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# Perturbation theory calculations of model pair potential systems

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**Perturbation theory calculations of model pair potential systems**

by

**Jianwu Gong**

A thesis submitted to the graduate faculty  
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Physical Chemistry

Program of Study Committee:

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Robert Jernigan

Iowa State University

Ames, Iowa

2016

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## DEDICATION

I would like to dedicate this thesis to my father Wei Gong who unconditionally supports me both in moral and in financial so that I could be able to complete this work.

I would also like to dedicate this thesis to Jiamin Huang. Thank you for being my sunshine and making me happy when skies are grey.

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## ABSTRACT

Helmholtz free energy is one of the most important thermodynamic properties for condensed matter systems. It is closely related to other thermodynamic properties such as chemical potential and compressibility. It is also the starting point for studies of interfacial properties and phase coexistence if free energies of different phases can be obtained.

In this thesis, we will use an approach based on the Weeks-Chandler-Anderson (WCA) perturbation theory to calculate the free energy of both solid and liquid phases of Lennard-Jones pair potential systems and the free energy of liquid states of Yukawa pair potentials. Our results indicate that the perturbation theory provides an accurate approach to the free energy calculations of liquid and solid phases based upon comparisons with results from molecular dynamics (MD) and Monte Carlo (MC) simulations.

## CHAPTER 1. GENERAL INTRODUCTION

### **Research Motivation**

Interfacial properties between different phases are crucial to phase transformation studies such as nucleation and crystal growth, which use the bulk free energy calculations as the starting point. There are many different methodologies to compute the free energy. For example, molecular dynamics (MD) and Monte Carlo (MC) simulations can give numerically exact results, however, these methods are generally time-consuming. Thus, theoretical approaches may offer an alternate route for obtaining the free energy calculations efficiently. Here a method based on the Weeks-Chandler-Anderson perturbation theory to compute free energy is used to illustrate such a theoretical approach.

The systems we are interested in are Lennard-Jones pair potential as well as the Yukawa pair potential. Lennard-Jones pair potential is one of the most common pair potentials with both a repulsive short-range part and an attractive long-range part. On the other hand, Yukawa pair potential used here is a potential which only has a repulsive term. The two pair potentials are quite representative interactions of various thermodynamic systems.

Our interests in the phase transformation and interfacial properties of such model systems require accurate bulk free energies as inputs. However, due to the time limit of a Master's degree, I am not able to finish the interfacial property studies. I only report my work on the bulk free energy calculations of these model systems.

## **Thesis Organization**

Chapter 2 introduces our general method used for the free energy computation as well as a brief review of relevant literature. Chapter 3 contains a more detailed introduction to the Lennard-Jones pair potential calculation for both solid and liquid phases. Chapter 4 discusses my preliminary calculations for the liquid phase of Yukawa pair potential. A summary and more discussions could be found in Chapter 5. Conclusions, future plan and acknowledgement are also presented in Chapter 5. All references are listed at the end of the thesis.



## CHAPTER 2. GENERAL METHODS

**General Methods**

Let's assume the pair potential of the system is  $\Phi(r)$ , it could be a Yukawa pair potential or a Lennard-Jones pair potential or other kinds of pair potentials. According to the WCA perturbation theory, the pair potential could be separated into a short-range repulsive part and a long-range attractive part. The short-range repulsive part is used as the reference potential and the long-range attractive part as the perturbative potential, which are labeled as  $\Phi_r(r)$  and  $\Phi_p(r)$  respectively:

$$\Phi(r) = \Phi_r(r) + \Phi_p(r). \quad (1)$$

The exact definition of these two parts is:

$$\Phi_r(r) = \begin{cases} \Phi(r) - V(r), & r \leq \lambda \\ 0, & r > \lambda \end{cases} \quad (2)$$

and

$$\Phi_p(r) = \begin{cases} V(r), & r \leq \lambda \\ \Phi(r), & r > \lambda \end{cases} \quad (3)$$

where the parameter  $\lambda$  can be tuned to yield accurate free energies.  $V(r)$  is a function defined by  $\Phi(r)$  and  $\lambda$  as:

$$V(r) = \Phi(\lambda) - \frac{d\Phi(r)}{dr} \Big|_{r=\lambda} (\lambda - r), \quad (4)$$

which makes the reference potential and the perturbative potential continuous at  $r = \lambda$  position.

The free energy of system  $F[\rho(\vec{r})]$  could be written as the sum of the reference system free energy and a perturbation part in terms of the pair distribution function  $\rho_0^{(2)}(\vec{r}_1, \vec{r}_2)$  of the reference system,

$$F[\rho(\vec{r})] = F_0[\rho(\vec{r})] + \frac{1}{2} \int d\vec{r}_1 d\vec{r}_2 \Phi_p(r_{12}) \rho_0^{(2)}(\vec{r}_1, \vec{r}_2), \quad (5)$$

where  $F_0[\rho(\vec{r})]$  is the free energy of the reference system.

The free energy per particle can be simplified by using the angle-averaged correlation function in the reference system  $g_0(r_{12})$ :

$$F[\rho(\vec{r})]/N = F_0[\rho(\vec{r})]/N + \frac{1}{2} \rho \int d\vec{r} \Phi_p(\vec{r}) g_0(\vec{r}), \quad (6)$$

where  $g_0(r_{12})$  is defined as:

$$g_0(r_{12}) = \frac{1}{4\pi V \rho^2} \int d\Omega \int d\vec{r}_1 \rho_0^{(2)}(\vec{r}_1, \vec{r}_2). \quad (7)$$

Normally the reference system is mapped to a hard-sphere system due to its availability of accurate thermodynamic properties both for the liquid and the solid phases. The pair potential of a hard-sphere system is defined as:

$$\Phi_{HS}(r) = \begin{cases} +\infty & , \quad r \leq d \\ 0 & , \quad r > d \end{cases} \quad (8)$$

where the hard-sphere diameter  $d$  depends on the thermodynamic state of the reference system and the mapping procedure.

For the WCA perturbation theory, the way to determine the hard-sphere diameter is based on the following equation:

$$\int d\vec{r} (e^{-\beta\Phi_r(r)} - e^{-\beta\Phi_{HS}(r)}) y_{HS}(r/d) = 0, \quad (9)$$

where  $y_{HS}(r/d)$  is the cavity function [17-18] and equation (9) leads to  $F_0 = F_{HS} + O(\delta^2)$  so that we could approximate  $F_0$  by  $F_{HS}$ . Furthermore this condition also yields  $g_0 = g_{HS} + O(\delta)$ , where  $\delta$  [1, 4] is a small number defined as:

$$\delta = \int_0^\lambda dr \left(\frac{r}{d_B} - 1\right)^2 \frac{d}{dr} e^{-\beta\Phi_0(r)}, \quad (10)$$

where  $d_B$  in the above equation is the Barker-Henderson diameter [16]. In solid state calculations we can directly use this Barker-Henderson diameter as the hard-sphere diameter while in liquid states some correction to the Barker-Henderson diameter provides a better hard-sphere diameter choice, which is defined as:

$$d = d_B \left(1 + \frac{\sigma_1}{2\sigma_0} \delta\right), \quad (11)$$

where

$$\sigma_0 = y_{HS}(r = d), \quad (12)$$

$$\sigma_1 = 2\sigma_0 + \left[\frac{dy_{HS}}{dx}\right]_{x=\frac{r}{d}=1}. \quad (13)$$

Using these approximations, we can rewrite Eq. (6) as:

$$\frac{F[\rho(\vec{r})]}{N} = \frac{F_{HS}[\rho(\vec{r})]}{N} + \frac{1}{2}\rho \int d\vec{r} \Phi_p(\vec{r}) g_{HS}\left(\frac{\vec{r}}{d}\right). \quad (14)$$

Hence the calculation of the free energy of a pair potential is reduced to the calculation of an effective hard sphere system free energy and its radial distribution function. I will discuss on how to compute the hard-sphere free energy and the perturbation free energy for both solid and liquid phases in details in Chapter 3 using the Lennard-Jones pair potential. In Chapter 4 I will discuss how to apply the perturbation theory to a pure repulsive pair potential such as the Yukawa potential.

## CHAPTER 3. LENNARD-JONES SYSTEM

**Overall Introduction**

For a Lennard-Jones pair potential:

$$V_{LJ}(r) = 4\varepsilon \left( \frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6} \right), \quad (15)$$

where  $\frac{\sigma^{12}}{r^{12}}$  is the short-ranged repulsive part and  $-\frac{\sigma^6}{r^6}$  being the long-ranged attractive part.

According to the discussion in Chapter 2, we have:

$$\Phi_r(r) = \begin{cases} 4\varepsilon \frac{\sigma^{12}}{r^{12}} - 4\varepsilon \frac{\sigma^{12}}{\lambda^{12}}, & r \leq \lambda \\ 0, & r > \lambda \end{cases} \quad (16)$$

$$\Phi_p(r) = \begin{cases} -4\varepsilon \frac{\sigma^6}{r^6} + 4\varepsilon \frac{\sigma^{12}}{\lambda^{12}}, & r \leq \lambda \\ V_{LJ}(r), & r > \lambda \end{cases} \quad (17)$$

where  $\lambda$  is chosen as the position where the potential reaches its minimal value of  $V_{LJ}(r)$ .

Here is an example of how the reference potential looks like (see Fig. 1).

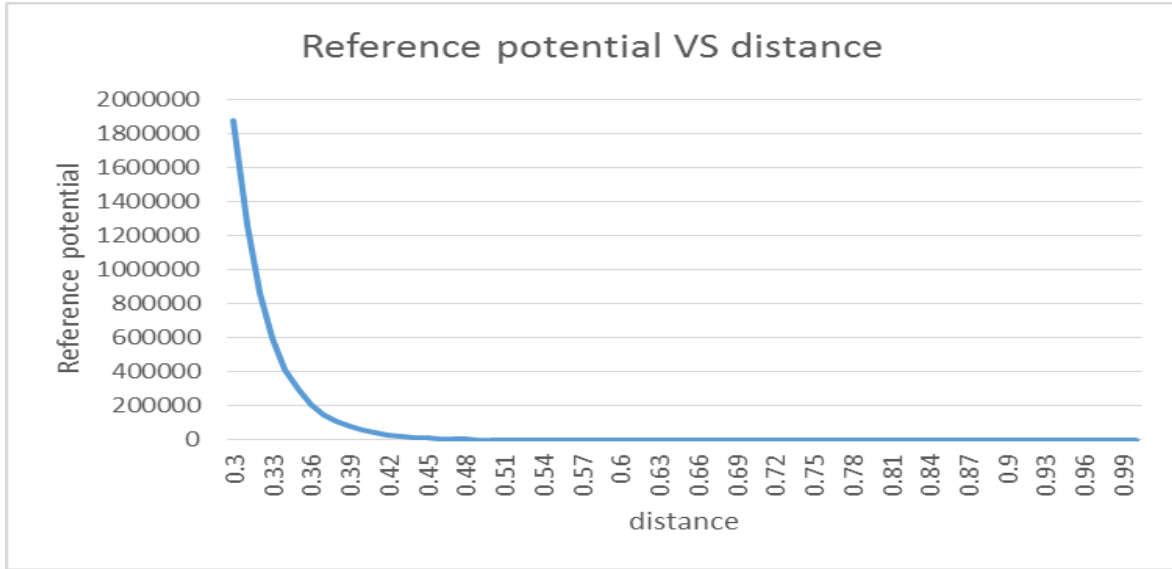


Fig.1 an example curve of reference potential under  $\epsilon=0.25$ ,  $\sigma=1$  and  $\lambda=0.5$ .

### Method on BCC Solid Reference Free Energy

From Eq. (14), the total free energy is divided into two parts:  $F_{HS}[\rho(\vec{r})]/N$  represents the hard sphere reference free energy and  $\frac{1}{2}\rho \int d\vec{r} \Phi_p(\vec{r})g_{HS}(\vec{r}/d)$  represents the perturbation free energy. In this part, we will discuss the computation of the hard sphere reference free energy.

Evans [19] pointed out that the classical density functional theory (DFT) is powerful tool for computing the thermodynamic properties of solids as well as liquid phases. According to the DFT theory, if we know the one body density  $\rho(\vec{r})$ , the hard sphere free energy  $F_{HS}[\rho(\vec{r})]$  is a functional of the one body density  $\rho(\vec{r})$ . Especially we can separate the free energy functional into two parts: an ideal-gas contribution  $F_{id}[\rho(\vec{r})]$  and an excess free energy functional  $F_{ex}[\rho(\vec{r})]$ :

$$F_{HS}[\rho(\vec{r})] = F_{id}[\rho(\vec{r})] + F_{ex}[\rho(\vec{r})]. \quad (18)$$

The ideal-gas contribution can be obtained exactly:

$$F_{id}[\rho(\vec{r})] = k_B T \int dV \rho(\vec{r}) \{ \ln[\rho(\vec{r})] - 1 \}. \quad (19)$$

As the excess free energy functional is not known exactly, many different approximations have been developed [20-24]. The functional we use here is the fundamental measure density functional proposed by Rosenfeld [25], and further developed by a few different groups [26-28]. The fundamental measure theory can be implemented in the following steps.

First, a series of weighted densities are calculated from one body density:

$$n_\alpha(\vec{r}) = \int d\vec{r}' \rho(\vec{r}') \omega_\alpha(\vec{r} - \vec{r}'), \quad (20)$$

where  $\omega_\alpha(\vec{r} - \vec{r}')$  are density-independent weight functions which are presented here in details:

$$\omega_2(y) = \delta\left(\frac{d}{2} - y\right), \quad (21)$$

$$\omega_3(y) = \theta\left(\frac{d}{2} - y\right), \quad (22)$$

$$\vec{\omega}_{v_2}(y) = \vec{e}_y \delta\left(\frac{d}{2} - y\right), \quad (23)$$

$$\vec{\omega}(y) = \vec{e}_y \vec{e}_y \delta\left(\frac{d}{2} - y\right), \quad (24)$$

where  $\delta(x)$  is the Dirac delta function and  $\theta(x)$  the Heaviside step function.  $\vec{e}_y$  is a unit vector along y-axis in the system coordinate system. Eqs. (21) and (22) define 2 scalar functions while Eq. (23) represents a vector function and Eq. (24) being a tensor function.

Then the excess free energy functional can be obtained as:

$$F_{ex}[\rho(\vec{r})] = k_B T \sum_{i=1}^3 \int d\vec{r} \Phi_i[n_\alpha(\vec{r})], \quad (25)$$

where  $\Phi_i$  functions are defined as:

$$\Phi_1 = \frac{n_2}{\pi d^2} \ln(1 - n_3), \quad (26)$$

$$\Phi_2 = \frac{n_2^2 - n_{v_2}^2}{2\pi d(1 - n_3)}, \quad (27)$$

$$\Phi_3 = f_3 \varphi_3(n_3). \quad (28)$$

As you may have noticed,  $\Phi_3$  function doesn't come with a specific equation. That is because the theory has been developed in various versions with different applications. In my code, we use the T2 version of  $f_3$  [28] defined as:

$$f_3^{(T2)} = \frac{3}{16\pi} [\overrightarrow{n_{v_2}} \overrightarrow{n} \overrightarrow{n_{v_2}} - n_2 \overrightarrow{n_{v_2}}^2 - \text{tr}(\overrightarrow{n}^3) + n_2 \text{tr}(\overrightarrow{n}^2)], \quad (29)$$

and  $\varphi_3(n_3)$  used in my code is called CS (Carnahan-Starling) edition [16]:

$$\varphi_3^{(CS)} = \frac{2}{3} \times \left[ \frac{n_3}{(1 - n_3)^2} + \ln(1 - n_3) \right], \quad (30)$$

which are known to yield accurate thermodynamic properties for the hard sphere system.

For the one body density  $\rho(\vec{r})$  in a solid phase, it is reasonable to take the sum of identical Gaussian profiles centered at the lattice sites  $\vec{R}_l$  as the density profile, namely

$$\rho(\vec{r}) = \sum_i \rho_{\Delta}(\vec{r} - \vec{R}_l) = \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} \sum_i e^{-\alpha(\vec{r} - \vec{R}_l)^2}. \quad (31)$$

Then, we can also compute the weighted density based on the lattice structure of a solid phase:

$$n_{\alpha}(\vec{r}) = \sum_i n_{\Delta}^{(\alpha)}(\vec{r} - \vec{R}_l). \quad (32)$$



If we could map a BCC solid of a reference potential to a BCC solid with hard sphere potential, we could use the DFT discussed above to compute the reference free energy. For a fixed reduced density  $\rho d^3$  the hard sphere reference free energy can be obtained from the Gaussian parameter  $\alpha$  minimization of the hard sphere free energy functional.

### Method on BCC Solid Perturbation Free Energy

In order to calculate the BCC solid perturbation free energy  $\frac{1}{2}\rho \int d\vec{r} \Phi_p(\vec{r})g_{HS}(\vec{r}/d)$ , we need to calculate the angle-averaged pair distribution function  $g_{HS}(\vec{r}/d)$ .

The correlation function is calculated by applying the approach of Rascon *et al.* [29-30]. In contrast to a liquid phase, the structural property of a solid state is mainly determined by one particle density  $\rho(\vec{r})$ . At a large separation, a reasonable approximation to the angle-averaged probability distribution is:

$$g^{(0)}(r) = \frac{1}{4\pi V \rho^2} \int d\vec{r}_1 d\Omega \rho(\vec{r}_1) \rho(\vec{r}_1 + \vec{r}), \quad (33)$$

If we put Eq. (31) into Eq. (33), we could get the sum of contributions  $g_i^{(0)}$  for the  $i$ -th shell.

If  $n_i$  is the coordination number of the  $i$ -th shell and  $R_i$  is the corresponding radius, we have the equation of  $g_i^{(0)}$ .

$$g_i^{(0)} = \frac{n_i}{4\pi\rho R_i} \left(\frac{\alpha}{2\pi}\right)^{1/2} \frac{e^{-\alpha(r-R_i)^2/2} + e^{-\alpha(r+R_i)^2/2}}{r}. \quad (34)$$

Then the total correlation function  $g_{HS}$  :

$$g_{HS}(r) = \sum_i g_i^{(0)}(r). \quad (35)$$

The calculation of perturbation energy can be performed by combining Eq. (35) and Eq. (17).

### Results of BCC Solid Free Energy of LJ System

For the reduced temperature  $T^* = k_B T / \varepsilon = 2.74$ , the excess free energy per particle  $\frac{\beta F_{ex}}{N}$  is calculated and a comparison with Monte Carlo simulations is presented in Table 1[1].

Table 1. A comparison between MC simulations and this work on excess free energy per particle in solid states for the reduced temperature  $T^* = k_B T / \varepsilon = 2.74$ .

$\rho^* = \rho \sigma^3$	$\frac{\beta F_{ex}}{N}$ (MC)	$\frac{\beta F_{ex}}{N}$ (Thesis)	Deviation percentage	$\eta$
1.2	3.138	3.162	0.8%	0.541
1.3	4.074	4.052	0.5%	0.564
1.4	5.31	5.19	2.2%	0.584
1.6	9.01	9.04	0.3%	0.620
1.8	14.91	14.95	0.3%	0.643
2.0	23.74	23.79	0.2%	0.660

### Method on Liquid Hard Sphere Free Energy

The hard sphere free energy of the liquid phase also has two parts: an ideal-gas contribution and the excess free energy. If density  $\rho d^3$  is given, then the packing fraction can be obtained as  $\eta = \frac{\pi \rho d^3}{6}$ .

The ideal-gas contribution is

$$\frac{\beta F_{id}}{N} = \ln(\rho d^3) - 1, \quad (36)$$

and the excess free energy can be obtained from the Carnahan-Starling equation:

$$\frac{\beta F_{ex}}{N} = \frac{\eta(4-3\eta)}{(1-\eta)^2}, \quad (37)$$

which is known to yield accurate excess free energies of a hard sphere liquid state.

### Method on Liquid Perturbation Free Energy

For liquid perturbation calculation, the hard sphere pair distribution function is obtained by using the Percus perspective [16]. Namely, the  $g(r)$  can be obtained from an inhomogeneous one body density profile in the presence of a tagged particle potential at the origin,

$$g(r) = \frac{\rho(r)}{\rho}. \quad (38)$$

According to literature [1, 2, 3, 4], the density distribution function  $\rho(r)$  could be derived from the following equation:

$$\rho(r) = \exp \left\{ -\frac{\delta \beta F^{(ex)}[\rho(\vec{r})]}{\delta \rho(\vec{r})} + \beta(\mu - \Phi_{HS}(r)) \right\}, \quad (39)$$

where  $\beta\mu$  function is defined as:

$$\beta\mu = \ln(\rho d^3) + \eta \frac{8-9\eta+3\eta^2}{(1-\eta)^3}. \quad (40)$$

Thus we can compute  $g(r)$  of a hard sphere liquid state using the density functional theory and the perturbation free energy would equal to  $\frac{1}{2}\rho \int d\vec{r} \Phi_p(\vec{r})g_{HS}(\vec{r}/d)$ .

### Results of Liquid Free Energy of LJ System

Using the above method, the calculated  $g(r)$  at various liquid densities are presented in Fig. 2.

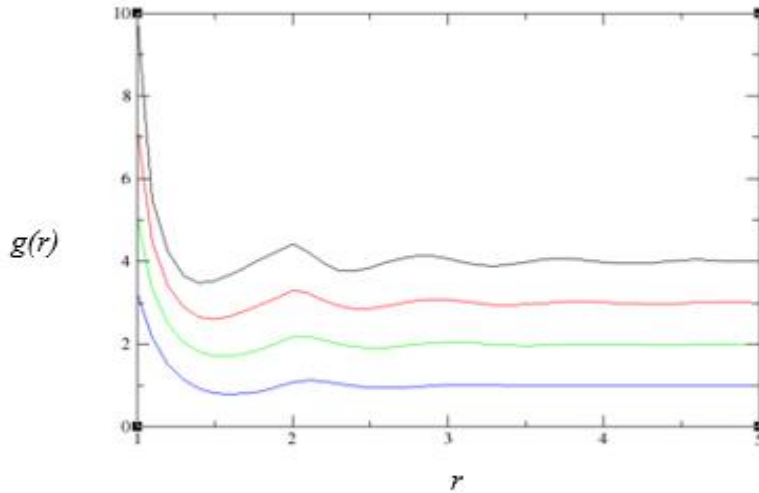


Fig. 2 Pair distribution functions at  $\rho d^3=1.0, 0.9, 0.8, 0.7$  (from top to the bottom). The top 3 curves have been shifted by 3.0, 2.0, 1.0 on the y-axis respectively for clear illustration.

In Table 2, the pair distribution function at  $\rho d^3=1.0$  is compared with the published results from MC simulations [5, 6].

Table 2. A comparison between the MC published  $g(r)$  values with my thesis'  $g(r)$  values for the reduced density  $\rho d^3=1.0$ .

$r/d$	Published paper(MC)	My result
1	9.8	9.827
1.5	3.6	3.532
2	4.5	4.418
2.5	3.8	3.853
3	4.0	4.080

For temperature  $T^* = k_B T / \varepsilon = 2.74$ , the excess free energy per particle  $\frac{\beta F_{ex}}{N} = \frac{\beta F}{N} - \ln(\rho d^3) + 1$  is compared with the MC results [1-4] in Table 3.

Table 3. A comparison between MC results and the thesis results for the excess free energy per particle in liquid state at  $T^* = k_B T / \varepsilon = 2.74$ .

$\rho^* = \rho \sigma^3$	$\frac{\beta F_{ex}}{N}(\text{MC})$	$\frac{\beta F_{ex}}{N}(\text{Thesis})$	Deviation percentage	$\eta$
0.2	-0.04	-0.04	~0	0.098
0.4	-0.01	-0.01	~0	0.194
0.7	0.38	0.35	7.9%	0.337
0.8	0.65	0.63	3.1%	0.384
0.9	1.05	1.03	1.9%	0.429
1.0	1.58	1.58	~0	0.473
1.1	2.31	2.27	1.7%	0.504

### Conclusions

As shown above, my computation on both solid and liquid states of a Lennard-Jones system are accurate when compared with published MC results [1, 4]. From these bulk free energies the phase coexistence conditions can be determined.

The way to find the coexistence conditions is called double tangent method, or the Maxwell construction. For a fixed temperature, we plot both  $\frac{\beta F}{N}(\text{solid})-\rho^*$  curve and  $\frac{\beta F}{N}(\text{liquid})-\rho^*$  curve together, the common tangent line for these two curves will yield the coexistence densities and the slope of the common tangent line naturally leads to the coexistence pressure (see Fig.3).

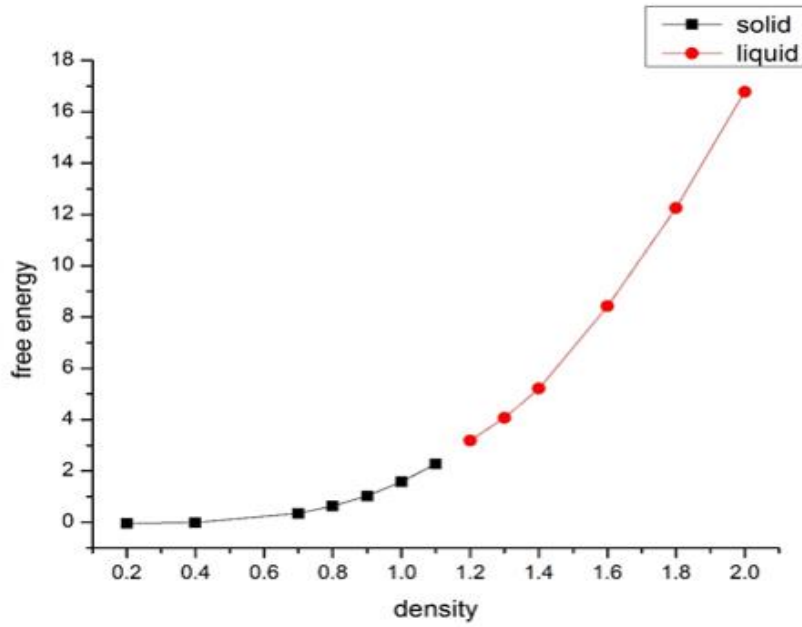


Fig 3. Free energies of liquid and solid phases against density at  $T^* = k_B T / \varepsilon = 2.74$ .

After drawing a double tangent line for both curves, we get the coexisting density at  $\rho_s^* = 1.122$  for solid and  $\rho_l^* = 1.236$  for liquid, which agrees with the published result [1]  $\rho_s^* = 1.155$  for solid and  $\rho_l^* = 1.214$  for liquid at  $T^* = k_B T / \varepsilon = 2.74$ . This result provides a clear demonstration on the accuracy of our perturbation theory.

## CHAPTER 4. YUKAWA SYSTEMS

A Yukawa pair potential can be written as [5, 6]:

$$\Phi(r) = \frac{Q^2}{4\pi\epsilon r} \exp\left(-\frac{r}{\lambda_D}\right). \quad (41)$$

If we introduce the Wigner-Seitz radius  $a = \left(\frac{3}{4\pi\rho}\right)^{1/3}$  as the unit of distance and define two dimensionless parameters  $\kappa$  and  $\Gamma$  as following:

$$\kappa = a/\lambda_D \text{ and } \Gamma = \frac{Q^2}{4\pi\epsilon a k T} \quad (42)$$

where  $\lambda_D$  is the Debye length.

Then a dimensionless Yukawa pair potential is:

$$\beta\Phi(r') = \frac{\Gamma}{r'} \exp(-\kappa r'), \quad (43)$$

where  $r' = r/a$ .

#### Amendment on General Methods When Applied to Yukawa System

Most parts of the calculations for the Yukawa system are exactly the same as the Lennard-Jones system. However, the Yukawa potential studied here is a pure repulsive potential and could be really soft for small  $\kappa$ . Here is an example of how soft the Yukawa potential could be (see Fig. 4).



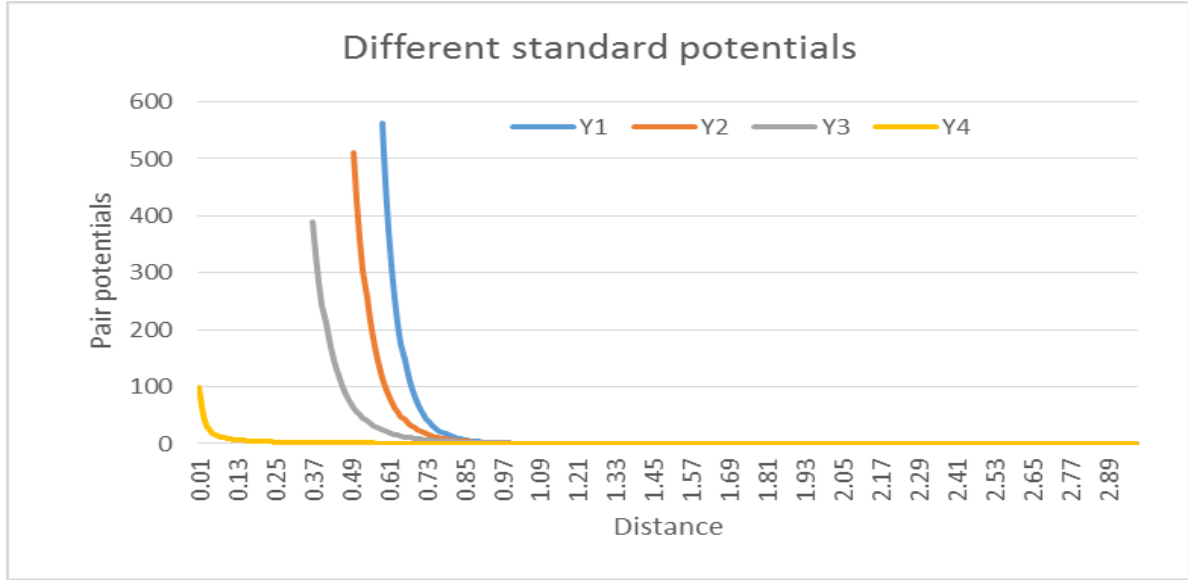


Fig 4. The comparison of four kinds of potentials (left to right:  $y_1 = \frac{1}{r^{12}}$   $y_2 = \frac{1}{r^9}$   $y_3 = \frac{1}{r^6}$   $y_4 = \frac{1}{r} \exp(-r)$ ), thus,  $\kappa = 1$  is softer than  $1/r^6$ .

To develop a consistent perturbation theory for various  $\kappa$  of the Yukawa systems, we choose to use the following harder potential as the reference and the corresponding perturbation potential:

$$\Phi_r(r) = \begin{cases} \frac{1}{r^{12}} - \frac{1}{r_c^{12}}, & r \leq r_c \\ 0, & r > r_c \end{cases} \quad (44)$$

$$\Phi_p(r) = \begin{cases} \Phi(r) - \frac{1}{r^{12}} + \frac{1}{r_c^{12}}, & r \leq r_c \\ \Phi(r), & r > r_c \end{cases} \quad (45)$$

### Issue of Units

The reason I would like to discuss the units issue here is because I struggled a lot on the unit. So I just want to make it clear about the unit for most important parameters.

As we mentioned at the beginning of this chapter, we have two dimensionless ratios  $\kappa$  and  $\Gamma$ . Hamaguchi *et al* [5,6] mentioned that the unit for energy should be  $\frac{Q^2}{4\pi\epsilon a}$  and  $a$  is the distance unit, thus we also use them as the units for energy and distance. That works for all of our distance and energy outputs.

### Results of Liquid Free Energy of Yukawa System

As we want to compare our results with the MD simulation results published before [5, 6, 31], we will use their dimensionless parameters  $\kappa$  and  $\Gamma$  as the way to specify corresponding thermodynamic states which are related to the conventional thermodynamic states specification via temperature  $k_B T$  and density  $\rho d^3$ .  $k_B$  is the Boltzmann constant here.

We start with a series of conditions at  $\Gamma=200$  and  $\kappa$  varies from 1.2 all the way to 4.0. As  $\frac{Q^2}{4\pi\epsilon a}$  is the unit of energy, we just assume it to be 1. Thus we have  $\Gamma = \frac{1}{k_B T} = 200$  and the temperature has been determined.

The next step we need to do is to determine the density as well as the packing fraction. According to Hansen *et al* [16], we choose the Wigner-Seitz radius  $a$  to be  $4.05 \times a_B = 2.1465 \text{ \AA}$ , where  $a_B$  is the Bohr radius. So the density now is  $\rho = \frac{3}{4\pi a^3} = 0.024 \text{ \AA}^{-3}$ .

The choice of  $r_c$  as mentioned before usually starts with a large  $r_c$ , then we try a relatively smaller  $r_c$  and run the code again. If the free energy we get finally converge as the  $r_c$  keeps decreasing, that should be the right free energy as well as the good  $r_c$  value. In my thesis here,  $r_c = 1.69\text{\AA}$ .

The following Table presents some of my results at  $\Gamma=200$  and various  $\kappa$ .

Table 4. Hard-sphere diameters, packing fractions and free energy at various  $\kappa$

$\kappa$	$d/a$	$d (\text{\AA})$	$\eta$	$\beta F$
1.2	1.656	3.555	0.5646	116.59
1.4	1.6486	3.539	0.557	71.6
2.0	1.612	3.460	0.5205	17.4
2.6	1.549	3.325	0.462	4.21
3.0	1.491	3.200	0.412	1.58
3.6	1.388	2.979	0.332	0.35
4.0	1.313	2.818	0.281	0.126

The following Table presents a comparison between our results and the published MD results [5-6].

Table 5, Comparison of MD result with our result under varied  $\kappa$ 

$\kappa$	$\beta F$ (MD)	$\beta F$ (Thesis)	Absolute difference
1.2	124.69	116.59	8.1
1.4	79.5	71.6	7.9
2.0	24.36	17.4	6.96
2.6	8.58	4.21	4.37
3.0	4.325	1.58	2.745
3.6	1.19	0.35	0.84
4.0	0.065	0.126	0.061

### Conclusions

According to the data we obtained, it seems that our result doesn't agree with the MD results very well, especially the difference is quite large when  $\kappa$  is relatively small. The MD results also indicate that when  $\Gamma=200$ ,  $\kappa < 2.6$  part is more stable in the bcc solid state. That's why I think the reason for a big deviation may due to the liquid state for small  $\kappa$  is indeed a metastable state.

Meanwhile, the choice of Wigner-Seitz radius and  $r_c$  may also present a problem for the computation of free energy. As the MD article doesn't give a specific Debye length for the plasma and that parameter could vary a lot in different plasmas, thus it makes it much harder for us to give a good prediction on the value of Wigner-Seitz radius, which is still under investigation.

## CHAPTER 5. GENERAL CONCLUSION

### General Discussions

According to the results presented in the Lennard-Jones potential part, we find that DFT method is not only very accurate and powerful for free energy calculations, but also not time-consuming in contrast to MC or MD method.

For the Yukawa potential part, we change the pair potential to a much softer pure repulsive potential, thus we need to separate the pair potential to a relatively hard reference potential (usually not softer than  $\frac{1}{r^4}$ ) and the corresponding perturbation free energy. After the separation of the potential energy, a series of convergence test on cutoff distance are required, which is different from the Lennard-Jones potential situation.

Also for soft pair potential like Yukawa potential, the HS-DFT theory might not work for all possible pair potentials. For example, it may not work when  $\kappa$  is very small due to the long-range nature of the potential. This may be the reason for the inaccuracy of my free energy calculations indicated by a relatively large difference between the published MC results and my calculated results. It is interesting to find out the limit of how soft the potential is where the perturbation theory still holds.

### Future Research

Based upon my experience of my research I would like to point out some future research directions.

For the Lennard-Jones system, I would like to pursue studies on other kinds of crystal structures. For example, some natural materials with relatively more complex crystal structures could be interesting. By doing so, we might be able to know why the material exists in its particular crystal lattices. So far, the systems I studied are one component systems, it will be interesting to study multicomponent systems, which represents most of materials in nature.

For the Yukawa system, my results are not good so far. I will be interested in pursuing better strategies to improve the calculations. Furthermore, it will be interesting to study the coexisting conditions of the Yukawa systems and to compare with the phase diagram of the Yukawa systems from simulations. It will also be rewarding to do further studies on the lowest limit of  $\kappa$  value under a specific  $\Gamma$  value. It will relate to how soft the pair potential could be if we still want to use the hard-sphere reference system to compute it.

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