($\frac{\delta P}{P}$) is also included. The plots of pressure vs density of simulation is shown in figure 5.1.

T*	Numerical results					Reference Values				
	$\rho_f - \rho_i$	$\frac{\delta P}{P}(\%)$	$\frac{\Delta F}{N}$	$\frac{P_f}{\rho_f} - \frac{P_i}{\rho_i}$	$\Delta\mu$	$\Delta\mu_{id}$	$\Delta\mu_{ex}$	$\Delta\mu_{ex}^{(jk)}$ [7]	$\Delta\mu_{ex}^{(s)}$ [3]	$\Delta\mu_{ex}^{(c)}$ [3]
2.74	0.1 - 0.2	0.012	1.881	0.064	1.944	1.899	0.045	0.027	0.003	-0.006
	0.2 - 0.3	0.032	1.154	0.223	1.376	1.111	0.265	0.244	0.075	0.066
	0.3 - 0.4	0.059	0.909	0.418	1.327	0.788	0.538	0.513	0.179	0.169
	0.4 - 0.5	0.082	0.834	0.748	1.582	0.611	0.971	0.944	0.335	0.321
	0.5 - 0.6	0.101	0.859	1.239	2.099	0.499	1.599	1.573	0.567	0.546
	0.6 - 0.7	0.109	0.967	1.941	2.908	0.422	2.486	2.461	0.893	0.864
	0.7 - 0.8	0.111	1.155	2.923	4.079	0.366	3.713	3.690	1.328	1.311
	0.8 - 0.9	0.105	1.432	4.163	5.595	0.323	5.273	5.248	1.905	1.921
	0.9 - 1.0	0.0986	1.806	5.855	7.661	0.289	7.372	7.344	2.663	2.743

Table 5.5. Numerical results for LJ liquid

$\Delta\mu_{ex}^{(jk)}$ are results using equation of state in reference paper [7] as given in section 5.2.2

$\Delta\mu_{ex}^{(s)}$ are simulation results of reference paper[3]

$\Delta\mu_{ex}^{(c)}$ are calculated results of reference paper[3]

Figure 5.2 shows desired pattern for pressure values for each density range. The results in table 5.5 shows deviation from the values from paper by Gari Sarkisov [3], However, on the other hand, the numerical results are close to the values which are obtained using the analytical expression given in paper by J. Karl Johnson et. al[7] for LJ liquids. In addition, the method gives correct results for Hard-sphere liquids as mentioned in section 5.2.1 and 5.2.3. The method also satisfies the test check for simulation outputs and for change in free energy($\Delta F/N$) in section 5.2.1 and 5.2.2 respectively. The deviation from reference results

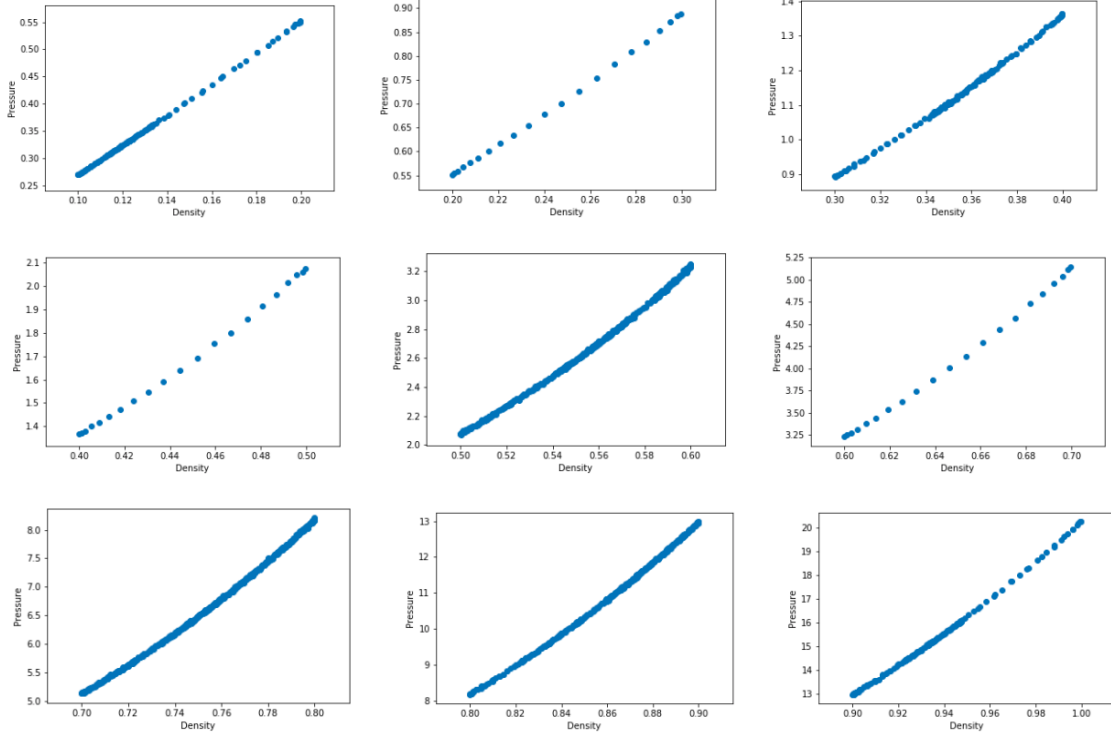


Figure 5.2: Pressure vs Density plots for each density range

$(\Delta\mu_{ex}^{(jk)})$ should be because of cut-off radius as it is observed that as the cut-off is increased, deviation from reference values is decreased which also supports the fact that with increasing cut-off radius, more interactions within liquid are measured and numerical results should approach to reference values. Another source of deviation can be because of the reason that in paper[7], cut and shifted potential is used, while cut and smooth truncation is used in this work. The other source of deviation can be due to the simulation time, as it is also observed during the work that with increasing simulation time, the results approach the literature values. However, a sufficient simulation time is used. Moreover, the average percentage value of relative unbiased estimate of variance ($\frac{\delta P}{P}$) are either close to 0.1 or smaller. This also supports the correctness of simulation results.

5.3 Other routes to Thermodynamic Integration

In simulations, we are not limited to physical integration path, rather we can use all parameters in the potential energy function as thermodynamic variables. We consider potential energy function U to depend on coupling parameter λ linearly. The reference system is denoted by $\lambda = 0$, while $\lambda = 1$ corresponds to our system of interest.

$$U(\lambda) = (1 - \lambda)U_0 + \lambda U_1$$

So we can write partition function for this system :

$$Q(N, V, T, \lambda) = \frac{1}{\Lambda^{3N} N!} \int dr^N \exp[-\beta U(\lambda)]$$

So the derivative of Helmholtz free Energy with respect to λ :

$$\left(\frac{\partial F(\lambda)}{\partial \lambda}\right)_{N,V,T} = -\frac{1}{\beta} \frac{\partial}{\partial \lambda} \ln Q(N, V, T, \lambda) = \frac{1}{\beta Q(N, V, T, \lambda)} \frac{\partial Q(N, V, T, \lambda)}{\partial \lambda}$$

$$\begin{aligned}
&= \frac{\int dr^N (\partial U(\lambda)/\partial \lambda) \exp[-\beta U(\lambda)]}{\int dr^N \exp[-\beta U(\lambda)]} \\
&= \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_{\lambda}
\end{aligned}$$

and we can write free energy difference as :

$$F(\lambda = 1) - F(\lambda = 0) = \int_{\lambda=0}^{\lambda=1} d\lambda \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_{\lambda} \quad (5.2)$$

If we consider LJ fluids, the Lennard jones potential between two particles of species i and species j is represented by

$$U_{LJ}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

For example, we can choose interaction strength ϵ_{ij} as a coupling parameter to vary it from 0 to 1 and calculate ensemble average of potential energy $\left\langle \frac{U(\epsilon)}{\partial \epsilon} \right\rangle_{\epsilon}$ using simulation and calculate free energy difference with equation(5.2) using numerical integration schemes. Thermodynamic Integration method gives us flexibility to use different variables as parameters and expresses free energy difference in terms of ensemble average which can be calculated using simulations.

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