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DEDICATION

To the memory of my dear father

HOU-LEH HSIEH

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

Figure | Page

CHAPTER I

INTRODUCTION:

COHN'S THEORY OF THE RADIAL DISTRIBUTION FUNCTION

The construction of a general statistical theory of dense system, such as the dense gases and liquids, has been much developed,[1,2] yet severe mathematical difficulties still stand in its way. In the dilute system, the particles are always far separated, so that the kinetic energy is very large compared with the interacting potential energy. In the dense system, the potential energy of particle interaction is significantly large and complicated, which gives the construction of the partition function unintegrable. So the thermodynamic properties derived from the partition function are very difficult.

An alternative method for evaluating the thermodynamic properties is by the radial distribution function, $\rho(r,n,T)$, which is defined as the distribution of particles around a given particle, called the central particle. If the local average number density at a distance r from the central particle is $n(r)$, then

$$\rho(r) \equiv \frac{n(r)}{n} \qquad (1.1)$$

is the radial distribution function of a system at some fixed temperature T and macroscopic number density n. If particles are moved far apart, correlation between them having broken down, so $\rho(r) = 1$ as $n(r) = n$ for $r \rightarrow \infty$. But if particles are moved to the central particle,

$\rho(r) = 0$ as $n(r) = 0$ for $r \leq \sigma$, where σ is the hard core distance between two particles.

The thermodynamic properties (or thermodynamic functions) of a fluid, such as pressure p, internal energy E, chemical potential μ, can be expressed in terms of the radial distribution function as follows:[2,3,4]

$$\frac{p}{kT} = n - \frac{n}{6kT} \int_0^\infty r \frac{dU(r)}{dr} \rho(r,n,T)\ 4\pi r^2 dr \tag{1.2}$$

$$\frac{E}{NkT} = \frac{3}{2} + \frac{n}{2kT} \int_0^\infty U(r)\ \rho(r,n,T)\ 4\pi r^2 dr \tag{1.3}$$

$$\frac{\mu}{kT} = \ln n\Lambda^3 + \frac{n}{kT} \int_0^1 \int_0^\infty U(r)\ \rho(r,n,T;\xi)\ 4\pi r^2 dr d\xi \tag{1.4}$$

where ξ is the charging or coupling parameter, $0 \leq \xi \leq 1$, this means that the "discharged" state for a particle is $\xi = 0$ and the "charged" state for a particle is $\xi = 1$. U(r) is the pair potential between two particles. $\Lambda = (h^2/2\pi mkT)^{\frac{1}{2}}$, h is Planck's constant, k is Boltzman's constant. We will use $\beta = 1/kT$ later.

In the expressions in eqs. (1.2) to (1.4), the first term in the right hand side refers to condition for a dilute gas, while the second term refers to dense gases and liquids arising from the interaction between pairs of particles. The above formulas just involve the pair interaction and are good only for applying to simple liquids, such as liquid argon. For more complex liquids, such as metallic solution, the interaction between triplets or higher order interactions has to be considered, because the interactions are between different composed atoms.

The experimental determination of the radial distribution function can be obtained according to the methods of neutron diffraction[5] or X-ray scattering[6]. The scattered intensity I(s) depends on the angle of the incident and scattered beams. This angle may be replaced by a parameter s. We can obtain the experimental values of $I_m(s)$ and I(s), the scattered intensities at zero density and at some density, respectively. Their relation is

$$I = I_m \{1 + \frac{4\pi n}{s} \int_0^\infty [\rho(r) - 1] \, r \sin(sr) \, dr\}$$

By a Fourier inversion, we have

$$\rho(r) = 1 + \frac{1}{2\pi^2 nr} \int_0^\infty \left[\frac{I(s)}{I_m(s)} - 1\right] s \sin(sr) \, ds$$

This is the way to get the experimental curves of the radial distribution function. So we can compare thermodynamic properties calculated from the experimental radial distribution function and the theoretical radial distribution function.

In this paper, the main purpose is to extend Cohn's theory of the radial distribution function. So we will first give a brief description of Cohn's theory as follows:

<u>Cohn's Theory of the Radial Distribution Function:</u>[7]

Consider a thermodynamic system composed of N identical and structureless particles interacting with a pair potential U(r) in a volume V. We devide the volume V into τ cells (Ranging from 0,1,2,... to t cell. There are $\tau - 1$ cells from 1 to t.), each of volume v, around a central particle 0. In the thermodynamic limit, the cell volume is $v = V/\tau$ = a finite quantity as $V \to \infty$ and $N \to \infty$. Each cell is so small that at most only one particle can be in it. We also assume that as each particle moves around in a cell, the total potential energy V_p does not change significantly. So, from classical statistical mechanics, we can write the probability P of realizing a particular distribution of particles about the central particle as

$$P = Av^{N-1} (N - 1)! \exp(-\beta V_p) \tag{1.5}$$

where A is a normalization factor. So eq. (1.5) is true as far as the neighboring cells are not simultaneously occupied, the contributions coming from two neighboring cells being occupied simultaneously is ignored. It is also true, even though two or more particles are very close, if the pair potential between two particles is sufficiently slowly varying.

Let U_{ij} be the pair potential between particles in the i th and j th cells, then

$$V_P = \tfrac{1}{2}\sum_{i\neq j} \mu_i\mu_j U_{ij} = \tfrac{1}{2}\sum_{i=0}\mu_i\phi_i \tag{1.6}$$

and $$\phi_i = \sum_{j\neq i} U_{ij}\mu_j \tag{1.7}$$

Here, and from now on unless it is specified, the upper limit of the sum is to the numbers of cells t (or τ-1). And ϕ_i is the potential energy of a particle in any cell i due to interaction with all other particles. μ_i is the cell occupation number of cell i. μ_i=0, +1 if the cell is unoccupied or occupied, respectively. For the central particle, $\mu_0 = +1$. A factor ½ in eq. (1.6) is to avoid over counting in the double sum.

Expanding V_p of eq. (1.6) in terms of the average values of μ_i, and ϕ_i, denoted respectively as $<\mu_i>$ and $<\phi_i>$, by Taylor's expansion, we rewrite eq. (1.5) as

$$P = Av^{N-1}\ (N-1)!\ \exp\left[-\beta \sum_{j=1} \mu_j<\phi_j> + \frac{\beta}{2} \sum_{j=i} <\mu_j>\ <\phi_j> - \frac{\beta}{2}\ \mu_o<\phi_o>+\Delta\right] \tag{1.8}$$

where $$\Delta \equiv -\frac{\beta}{2} \sum_{j\neq k\neq 0} U_{jk}\ (\mu_j-<\mu_j>)(\mu_k-<\mu_k>) \tag{1.9}$$

$$<\phi_j> = \sum_{k\neq j} U_{jk}\ <\mu_k> \tag{1.10}$$

and $$<\mu_j> = \frac{\Sigma\mu_j P}{\Sigma P} \tag{1.11}$$

Δ is the fluctuation term of a given distribution about the average. In eq. (1.8), if Δ=0, we use P_o for P. The average of this type will have a superscript zero, i,e.

$$<\mu_j>^0 = \frac{\Sigma\mu_j P_o}{\Sigma P_o} = \frac{\Sigma\mu_j \tilde{P}_o}{\Sigma\tilde{P}_o} = -\frac{1}{\beta}\ \frac{\partial \ln(\Sigma\tilde{P}_o)}{\partial<\phi_j>} \tag{1.12}$$

where $$\tilde{P}_o = \exp -\beta \sum_j \mu_j<\phi_j> \tag{1.13}$$

Using the method of steepest descents[7,8] to evaluate ΣP_o, we then have,

$$<\mu_j>^o = \frac{ze^{-\beta<\phi_j>}}{1+ze^{-\beta<\phi_j>}} \tag{1.14}$$

where the parameter $z = \xi_o e^{\beta h}$ and $\xi_o = \frac{nv}{1-nv}$ (1.15)

by assuming $<\phi_j> = h$, a constant as $r \to \infty$.

By eqs. (1.8) and (1.13), we write eq. (1.11) as

$$<\mu_j> = \frac{\Sigma\mu_j\tilde{P}_o e^{\Delta}}{\Sigma\tilde{P}_o e^{\Delta}} = \frac{\Sigma\mu_j\tilde{P}_o(1+\Delta+\frac{1}{2!}\Delta^2+\ldots..)}{\Sigma\tilde{P}_o(1+\Delta+\frac{1}{2!}\Delta^2+\ldots...)} \tag{1.16}$$

$$<\mu_j> \simeq <\mu_j>^0 \quad \text{if } \Delta \simeq 0 \tag{1.17}$$

We know $$<\mu_j> = nv\rho(r) \tag{1.18}$$

where r is the distance of cell j from the central particle. Then by eqs. (1.14), (1.17) and (1,18), we have

$$nv\rho(r) = \frac{ze^{-\beta\phi}}{1+ze^{-\beta\phi}} \quad \text{or } nv\rho(r) = \frac{\xi_o e^{-\beta(\phi-h)}}{1+\xi_o e^{-\beta(\phi-h)}} \tag{1.19}$$

here, for convenience, the bracket < > and the subscript j are dropped from $<\phi_j>$. By eqs. (1.15) and (1.19),

$$\phi(r) - h = \frac{1}{\beta}\ln\frac{1+\xi_o-\xi_o\rho(r)}{\rho(r)} \tag{1.20}$$

Another expression[7] for $\phi(r)$ in an integral form is derived by considering the potential energy of any particle at a distance r from the central particle due to all other particles (excluding the central particle) and the contribution U(r) from the central particle. This $\phi(r)$ is written as (See Appendix A)

$$\phi(r) = U(r) + \frac{2\pi n}{r}\int_\sigma^\infty x\,\rho(x)\,K(x,r)\,dx \tag{1.21}$$

Combining eqs. (1.20) and (1.21), we have

$$h+\frac{1}{\beta}\ln\frac{1+\xi_o-\xi_o\rho(r)}{\rho(r)} = U(r) + \frac{2\pi n}{r}\int_\sigma^\infty x\,\rho(x)K(x,r)\,dx \tag{1.22}$$

or $$\frac{r}{\beta}\ln\frac{1+\xi_o-\xi_o\rho(r)}{\rho(r)} = rU^\circ(r) + 2\pi n\int_\sigma^\infty x\,\rho(x)K(x,r)\,dx \tag{1.23}$$

This is Cohn's integral equation, where

$$U^{\circ}(r) = U\,(r) - h \tag{1.24}$$

$$K(x,r) = \int_{|x-r|}^{x+r} \xi U(\xi)\; d\xi + G(x,r) \int_{\sigma}^{|x-r|} \xi U(\xi)\; d\xi \tag{1.25}$$

$$G(x,r) = 0 \quad \text{when } |x-r| \geq \sigma$$
$$= 1 \quad \text{when } |x-r| < \sigma \tag{1.26}$$

For a linearized version, we consider the case where we can write

$$\rho(r) = 1 + \omega(r) \qquad \text{for } \omega(r) << 1 \tag{1.27}$$

then eq. (1.23) can be linearized. So, for low density, we have[7]

$$\rho(r) = 1 - \beta\left[1+\xi_0\right]^{-1}\overset{\circ}{U}(r)+\lambda \int_1^{\infty} x\bar{\Lambda}(x,\tfrac{r}{\sigma})\left[1-\beta(1+\xi_0)^{-1}U^{\circ}(\sigma x)\right] dx \tag{1.28}$$

where

$$\bar{\Lambda}(x,y) = \frac{\beta(1+\xi)^{-1}}{y\sigma^2} \left\{\int_{\sigma|x-y|}^{\sigma(x+y)} \xi U(\xi)d\xi + G(\sigma x,\sigma y)\int_{\sigma}^{\sigma|x-y|}\xi U(\xi)\,d\xi\right\} \tag{1.29}$$

The numerical calculation[9] for dilute argon, using modified Buckingham potential function[9,10] for eq. (1.23), showed the good result. Cure,[13] using Lennard - Jones potential[10], found that the comparison of the pressure and internal energy obtained from Cohn's theory is excellent related to MC (Monte Carlo)[14] and PY (Percus-Yevick)[15] methods, but not the coefficient of compressibility.

In order to see how Cohn's integral equation is different from the others, we give some current ones as follows:

(a) B-G-Y (Born-Green-Yvon) and K (Kirkwood) Equations:[4]

$$\ln\rho(r,\xi) = -\beta\xi U(r) + \frac{\pi n}{r}\int_0^{\infty}\left[K(r-R,\xi\,)-K(r+R,\xi)\right] R\left[\rho(R)-1\right]dR \tag{1.30}$$

where

$$K(t,\xi) = \beta\xi\int_{|t|}^{\infty} (s^2-t^2)\overset{\circ}{U}(s)\rho(s,\xi)\,ds \qquad \text{(B-G-Y)} \tag{1.31}$$

$$K(t,\xi) = -2\beta\int_0^{\xi}\int_{|t|}^{\infty} sU(s)\rho(s,\xi)\,ds\,d\xi \qquad \text{(Kirkwood)} \tag{1.32}$$

(b) HNC (Hyper-Netted Chain) Equation[2,16]:

$$\ln \rho(\underline{r}_{12}) = -\beta U(\underline{r}_{12}) + n\int_0^\infty \{\rho(\underline{r}_{13}) - \ln \rho(\underline{r}_{13}) - 1 - \beta U(\underline{r}_{13})\}\{\rho(\underline{r}_{23}) - 1\} d\underline{r}_3 \tag{1.33}$$

(c) P-Y (Percus-Yevick) Equation[2,15]:

$$\rho(\underline{r}_{12})\, e^{\beta U(\underline{r}_{12})} = 1 - n\int_0^\infty \{e^{\beta U(\underline{r}_{13})} - 1\}\{\rho(\underline{r}_{23}) - 1\}\rho(\underline{r}_{13})\, d\underline{r}_3 \tag{1.34}$$

These are nonlinearized equations. We see that Cohn's integral equation has the advantage of being linear in the radial distribution function.

The original Cohn's assumptions: neighboring cells being not simultaneously occupied and letting $\Delta = 0$, make his theory applied to a limit number density only. In Chapter II, we will consider it when $\Delta = 0$. In Chapter III, we will consider it when $\Delta \neq 0$. In Chapter IV, we will consider a difference $\delta(r)$ between $\langle\mu_i\rangle$ and $\langle\mu_i\rangle^o$ and add it in Cohn's integral equation. In Chapter V, a conclusion is made. Finally, some mathematical derivations are included in Appendix.

CHAPTER II

CONSIDERATION WHEN $\Delta = 0$

In this chapter, we will calculate the average value of cell occupation number by using a grand partition function when $\Delta = 0$, and derive a relation, when $\Delta = 0$, concerning the average of the product of the cell occupation numbers. An application of this relation will be discussed.

A. Grand Partition function with $\Delta = 0$

The partition function can be separated into momentum part and configurational part. The momentum partition function is a constant and can be evaluated easily. So we may just use the configurational partition function when we will find the average of some quantity. From eq.(1.5), neglecting the constant part, we may define $\exp(-\beta V_p)$ as the relative probability of our particular distribution. Then we can write a configurational partition function of N particles with one fixed (central particle) and N-1 particles distributed around it as

$$Z_N(V,T) = C \sum_{\{\mu_j\}} e^{-\beta V_p\{\mu_j\}} \qquad (2.1)$$

where C is a constant factor depending on the cell volume v, V_p is defined in eq.(1.6), $\{\mu_j\}$ is a set of cell occupation number, $\mu_j = \mu_1, \mu_2 \ldots\ldots \mu_t$, and $\{\mu_j\}$ under the sum means that μ_j is subjected to two constraints:

$$\mu_j = 0, \text{ or } +1 \qquad \text{for } j = 1,2,\ldots\ldots,t. \tag{2.2a}$$

$$\sum_{j=1} \mu_j = N - 1 \tag{2.2b}$$

Expanding V_p in terms of $<\mu_i>$ and $<\phi_i>$, we rewrite eq.(2.1) as

$$Z_N(V,T) = C\Omega \sum_{\{\mu_j\}} \exp\{-\beta \sum_{j=1} \mu_j <\phi_j>\} e^{\Delta} = C\Omega\Sigma\tilde{P}_o e^{\Delta} \tag{2.3}$$

where

$$\Omega = \exp\{\frac{\beta}{2} \sum_{j=1} <\mu_j><\phi_j> - \frac{\beta}{2} \mu_o <\phi_o>\} = \text{a constant for N particles.} \tag{2.4}$$

and Δ and $\tilde{P}_o$ have been defined in eqs.(1.9) and (1.13) respectively.

If we fix the central particle at any definite cell, i,e,0, then the configurational partition function of the other N-1 particles is

$$Z_{N-1}(V,T) = C\Omega_o \sum_{\{\mu_j\}} \exp\{-\beta \sum_{j=1} \mu_j <\phi_j>\} e^{\Delta} \tag{2.5}$$

where

$$\Omega_o = \exp\{\frac{\beta}{2} \sum_{j=1} <\mu_j><\phi_j>\} = \text{a constant for N-1 particles.} \tag{2.6}$$

The above form of partition function is called configurational canonical partition function which is applied to a system having a fixed number of particles. The more general form called grand partition function can be applied to any number of particles in the system and is more able to describe a general situation, like two different phases coexisting in the same system, as binary alloy.

We define the grand partition function as

$$G(z,V,T) = \sum_{N=0}^{\infty} z^N Z_N = \sum_{N=1}^{\infty} z^{N-1} Z_{N-1} \tag{2.7}$$

where z is the fugacity parameter, which will be identified later. The constraints in eq.(2.3) are valid here, too.

For the case $\Delta=0$, Z and G will also have a superscript zero, i.e.

$$Z_N^o\,(V,T) = \Omega_{\{\mu_j\}}\sum \exp\{-\beta \sum_{j=1} \mu_j\langle\phi_j\rangle\} \tag{2.8}$$

$$Z_{N-1}^o(V,T) = \Omega_o \sum_{\{\mu_j\}} \exp\{-\beta \sum_{j=1}\mu_j\langle\phi_j\rangle\} \tag{2.9}$$

$$G^o(z,V,T) = \sum_{N=1}^{\infty} z^{N-1}\, Z_{N-1}^o \tag{2.10}$$

$$= \Omega_o \sum_{N=1}^{\infty} \sum_{\{\mu_j\}} z^{N-1} \exp\{-\beta \sum_{j=1} \mu_j\langle\phi_j\rangle\}$$

$$= \Omega_o \sum_{N=1}^{\infty} \sum_{\{\mu_j\}} \prod_{j=1} (ze^{-\beta\langle\phi_j\rangle})^{\mu_j} \qquad \text{by eq.(2.2b)}$$

$$= \Omega_o \prod_{j=1} \{ \sum_{\mu_j} (ze^{-\beta\langle\phi_j\rangle})^{\mu_j}\}$$

$$\text{or } G^o(z,V,T) = \Omega_o \prod_{i=1} (1 + ze^{-\beta\langle\phi_i\rangle}) \qquad \text{by eq.(2.2a)} \tag{2.11}$$

Note, the sum $\sum_{\{\mu_j\}}$ is equivalent to $\sum_{\mu_1}\sum_{\mu_2}\sum_{\mu_3}\cdots\cdots$ Each μ_i ranges over the values 0 or +1.

B. Average Occupation Number

The occupation number in each cell is 0 or +1. We will find the average occupation number in each cell, at a distance r from the central particle.

Using the grand partition function, we find

$$\langle\mu_j\rangle^o = \frac{1}{G^o}\,\Omega_o \sum_{N=1}^{\infty} z^{N-1} \sum_{\{\mu_j\}} \mu_j e^{-\beta \sum_{j=1}\mu_j\langle\phi_j\rangle} \tag{2.12}$$

$$= -\frac{1}{\beta}\frac{\partial}{\partial\langle\phi_j\rangle}\ln G^o \tag{2.13}$$

By (2.11) and (2.13)

$$\langle\mu_j\rangle^o = \frac{ze^{-\beta\langle\phi_j\rangle}}{1+ze^{-\beta\langle\phi_j\rangle}} \tag{2.14}$$

Now we have to find how z is related to the density n. Let us consider a cell j at a distance very far away from the central particle. In that cell, $\rho(r) = 1$ as $r \to \infty$ and $<\mu_j> = nv\rho(r) = nv = <\mu_j>^o$.

We have mentioned before that $<\phi_j>$ actually will never be zero no matter how dilute the system is, since there is an interaction potential between two particles. So, $<\phi_j>$ approaches a constant value h if cell j is very far away from the central particle. i.e.

$h = <\phi_j> \big|_{r\to\infty}$. So, by eq. (2.14)

$$nv = \frac{ze^{-\beta h}}{1+ze^{-\beta h}} \qquad \text{or}$$

$$z = \xi_o e^{\beta h} \qquad \text{and} \qquad \xi_o = \frac{nv}{1-nv} \tag{2.17}$$

Note, h is found[9] as a constant times the number density n. This agrees with eqs. (1.14) and (1.15), which are derived from the method of steepest descents.

C. Product Relation of Average Occupation Number

For the product of two cell occupation numbers, we may use the grand partition function to find its average.

$$<\mu_i\mu_j>^o = \frac{1}{G^o}\ \Omega_o \sum_{N=1}^{\infty} z^{N-1} \sum_{\{\mu_k\}} \mu_i\mu_j e^{-\beta\sum_{k=1} \mu_k<\phi_k>} \tag{2.16}$$

$$= \frac{1}{G^o}\left(\frac{-1}{\beta}\right)^2 \frac{\partial^2 G^o}{\partial<\phi_i>\partial<\phi_j>}$$

$$= \frac{1}{\beta^2}\left\{ \frac{\partial}{\partial<\phi_i>}\left(\frac{1}{G^o}\frac{\partial G^o}{\partial<\phi_j>}\right) - \frac{\partial(1/G^o)}{\partial<\phi_i>}\frac{\partial G^o}{\partial<\phi_j>} \right\}$$

$$= \frac{1}{\beta^2}\left\{ \frac{\partial}{\partial<\phi_i>}\frac{\partial\ln G^o}{\partial<\phi_j>} + \frac{\partial\ln G^o}{\partial <\phi_i>}\frac{\partial\ln G^o}{\partial<\phi_j>} \right\}$$

$$= -\frac{1}{\beta}\frac{\partial\langle\mu_j\rangle^0}{\partial\langle\Phi_i\rangle} + \langle\mu_i\rangle^0\langle\mu_j\rangle^0 \quad \text{by eq.(2.13)} \tag{2.17}$$

By eq.(2.14), we have

$$-\frac{1}{\beta}\frac{\partial\langle\mu_j\rangle^0}{\partial\langle\Phi_i\rangle} = \delta_{ij}\{\langle\mu_i\rangle^0 - \langle\mu_i\rangle^{02}\} \tag{2.18}$$

where δ_{ij} is the Kronecker delta.

$$\therefore \quad \langle\mu_i\mu_j\rangle^0 = \delta_{ij}\{\langle\mu_i\rangle^0 - \langle\mu_i\rangle^{02}\} + \langle\mu_i\rangle^0\langle\mu_j\rangle^0 \tag{2.19}$$

$$\begin{aligned} \text{or} \quad \langle\mu_i\mu_j\rangle^0 &= \langle\mu_i\rangle^0\langle\mu_j\rangle^0 \quad \text{if } i \neq j \\ &= \langle\mu_i\rangle^0 = \langle\mu_j\rangle^0 \text{ if } i = j \end{aligned} \tag{2.20}$$

Thus, if $\Delta=0$, and $i\neq j$, the occupation numbers are uncorrelated, the average of the product of two cell occupation numbers is equal to the product of two average cell occupation numbers.

This has some physical meaning: Because μ_i, μ_j = 0 or +1, so also μ_i^2, μ_j^2 = 0 or +1. If $i \neq j$, $\langle\mu_i\mu_j\rangle^0$ has $\langle(0)(1)\rangle^0$ or $\langle(1)(0)\rangle^0$. If $i=j$, $\langle\mu_i\mu_j\rangle^0$ has $\langle(0)(0)\rangle^0$ or $\langle(1)(1)\rangle^0$. When $i=j$, notice $\langle\mu_i\mu_j\rangle^0$ = $\langle\mu_i^2\rangle^0 = \langle\mu_i\rangle^0 = \langle\mu_j\rangle^0$ does not mean that two particles can be in the same cell, but it means only that, mathematically, the average of the square of a cell occupation number is the same as the average of a cell occupation number, if $\Delta=0$. Otherwise, $\langle\mu_i\mu_j\rangle^0 = \langle\mu_i\rangle^0\langle\mu_j\rangle^0$, if $i\neq j$. This is similar to the discussion by Landau and Lifshitz.[17]

For the product of three cell occupation numbers, by the same procedure as above, we have

$$\langle\mu_i\mu_j\mu_k\rangle^0 = \frac{1}{G^0}\,\Omega_0 \sum_{N=1}^{\infty} z^{N-1} \sum_{\{\mu_l\}} \mu_i\mu_j\mu_k\, e^{-\beta\sum_{l=1}\mu_l\langle\Phi_l\rangle} \tag{2.22}$$

$$= \frac{1}{G^o}\left(\frac{-1}{\beta}\right)^3 \frac{\partial^3 G^o}{\partial<\phi_i>\partial<\phi_j>\partial<\phi_k>}$$

$$= \left(\frac{-1}{\beta}\right)^3 \left\{\frac{\partial}{\partial<\phi_i>}\left(\frac{1}{G^o}\frac{\partial^2 G^o}{\partial<\phi_j>\partial<\phi_k>}\right) - \frac{-1}{G^{o2}}\frac{\partial G^o}{\partial<\phi_i>}\frac{\partial^2 G^o}{\partial<\phi_j>\partial<\phi_k>}\right\}$$

$$= -\frac{1}{\beta}\frac{\partial}{\partial<\phi_i>}(<\mu_j\mu_k>^o) + <\mu_i>^o<\mu_j\mu_k>^o \tag{2.23}$$

$$= <\mu_i>^o<\mu_j>^o<\mu_k>^o + \delta_{jk}\{\delta_{ji}(<\mu_j>^o - <\mu_j>^{o2})(1-2<\mu_j>^o)\}$$

$$+ \delta_{ji}(<\mu_j>^o - <\mu_j>^{o2})<\mu_k>^o + \delta_{ki}(<\mu_k>^o - <\mu_k>^{o2})<\mu_j>^o$$

$$+ \delta_{jk}(<\mu_j>^o - <\mu_j>^{o2})<\mu_i>^o \qquad \text{by eq. (2.19)} \tag{2.24}$$

or

$$\left.\begin{aligned} <\mu_i\mu_j\mu_k>^o &= <\mu_i>^o<\mu_j>^o<\mu_k>^o && \text{if } i\neq j\neq k \\ &= <\mu_i>^o<\mu_j>^o && \text{if } i\neq j, \text{ either } k=i \text{ or } k=j \\ &= <\mu_i>^o && \text{if } i=j=k \end{aligned}\right\} \tag{2.25}$$

By the same method as above, we can deduce, for example, that

$$\begin{aligned} <\mu_i\mu_j\mu_k\mu_l\ldots>^o &= <\mu_i>^o<\mu_l>^o, \text{ if } i=j=k\neq l\neq\ldots. \\ &= <\mu_i>^o<\mu_j>^o<\mu_k>^o<\mu_l>^o\ldots, \text{ if } i\neq j\neq k\neq l\neq\ldots \end{aligned} \tag{2.26}$$

Therefore, if $\Delta=0$, the average of the product of the different cell occupation numbers is equal to the product of these average cell occupation numbers. Their correlation is zero.

D. Applications

Here we will apply the above product relation of average cell occupation numbers to derive an equation for $\delta(r)$, which is a difference between $<\mu_i>$ and $<\mu_i>^o$. From eq. (1.16), we may write

$$<\mu_j> = \frac{<\mu_j>^o + <\mu_j\Delta>^o + <\mu_j\Delta^2>^o/2! + ..}{1 + <\Delta>^o + <\Delta^2>^o/2! + ...} \quad (2.27)$$

In order to calculate $<\mu_j>$ as accurately as possible, we have to calculate $<\Delta>^o$, $<\Delta^2>^o$, $<\mu_j\Delta>^o$, $<\mu_j\Delta^2>^o$...etc. Rewrite eq.(2.27) as

$$<\mu_j>=\{<\mu_j>^o+<\mu_j\Delta>^o+\frac{1}{2!}<\mu_j\Delta^2>^o+...\}\{1-<\Delta>^o-\frac{1}{2!}<\Delta^2>^o+<\Delta>^{o2}+..\} \quad (2.28)$$

or $$<\mu_j>=<\mu_j>^o+\{<\mu_j\Delta>^o-<\mu_j>^o<\Delta>^o\}+\frac{1}{2!}\{<\mu_j\Delta^2>^o-<\mu_j>^o<\Delta^2>^o\}$$

$$+\{<\mu_j>^o<\Delta>^{o2}-<\mu_j\Delta>^o<\Delta>^o\} \qquad \text{to } O(\Delta^2) \quad (2.29)$$

By the relation in eqs.(2.20),(2.25) and (2.26), we can calculate

$$<\Delta>^o = \frac{\Sigma\Delta\tilde{P}_o}{\Sigma\tilde{P}_o} = \frac{1}{\Sigma\hat{P}_o}(-\frac{\beta}{2})\Sigma\tilde{P}_o\{\sum_{k\neq l\neq 0}U_{kl}(\mu_k-<\mu_k>)(\mu_l-<\mu_l>)\}$$

$$=\frac{-\beta}{2}\sum_{k\neq l\neq 0}U_{kl}\{<\mu_k\mu_l>^o-<\mu_k>^o<\mu_l>-<\mu_k><\mu_l>^o+<\mu_k><\mu_l>\}$$

or $$<\Delta>^o = -\frac{\beta}{2}\sum_{k\neq l\neq 0}U_{kl}\{<\mu_k>^o<\mu_l>^o-<\mu_k>^o<\mu_l>-<\mu_k><\mu_l>^o+<\mu_k><\mu_l>\} \quad (2.30)$$

and $$<\mu_j\Delta>^o = \frac{\Sigma(\mu_j\Delta)\tilde{P}_o}{\Sigma\hat{P}_o} = \frac{1}{\Sigma\hat{P}_o}(-\frac{\beta}{2})\Sigma\tilde{P}_o\{\sum_{k\neq l\neq 0}U_{kl}\mu_j(\mu_k-<\mu_k>)(\mu_l-<\mu_l>)\}$$

$$= -\frac{\beta}{2}\sum_{k\neq l\neq 0}U_{kl}\{<\mu_j\mu_k\mu_l>^o-<\mu_j\mu_k>^o<\mu_l>-<\mu_j\mu_l>^o<\mu_k>+<\mu_j>^o<\mu_k><\mu_l>\}.$$

or $$<\mu_j\Delta>^o= -\frac{\beta}{2}\sum_{j\neq k\neq l\neq 0}U_{kl}\{<\mu_j>^o<\mu_k>^o<\mu_l>^o-<\mu_j>^o<\mu_k>^o<\mu_l>-<\mu_j>^o<\mu_l>^o<\mu_k>$$

$$+<\mu_j>^o<\mu_k><\mu_l>\}$$

$$-\frac{\beta}{2}\sum_{\substack{k\neq l\\ j=k,j\neq l}}U_{kl}\{<\mu_k>^o<\mu_l>^o-<\mu_k>^o<\mu_l>-<\mu_k>^o<\mu_l>^o<\mu_k>+<\mu_k>^o<\mu_k><\mu_l>\}$$

$$-\frac{\beta}{2}\sum_{\substack{k\neq l\\ j=l,j\neq k}}U_{kl}\{<\mu_l>^o<\mu_k>^o-<\mu_l>^o<\mu_k>^o<\mu_l>-<\mu_l>^o<\mu_k>+<\mu_l>^o<\mu_k><\mu_l>\}$$

(2.31)

The above calculations are to be used in the right hand side of eq.(2.29). Because the calculations of $<\Delta^2>^o$, $<\mu_j\Delta^2>^o$..etc. are very long and complicated, and they are much smaller than the terms of the first order of Δ, so they are neglected. We may rewrite eq.(2.29) as

$$<\mu_j> = <\mu_j>^o + \{<\mu_j\Delta>^o - <\mu_j>^o<\Delta>^o\} \quad \text{to } O(\Delta) \tag{2.32}$$

or $$\delta_j = <\mu_j\Delta>^o - <\mu_j>^o<\Delta>^o \tag{2.33}$$

where we define $\delta_j \equiv <\mu_j> - <\mu_j>^o$ or $<\mu_j> = <\mu_j>^o + \delta_j$ (2.34)

Sustituting eq.(2.34) into eqs.(2.30) and (2.31), we have

$$<\Delta>^o = -\frac{\beta}{2}\sum_{k\neq l\neq 0} U_{kl}\delta_k\delta_l \tag{2.35}$$

$$\begin{aligned}<\mu_j\Delta>^o &= -\frac{\beta}{2}<\mu_j>^o\sum_{j\neq k\neq l\neq 0} U_{kl}\delta_k\delta_l - \frac{\beta}{2}<\mu_j>^o\sum_{\substack{l=1\\ j\neq l}} U_{jl}\{-\delta_l+<\mu_j>^o\delta_l+\delta_j\delta_l\} \\ &\quad - \frac{\beta}{2}<\mu_j>^o\sum_{\substack{k=1\\ j\neq k}} U_{jk}\{-\delta_k+<\mu_j>^o\delta_k+\delta_j\delta_k\} \\ &= -\frac{\beta}{2}<\mu_j>^o\{\sum_{\substack{k\neq l\neq 0\\ j\neq k, j\neq l}} U_{kl}\delta_k\delta_l+\sum_{\substack{l=1\\ l\neq j}} U_{jl}\delta_j\delta_l+\sum_{\substack{k=1\\ k\neq j}} U_{jk}\delta_j\delta_k\} \\ &\quad - \frac{\beta}{2}<\mu_j>^o(-1+<\mu_j>^o)\sum_{\substack{l=1\\ l\neq j}} U_{jl}\delta_l - \frac{\beta}{2}<\mu_j>^o(-1+<\mu_j>^o)\sum_{\substack{k=1\\ k\neq j}} U_{jk}\delta_k\end{aligned} \tag{2.36}$$

By eq.(2.35) and (2.36), we have

$$<\mu_j\Delta>^o - <\mu_j>^o<\Delta>^o = 2(-\frac{\beta}{2})<\mu_j>^o(-1+<\mu_j>^o)\sum_{\substack{l=1\\ l\neq j}} U_{jl}\delta_l \tag{2.37}$$

where the first term in eq.(2.36) just cancels $<\mu_j>^o<\Delta>^o$. By eqs. (2.33) and (2.37),

$$\delta_j = \beta(<\mu_j>^o-<\mu_j>^{o2})\sum_{\substack{l=1\\ l\neq j}} U_{jl}\delta_l \quad \text{to } O(\Delta) \tag{2.38}$$

We know it is very difficult to solve this equation for $\delta(r)$. For very large r, $\langle\mu_j\rangle^o \simeq nv$, so in this limit

$$\delta_j = \beta(nv - n^2v^2) \sum_{\substack{l=1 \\ l\neq j}} U_{jl}\, \delta_l \tag{2.39}$$

For very small r, $\langle\mu_j\rangle^o = nv\rho^o(r)$, so

$$\delta_j = \beta\, \{ nv - n^2v^2\rho^{o2}(r)\} \sum_{\substack{l=1 \\ l\neq j}} U_{jl}\, \delta_l \tag{2.40}$$

where we define $\rho^o(r)$ as the radial distribution without considering the fluctuation. $\rho^o(r)$ is used here in order to distinguish $\rho(r)$ in $\langle\mu_j\rangle = nv\rho(r)$. Because $\rho^o(r)$ is also a function we are looking for, so the equation becomes very complicated and hard to solve. In the next Chapter, we will derive a similar equation as eq.(2.38), and use a special potential function to solve for $\delta(r)$. So we will not go any further from eq.(2.38). It just shows us an application of the product of the average cell occupation numbers.

E. Condensation when $\Delta=0$

It is well known that the first order phase transition occurs at the singularity or discontinuity in the equation of state. For any finite system, no matter how large the volume of the system, we cannot easily recognize the first order phase transition unless the equation of state can be explicitly calculated.[18] The singularity is associated with the limit $V\to\infty$. For an infinite system, according to the condensation theory of Yang and Lee[18,19,20], we have to prove the uniform convergence of $V^{-1} \ln \mathcal{G}(z,V) \equiv F_\infty(z)$ as $V \to \infty$ so that we can write an equation of state for a single plase as $\beta\, p(z) = F_\infty(z)$ and $1/\bar{v}(z) = z\partial F_\infty(z)/\partial z$.

where $\tilde{v}(z)$ is the specific volume, $\tilde{v} = 1/n$. Because it is very difficult to prove the uniform convergence of $F_\infty(z)$ by using our grand partition function in eq.(2.11) for $\Delta=0$, so we will use the canonical partition function to discuss the condensation.

When $\Delta=0$, the partition function for N particles with one fixed, from eq.(2.8), can be written in an integral form as

$$Z_N^o = \tilde{\Omega}\int_V \exp\{-\beta \sum_{j=1}^{N} \langle\phi_j\rangle\}\, d\underline{r}_1 d\underline{r}_2 \ldots\ldots d\underline{r}_N \qquad (2.41)$$

where $\langle\phi_j\rangle$ is the average potential on each particle, instead on each cell as in eq.(2.8). $\tilde{\Omega}$ is another proportional constant. Or write

$$Z_N^o = \tilde{\Omega}\int_V e^{-\beta\langle\phi_1\rangle} d\underline{r}_1 \ldots \int_V e^{-\beta\langle\phi_N\rangle}\, d\underline{r}_N$$

$$= \tilde{\Omega}\prod_{i=1}^{N} \int_V e^{-\beta\langle\phi_i\rangle}\, d\underline{r}_i$$

$$= \tilde{\Omega}\,\{\int_V e^{-\beta\phi(r)}\, 4\pi r^2 dr\}^N \qquad (2.42)$$

We see that our system has a partition function of the same form as an ideal gas in an external field with potential energy $\langle\phi_i\rangle$ on i th particle.

For very large r, $\phi(r)$ has the form $U(r)+h$, where $U(r) \to 0$ as $r\to\infty$. Let R_1 be the point where $U(R_1) = 0$, and R be the radius of the volume V. (assuming we have a spherical system). The integral can then be written as

$$\int_V e^{-\beta\phi(r)}\, 4\pi r^2 dr = \int_\sigma^{R_1} e^{-\beta\phi(r)}\, 4\pi r^2 dr + e^{-\beta h}\int_{R_1}^{R} 4\pi r^2 dr$$

For an infinite system, $V \to \infty$ or $R \to \infty$, the first term will be a finite constant, the second term will be proportional to V, because its integral is $4\pi(R^3 - R_i^3)/3 \simeq 4\pi R^3/3 = V$ as $R \to \infty$. Therefore, eq.(2.42) can be written as

$$Z_N^o = \tilde{\Omega}\, \{ CV \}^N \quad \text{(C is a proportional constant)} \tag{2.43}$$

Then the free energy is

$$F = -kT \ln Z_N^o = -kT\, \{\text{a constant} + N \ln V\} \tag{2.44}$$

and the pressure is

$$p = -\frac{\partial F}{\partial V}\Big|_T = kTN/V \qquad \text{or } p = nkT \tag{2.45}$$

The pressure depends on temperature only and is independent of volume. Therefore there is no condensation when $\Delta = 0$.

CHAPTER III

CONSIDERATION WHEN $\Delta \neq 0$

In Chapter I, we have mentioned that the neighboring cells are not simultaneously occupied and let $\Delta=0$ in deriving Cohn's integral equation, eq.(1.23), will limit his theory for low density. In order to apply his theory for high density, we have to overcome these two assumptions. In Chapter II, we have tried to use the product relation of average cell occupation numbers, when $\Delta=0$, in the calculation of the fluctuation terms, and derive an equation, eq.(2.38), governing $\delta(r)$, the difference between $\langle\mu_i\rangle$ and $\langle\mu_i\rangle^o$, but it turns out difficulty to solve for $\delta(r)$, even the first order of fluctuation Δ is considered only. Here in this Chapter, we will avoid these difficulties. When the system is getting denser and denser, the fluctuation is very large. So we have to keep all the fluctuation terms as many as possible. The Einstein's formula[21] of the probability of fluctuations is used here to calculate the average cell occupation number $\langle\mu_i\rangle$ to all the orders of Δ, and from which we can derive an integral equation of $\delta(r)$ for general cases with general pair potential. Since the kernel $K(x,r)$ we use in the integral equation is so complex that we shall select a special potential function to solve the equation. This special potential has the form $U(r) = U_o$ for $r \leq \sigma$ and $U(r) = A\exp(-\mu r)/r$ for $r > \sigma$, where U_o and μ are positive constant and A is a negative constant. In the high density, it is very possible that two particles are in the neighboring cells, even in the same cell (this means the centers of two particles are in the same cell). So the special potential function we used here $U(r) = U_0$ for $r \leq \sigma$ is realistic. Then we solve $\delta(r)$ for very large r and $\delta(r)$ for very small r and their match point at $r = r_0$ can be found.

A. The Probability of Fluctuations

Before deriving the probability of fluctuations, we explain the ideas to calculate the fluctuation terms as follows: First, we define

$$x_i \equiv \mu_i - \langle\mu_i\rangle^o \quad \text{for all variable } x_i \text{ at i th cell} \tag{3.1}$$

where μ_i is either 0 or +1 and $\langle\mu_i\rangle^o \leq 1$, so x_i ranges from -1 to +1. Then we can write

$$\delta_i = \langle\mu_i\rangle - \langle\mu_i\rangle^o = \langle x_i\rangle \tag{3.2}$$

and so $x_i - \delta_i = \mu_i - \langle\mu_i\rangle$ (3.3)

By eq.(2.27), we can write

$$\langle\mu_i\rangle = \frac{\langle\mu_i e^{\Delta}\rangle^o}{\langle e^{\Delta}\rangle^o} = \frac{\langle(\langle\mu_i\rangle^o + x_i)e^{\Delta}\rangle^o}{\langle e^{\Delta}\rangle^o} = \langle\mu_i\rangle^o + \frac{\langle x_i e^{\Delta}\rangle^o}{\langle e^{\Delta}\rangle^o} \tag{3.4}$$

or
$$\langle\mu_i\rangle - \langle\mu_i\rangle^o = \delta_i = \frac{\langle x_i e^{\Delta}\rangle^o}{\langle e^{\Delta}\rangle^o} \tag{3.5}$$

In the dense system, we have to calculate $\langle\mu_i\rangle$ (or δ_i) as accurately as possible. From the above equation, we must calculate the average $\langle\ \rangle^o$ including Δ exactly. By eqs.(1.9) and (3.3), we may write

$$\Delta = -\frac{\beta}{2} \sum_{i\neq j\neq 0} U_{ij}\,(x_i - \delta_i)(x_j - \delta_j) \tag{3.6}$$

which is dependent of the variable x_i. Therefore, in order to calculate the average of some quantity including Δ, we must choose a probability function with the variables x_i. Because x_i is the deviation of μ_i from its average $\langle\mu_i\rangle^0$, so we can consider x_i as a local fluctuation of the i th cell occupation number. Let us denote $W\{x_i\}$ as the probability of fluctuations for this whole set of variables $\{x_i\} = x_1 x_2 \ldots\ldots x_t$. Then, according Einstein's formula[21], the probability of fluctuations in an isolated system is

$$W\{x_i\} = \hat{A} e^{\Delta s/k} \tag{3.7}$$

where $\tilde{A}$ is a proportional constant, Δs is the change of entropy from equilibrium associated with the fluctuations, the variables x_i, and k is the Boltzmann constant. The above formula is valid for all equilibrium situations.

For the calculations of the average $\langle\ \rangle^0$ of some quantity, say $f(\Delta)$, with fluctuationΔ, we may assume that

$$\langle f(\Delta)\rangle^0 = \int_{x_1=-1}^{+1} \cdots \int_{x_t=-1}^{+1} W\{x_i\} f(\Delta)\, dx_1 \ldots dx_t \tag{3.8}$$

This assumption should be all right as far as we can express $W\{x_i\}$ in terms of the variables x_i instead of Δ, because the left hand side, $\langle\ \rangle^0$, is the average by using the partition function when $\Delta = 0$. Now we will derive $W\{x_i\}$, from eq.(3.7), as follows:

We are considering fluctuation at constant T and V. Expanding the entropy S around its value at equilibrium, we have

$$S\{x_i\} = S(0) + \sum_i \left(\frac{\partial S}{\partial x_i}\right)_o x_i + \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 S}{\partial x_i \partial x_j}\right)_o x_i x_j + \cdots \qquad (3.9)$$

For an isolated system, the entropy is a maximum in equilibrium, so the second term vanishes. The change of entropy is then

$$\Delta S = S\{x_i\} - S(0) = \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 S}{\partial x_i \partial x_j}\right)_o x_i x_j \qquad (3.10)$$

Because the change of entropy and the change of energy has the relation,

$$\Delta S = \frac{1}{T} \Delta E = \frac{1}{T} [E\{x_i\} - E(0)] \quad \text{for constant } V \qquad (3.11)$$

So $$\frac{\partial^2 S}{\partial x_i \partial x_j} = \frac{1}{T} \frac{\partial^2 E}{\partial x_i \partial x_j} \qquad (3.12)$$

By eqs.(3.10) and (3.12) we may write eq.(3.7) as

$$W\{x_i\} = \tilde{A} e^{\frac{1}{2kT} \sum_{k,l=1}^{t} \Lambda_{kl} x_k x_l} \qquad (3.13)$$

where we define $$\Lambda_{kl} \equiv \left(\frac{\partial^2 E}{\partial x_i \partial x_j}\right)_o \qquad (3.14)$$

Now, we will evaluate Λ_{kl}. Define $U_{ij}=0$ for $i=j$, i.e. $U_{ii}=0$, then

$$E\{x_i\} = \frac{1}{2} \sum_{i,j=0}^{t} \mu_i \mu_j U_{ij}$$

$$= \frac{1}{2} \sum_{i,j=1}^{t} (\langle\mu_i\rangle^o + x_i)(\langle\mu_j\rangle^o + x_j) U_{ij} + \sum_{j=1}^{t} \mu_j U_{oj}$$

$$= \frac{1}{2} \sum_{i,j}^{t} \langle\mu_i\rangle^o \langle\mu_j\rangle^o U_{ij} + \frac{1}{2} \sum_{i,j}^{t} (x_i \langle\mu_j\rangle^o + x_j \langle\mu_i\rangle^o) U_{ij}$$

$$+ \frac{1}{2} \sum_{i,j}^{t} x_i x_j U_{ij} + \sum_{j=1}^{t} (\langle\mu_j\rangle^o + x_j) U_{jo} \qquad (3.15)$$

The variables x_i are not all independent. The sum of x_i is zero, i.e.

$$\sum_{i=1}^{t} x_i = \sum_{i=1}^{t} (\mu_i - \langle\mu_i\rangle^o) = 0$$

$$\text{or} \quad x_t = -\sum_{i=1}^{t-1} x_i \qquad (3.16)$$

Here t can be any cell (not necessary the farthest cell). In order to differentiate eq.(3.15) respect to any of its variable x_i, we have to change the upper limit of sum to t-1, so x_i will be independent variables.

$$E\{x_i = x_1 \ldots x_{t-1}\} = \frac{1}{2} \sum_{i,j} \langle\mu_i\rangle^o \langle\mu_j\rangle^o U_{ij}$$

$$+ 2(\tfrac{1}{2}) \sum_{i,j=1}^{t-1} x_i \langle\mu_j\rangle^o U_{ij} + 2(\tfrac{1}{2}) \sum_{j=1}^{t-1} x_t \langle\mu_j\rangle^o U_{jt}$$

$$+ 2(\tfrac{1}{2}) \sum_{i=1}^{t-1} x_i \langle\mu_t\rangle^o U_{it} + 2(\tfrac{1}{2}) x_t \langle\mu_t\rangle^o U_{tt}$$

$$+ \frac{1}{2} \sum_{i,j=1}^{t-1} x_i x_j U_{ij} + \frac{1}{2} \sum_{j=1}^{t-1} x_t x_j U_{tj} + \frac{1}{2} \sum_{i=1}^{t-1} x_i x_t U_{it} + \frac{1}{2} x_t x_t U_{tt}$$

$$+ \sum_{j=1}^{t-1} \langle\mu_j\rangle^o U_{jo} + \sum_{j=1}^{t-1} x_j U_{jo} + \langle\mu_t\rangle^o U_{to} - \sum_{i=1}^{t-1} x_i U_{to}$$

$$= \frac{1}{2} \sum_{i,j} \langle\mu_i\rangle^o \langle\mu_j\rangle^o U_{ij}$$

$$+ \sum_{i,j=1}^{t-1} x_i \langle\mu_j\rangle^o U_{ij} - \sum_{i,j=1}^{t-1} x_i \langle\mu_j\rangle^o U_{jt} + \sum_{i=1}^{t-1} x_i \langle\mu_t\rangle^o U_{it}$$

$$+ \frac{1}{2} \sum_{i,j=1}^{t-1} x_i x_j U_{ij} - \frac{1}{2} \sum_{i,j=1}^{t-1} x_i x_j U_{tj} - \frac{1}{2} \sum_{i,j=1}^{t-1} x_i x_j U_{it}$$

$$+ \sum_{j=1}^{t-1} \langle\mu_j\rangle^o U_{jo} + \sum_{j=1}^{t-1} x_j U_{jo} + \langle\mu_t\rangle^o U_{to} - \sum_{i=1}^{t-1} x_i U_{to} \qquad (3.17)$$

Now we are ready to differentiate respect to x_k and then x_1.

$$\frac{\partial E}{\partial x_k} = \sum_{j=1}^{t-1} \langle\mu_j\rangle^o U_{kj} - \sum_{j=1}^{t-1} \langle\mu_j\rangle^o U_{jt} + \langle\mu_t\rangle^o U_{kt}$$

$$+ \sum_{j=1}^{t-1} x_j U_{kj} - \frac{1}{2}\sum_{j=1}^{t-1} x_j U_{tj} - \frac{1}{2}\sum_{i=1}^{t-1} x_i U_{tk}$$

$$- \frac{1}{2}\sum_{j=1}^{t-1} x_j U_{kt} - \frac{1}{2}\sum_{i=1}^{t-1} x_i U_{it} + U_{ko} - U_{to} \qquad (3.18)$$

$$\frac{\partial^2 E}{\partial x_l \partial x_k} = U_{kl} - \frac{1}{2} U_{tl} - \frac{1}{2} U_{tk} - \frac{1}{2} U_{kt} - \frac{1}{2} U_{lt}$$

$$= U_{kl} - U_{tl} - U_{tk} \qquad (3.19)$$

$$\therefore\ \Lambda_{kl} \equiv \left(\frac{\partial^2 E}{\partial x_l \partial x_k}\right)_o = U_{kl} - U_{tl} - U_{tk} = \Lambda_{lk} \qquad (3.20)$$

Therefore, Λ_{kl} is a symmetric function, By eq.(3.13) we then have

$$W\{x_i\} = \tilde{A} e^{\frac{1}{2kT} \sum_{k,l=1}^{t-1} \Lambda_{kl} x_k x_l}, \text{ here } \{x_i\} \text{ is } x_1 .. x_{t-1} \qquad (3.21)$$

Next, we will use this probability of fluctuation to calculate the average of the fluctuation terms.

B. The Equation for $\delta(r)$

Here we will use $W\{x_i\}$ in eq.(3.21) to calculate $\langle e^{\Delta}\rangle^o$, from which we are able to derive an equation governing $\delta(r)$, By eq.(3.8),

$$\langle e^{\Delta}\rangle^o \cong \int_{x_1=-1}^{+1} \cdots \int_{x_{t-1}=-1}^{+1} W\{x_i\} e^{\Delta} dx_1 \ldots dx_{t-1} \qquad (3.22)$$

Because $W\{x_i\}$ is from x_1 to x_{t-1}, so we also have to calculate Δ as the sum from 1 to t-1. By eq.(3.6),

$$\Delta = -\frac{\beta}{2} \sum_{i,j=1}^{t} (x_i x_j U_{ij} - 2x_i \delta_j U_{ij} + \delta_i \delta_j U_{ij})$$

$$= -\frac{\beta}{2}\sum_{i,j=1}^{t-1} x_i x_j U_{ij} + \frac{\beta}{2}\sum_{i,j=1}^{t-1} x_i x_j U_{tj} + \frac{\beta}{2}\sum_{i,j=1}^{t-1} x_i x_j U_{ti}$$

$$+ \beta \sum_{i,j=1}^{t-1} x_i \delta_j U_{ij} + \beta \sum_{i=1}^{t-1} x_i \delta_t U_{it} - \beta \sum_{i,j=1}^{t-1} x_i \delta_j U_{tj}$$

$$- \frac{\beta}{2}\sum_{i,j=1}^{t} \delta_i \delta_j U_{ij}$$

$$= -\frac{\beta}{2}\sum_{i,j=1}^{t-1} x_i x_j (U_{ij} - U_{tj} - U_{ti}) + \beta \sum_{i,j=1}^{t-1} x_i \delta_j (U_{ij} - U_{it} - U_{tj})$$

$$- \frac{\beta}{2}\sum_{i,j=1}^{t} \delta_i \delta_j U_{ij}$$

$$\text{or } \Delta = -\frac{\beta}{2}\sum_{i,j=1}^{t-1} x_i x_j \Lambda_{ij} + \beta \sum_{i,j=1}^{t-1} x_i \delta_j \Lambda_{ij} - \frac{\beta}{2}\sum_{i,j}^{t} \delta_i \delta_j U_{ij} \qquad (3.23)$$

In the above derivation, we have used the condition that

$$\sum_{j=1}^{t} \delta_j = 0 \quad \text{or} \quad \delta_t = -\sum_{j=1}^{t-1} \delta_j \qquad (3.24)$$

Substituting eqs.(3.21) and (3.23) into eq.(3.8), we have

$$\langle e^{\Delta}\rangle^{0} = \tilde{A} \int_{x_1=-1}^{+1} \cdots \int_{x_{t-1}=-1}^{+1} W\{x_i\} e^{\Delta} dx_1 \ldots dx_{t-1}, \text{here } \{x_i\} = x_1 \ldots x_{t-1}$$

$$= \tilde{A} \exp\left(-\frac{\beta}{2}\sum_{i,j=1}^{t} \delta_i \delta_j U_{ij}\right) \int_{-1}^{+1} \cdots \int \exp\left(\beta \sum_{i=1}^{t-1} x_i \lambda_i\right) dx_1 \ldots dx_{t-1}$$

(3.25)

$$\text{where we define } \lambda_i \equiv \sum_{j=1}^{t-1} \Lambda_{ij} \delta_j \qquad (3.26)$$

$$\text{and } \int_{-1}^{+1} \cdots \int \exp\left(\beta \sum_{i=1}^{t-1} x_i \lambda_i\right) dx_1 \ldots dx_{t-1} = \prod_{i=1}^{t-1} \int_{-1}^{+1} \exp(\beta \lambda_i x_i) dx_i$$

$$= \prod_{i=1}^{t-1} \frac{1}{\beta \lambda_i} \left(e^{\beta \lambda_i} - e^{-\beta \lambda_i}\right)$$

$$= \prod_{i=1}^{t-1} \frac{2 \sinh \beta \lambda_i}{\beta \lambda_i} \qquad (3.27)$$

By eqs.(3.25) and (3.27), we have

$$<e^{\Delta}>^{o} = \hat{A} \exp(-\frac{\beta}{2} \sum_{i,j=1}^{t} \delta_i \delta_j U_{ij}) (2)^{t-1} \prod_{i=1}^{t-1} \frac{\sinh \beta\lambda_i}{\beta\lambda_i} \qquad (3.28)$$

By eqs.(3.25), we can find δ_i by

$$\delta_i = \frac{<x_i e^{\Delta}>^{o}}{<e^{\Delta}>^{o}} = \frac{1}{\beta} \frac{\partial \ln <e^{\Delta}>^{o}}{\partial \lambda_i} \qquad (3.29)$$

$$\ln <e^{\Delta}>^{o} = \ln \tilde{A} - \frac{\beta}{2} \sum_{i,j=1}^{t} \delta_i \delta_j U_{ij} + (t-1) \ln 2 + \sum_{i=1}^{t-1} \ln \frac{\sinh \beta\lambda_i}{\beta\lambda_i} \qquad (3.30)$$

$$\therefore \quad \delta_i = \coth \beta\lambda_i - \frac{1}{\beta\lambda_i} \qquad (3.31)$$

The right hand side is a Langevin function, i.e. $\mathcal{L}(\beta\lambda_i)$, so

$$\delta_i = \mathcal{L}(\beta\lambda_i) \quad \text{or} \quad \delta_i = \mathcal{L}(\beta \sum_{j=1}^{t-1} \Lambda_{ij}\delta_j) \qquad (3.32)$$

We call this as the equation for δ_i. This is an exact equation.

In order to solve this non-linear equation, we may expand the right hand side as $(\beta\lambda_i/3)-(\beta\lambda_i)^3/45+..$, but λ_i itself is a linear sum of δ_j, so it will be better to use the inverse Langevin in the left hand side and expand it as the order of δ_i, i.e.

$$\mathcal{L}^{-1}\delta_i = \beta \sum_{j=1}^{t-1} \Lambda_{ij}\delta_j \qquad (3.33)$$

Here $\mathcal{L}^{-1}\delta_i = A_1\delta_i + A_2\delta_i^2 + A_3\delta_i^3 + \ldots$, the constants, $A_1=3$, $A_2=0$, $A_3=9/5$ (see Appendix B). δ_i is the order of zero, so the second and third order of δ_i can be neglected.

Now, we may write eq.(3.33) as

$$\delta_i = \frac{\beta}{3} \sum_{j=1}^{t-1} \Lambda_{ij}\delta_j \quad \text{or} \quad \delta_i = \frac{\beta}{3} \sum_{j=1}^{t-1} (U_{ij}-U_{ti}-U_{tj})\delta_j = \frac{\beta}{3} \sum_{j=1}^{t} U_{ij}\delta_j \qquad (3.34)$$

According to the same method in Appendix A, we can derive

$$\sum_{j=1}^{t} U_{ij}\delta_j = \frac{2\pi}{rv} \int_{\sigma}^{\infty} x\delta(x)K(x,r)\,dx \qquad (3.35)$$

where K(x,r) is defined in eq.(1.25)

Combining eqs.(3.34) and (3.35), we have

$$\delta(r) = \frac{2\pi\beta}{3vr} \int_{\sigma}^{\infty} x\delta(x)K(x,r)\,dx \qquad (3.36)$$

or $$\Pi(r) = \lambda\int_{\sigma}^{\infty} \Pi(x)K(x,r)\,dx \qquad (3.37)$$

where we define $\Pi(r) \equiv r\delta(r)$ (3.38)

and $$\lambda = 2\pi\beta/3v \qquad (3.39)$$

Eq.(3.37) is the equation for $\Pi(r)$, then for $\delta(r)$. If this equation has the finite upper limit, then in general, this equation has but one solution $\Pi(r) = 0$. But there exists a set of characteristic constants $\lambda_1, \lambda_2, \ldots$, for each of which this equation has a finite solutions $\Pi_1(r), \Pi_2(r) \ldots$, called the characteristic functions. The solution is then obtained in the form $\Pi(r) = \sum_n C_n\Pi_n(r)$ where the C_n are arbitrary constant. But our equation has the upper limit ∞. So it might have a solution $\Pi(r)$ for certain λ.

It is very difficult to solve $\Pi(r)$ for all regions r, but for very large r and very small r, we can use a good approximation to simplify the kernel and use a special potential function to solve for $\Pi(r)$. In the following section we will first consider the case when r is very large. After that, we then will consider the case when r is very small. Then we can extend to all region r by using the condition that $\sum_{i=1}\delta_i = 0$.

C. Solution of $\Pi(r)$ for Very Large r

If r is very large, we can simplify the kernel K(x,r) so that $\Pi(r)$ can be solved easily. A special potential function is used here to solve the equation.

From eq.(3.37), we will first solve $\Pi(r)$ for very large r. Since K(x,r) in eq.(1.25), is so complex, - i.e.

$$\begin{aligned} K(x,r) &= \int_{\sigma}^{x+r} \xi U(\xi)\,d\xi \equiv K_I(x,r) \qquad \text{when } |x-r| < \sigma \\ &= \int_{|x-r|}^{x+r} \xi U(\xi)\,d\xi \equiv K_{II}(x,r) \qquad \text{when } |x-r| \geq \sigma \end{aligned} \tag{3.40}$$

We shall select a special potential function, which is nevertheless realistic qualitatively. we take

$$\begin{aligned} U(r) &= U_0 \qquad \text{for } r \leq \sigma \\ &= A\frac{e^{-\mu r}}{r} \qquad \text{for } r > \sigma \end{aligned} \tag{3.41}$$

where U_0 and μ are positive constants and A is a negative constant.

Because kernel K(x,r) is different in the regions $|x-r| < \sigma$ and $|x-r| \geq \sigma$, so we have to derive a kernel for all the region when r is very large. In the region, $r-\sigma$ to $r+\sigma$, since r is very large, $\Pi(r)$ is almost constant. So by eq.(3.40), we write eq.(3.37) as

$$\Pi(r) = \lambda\int_{|r-x|\geq\sigma} \Pi(x)K_{II}(x,r) + \lambda\Pi(r)\int_{r-\sigma}^{r+\sigma} K_I(x,r)\,dx \tag{3.42}$$

$$= \lambda\int_{\sigma}^{\infty}\Pi(x)K_{II}(x,r)\,dx - \lambda\Pi(r)\int_{|r-x|<\sigma}K_{II}(x,r)\,dx + \lambda\Pi(r)\int_{r-\sigma}^{r+\sigma}K_I(x,r)\,dx \tag{3.43}$$

Now, for very large r, we find (Appendix C)

$$\int_{r-\sigma}^{r+\sigma} K_I(x,r)\,dx = \frac{2\sigma A}{\mu} e^{-\mu\sigma} \qquad (\text{if } r \to \infty) \tag{3.44}$$

$$\int_{|r-x|<\sigma} K_{II}(x,r)\,dx = \frac{2U_0\sigma^3}{3} + \frac{2\sigma A}{\mu} e^{-\mu\sigma} \quad (\text{if } r \to \infty) \tag{3.45}$$

Substituting eqs.(3.44) and (3.45) into eq. (3.43), we have

$$\Pi(r) = \lambda\int_\sigma^\infty \Pi(x)K_{II}(x,r)\,dx - \frac{2U_0\sigma^3}{3}\lambda\Pi(r)$$

or $$\Pi(r) = \nu\int_\sigma^\infty \Pi(x)K_{II}(x,r)\,dx \tag{3.46}$$

where $$\nu \equiv \frac{\lambda}{1+(2U_0\sigma^3/3)\lambda} \tag{3.47}$$

In the following, we will derive a simple form for $K_{II}(x,r)$:

Using eq.(3.41), $K_{II}(x,r)$ in eq.(3.40) can be written

$$K_{II}(x,r) = \int_{|x-r|}^{\sigma} \xi U_0\,d\xi + \int_\sigma^{x+r} \xi A \frac{e^{-\mu\xi}}{\xi}\,d\xi \qquad \text{if } |x-r| < \sigma$$

$$= \int_{|x-r|}^{x+r} \xi A \frac{e^{-\mu\xi}}{\xi}\,d\xi \qquad \text{if } |x-r| \geq \sigma$$

or

$$K_{II}(x,r) = \begin{cases} U_0\{\frac{\sigma^2}{2} - \frac{|x-r|^2}{2}\} - \frac{A}{\mu}\{e^{-\mu(x+r)} - e^{-\mu\sigma}\} \equiv K_{II}^{(1)}(x,r) & \text{for } |x-r| < \sigma \\ -\frac{A}{\mu}\{e^{-\mu(x+r)} - e^{-\mu|x-r|}\} \equiv K_{II}^{(2)}(x,r) & \text{for } |x-r| \geq \sigma \end{cases} \tag{3.48}$$

Note, $\Pi(r) = r\delta(r)$, so $\Pi(r) = 0$ if $r = 0$. Also at the central cell, the occupation number is always +1, so $\delta(r) = 0$ if $r < \sigma$. i.e. $\Pi(r) = 0$ for $r < \sigma$. Then, from eq.(3.46), the lower limit σ in the integral can be replaced by 0, i.e.

$$\Pi(r) = \nu\int_0^\infty \Pi(x)K_{II}(x,r)\,dx \tag{3.49}$$

here the integral also includes the region r-σ to r+σ, i.e.

$$\int_{r-\sigma}^{r+\sigma} \Pi(x)K_{II}(x,r)\,dx \simeq \Pi(r)\int_{r-\sigma}^{r+\sigma} K_{II}\,(x,r)\,dx \tag{3.50}$$

Using $K_{II}^{(1)}$ and $K_{II}^{(2)}$ of eq.(3.48), we find, for very large r,

$$\int_{|r-x|\leq\sigma} K_{II}^{(1)}(x,r)\,dx = \frac{2U_o\sigma^3}{3} + \frac{2\sigma A e^{-\mu\sigma}}{\mu} \underset{\mu\to 0}{=} \frac{2U_o\sigma^3}{3} - 2\sigma^2 A + \frac{2A\sigma}{\mu} \tag{3.51}$$

$$\int_{|r-x|\leq\sigma} K_{II}^{(2)}(x,r)\,dx = \frac{2A}{\mu^2}\,(1 - e^{-\mu\sigma}) \underset{\mu\to 0}{=} \frac{2A\sigma}{\mu} \tag{3.52}$$

We assume $(\frac{2}{3}U_o\sigma^3 - 2\sigma^2 A) << \frac{2A\sigma}{\mu}$ (3.53)

Then we see that $K_{II} = K_{II}^{(2)}$ can be used throughout the region 0 to ∞,

$$K_{II}(x,r) = \frac{A}{\mu}\{e^{-\mu|x-r|} - e^{-\mu(x+r)}\} \qquad \text{for all } x \tag{3.54}$$

For very large r, we find

$$K_{II}(x,r) = \frac{A}{\mu}\,e^{-\mu(r-x)} \qquad \text{if } x<r \tag{3.55a}$$

$$K_{II}(x,r) = \frac{A}{\mu}\,e^{-\mu(x-r)} \qquad \text{if } x>r \tag{3.55b}$$

The reason is, for $x\geq r$, eq.(3.54) can be written as

$$K_{II}(x,r) = \frac{A}{\mu}\,e^{-\mu x}\{e^{\mu r} - e^{-\mu r}\} \simeq \frac{A}{\mu}\,e^{-\mu x}e^{\mu r}, \text{ because } e^{-\mu r}\to 0 \text{ as } r\to\infty$$

For $x\leq r$, eq.(3.54) can be written as

$$K_{II}(x,r) = \frac{A}{\mu}\,e^{-\mu r}(e^{\mu x} - e^{-\mu x}) = 0, \text{ if } x = 0$$

$$\simeq \frac{A}{\mu}\,e^{-\mu r}e^{\mu x}, \text{ if } x\neq 0, \text{ r is very large.}$$

Therefore, for very large r, $K_{II}(x,r)$ has the simple form,

$$K_{II}(x,r) \cong \frac{A}{\mu} e^{-\mu|x-r|} \quad \text{for all } x \tag{3.56}$$

Eq. (3.49) can then be written as

$$\Pi(r) = \frac{A\nu}{\mu} \int_0^r \Pi(x) e^{-\mu(r-x)} dx + \frac{A\nu}{\mu} \int_r^\infty \Pi(x) e^{-\mu(x-r)} dx \tag{3.57}$$

We can now convert this to a differential equation as follows:

Using Leibniz's formula, we differentiate $\Pi(r)$ twice, giving

$$\frac{d\Pi(r)}{dr} = \frac{A\nu}{\mu} \int_0^r \Pi(x)(-\mu) e^{-\mu(r-x)} dx + \frac{A\nu}{\mu} \Pi(r) + \frac{A\nu}{\mu} \int_r^\infty \Pi(x)(\mu) e^{-\mu(x-r)} dx$$

$$- \frac{A\nu}{\mu} \Pi(r)$$

or
$$\frac{d\Pi(r)}{dr} = -A\nu \int_0^r \Pi(x) e^{-\mu(r-x)} dx + A\nu \int_r^\infty \Pi(x) e^{-\mu(x-r)} dx \tag{3.58}$$

$$\frac{d^2\Pi(r)}{dr^2} = A\nu\mu \int_0^r \Pi(x) e^{-\mu(r-x)} dx - A\nu\Pi(r) + A\nu\mu \int_r^\infty \Pi(x) e^{-\mu(x-r)} dx$$

$$- A\nu\Pi(r) \tag{3.59}$$

By eqs.(3.57) and (3.58), we have

$$\frac{d^2\Pi(r)}{dr^2} + (-\mu^2 + 2A\nu)\, \Pi(r) = 0 \tag{3.60}$$

The solution for this equation is

$$\Pi(r) = \delta_0 e^{-\sqrt{\mu^2 - 2\nu A}\, r} \qquad \text{for } r \to \infty \tag{3.61}$$

where $\mu^2 - 2\nu A$ should be positive. $\Pi(r)$ will drop exponentially for very large r. And δ_0 is a constant.

or
$$\delta(r) = \delta_0 \frac{e^{-\sqrt{\mu^2 - 2\nu A}\, r}}{r} \qquad \text{for } r \to \infty \tag{3.62}$$

Now, the constant δ_0 can be found as follows:

Substituting eqs.(1.18), (1.14) and (3.62) into (3.2),

$$\delta_0 \frac{e^{-\sqrt{\mu^2 - 2\nu A}\ r}}{r} = n\nu\rho(r) - \frac{ze^{-\beta\phi(r)}}{1+ze^{-\beta\phi(r)}} \tag{3.63}$$

Let us assume for very large r that U(r) is very small, then

$$\rho(r) \cong e^{-\beta U(r)} \cong 1 - \beta U(r) \quad \text{(See Appendix D)} \tag{3.64}$$

and $\phi(r) \cong U(r) + h$ (3.65)

and by $z = \xi_0 e^{\beta h} = \frac{n\nu}{1-n\nu} e^{\beta h}$ eq. (1.15)

We can write eq.(3.63) as, to $O(\beta U)$,

$$\delta_0 \frac{e^{-\sqrt{\mu^2 - 2\nu A}\ r}}{r} \cong - n^2\nu^2\beta U(r) \tag{3.66}$$

By using the special potential in eq.(3.41) for U(r), we have

$$\delta_0 \frac{e^{-\sqrt{\mu^2 - 2\nu A}\ r}}{r} \cong - n^2\nu^2\beta A \frac{e^{-\mu r}}{r} \tag{3.67}$$

This can only be valid if

$$\mu^2 >> 2\nu A \tag{3.68}$$

and thus $\delta_0 = -n^2\nu^2\beta A$, a positive quantity ($A < 0$) (3.69)

Therefore $\delta(r) = \delta_0 \frac{e^{-\mu r}}{r}$ for $r \to \infty$, $\delta_0 > 0$ (3.70)

or $\Pi(r) = \delta_0\ e^{-\mu r}$ for $r \to \infty$ (3.71)

We see here, that $\delta(r)$ is proportional to the pair potential for very large r. It will drop very fast and approach 0 as $r \to \infty$. In the next section, we will derive a relation between $\delta(r)$ and a general pair potential U(r).

D. Relation between $\delta(r)$ and U(r) for Very Large r

Here we consider the relation between $\delta(r)$ and U(r) for a general potential function when r is very large. From eq.(3.2), we write

$$\delta(r) = \langle\mu(r)\rangle - \langle\mu(r)\rangle^{0} \tag{3.72}$$

where r is the distance of the i th cell from the central particle. We substitute eqs.(1.18) and (1.14) into eq.(3.72),

$$\delta(r) = nv\rho(r) - \frac{ze^{-\beta\phi(r)}}{1+ze^{-\beta\phi(r)}} \tag{3.73}$$

When r is very large, by eqs.(3.64), (3.65) and (1.15), we may write eq.(3.73) as

$$\delta(r) = nve^{-\beta U(r)} - \frac{(\frac{nv}{1-nv}e^{\beta h})e^{-\beta\{U(r)+h\}}}{1+(\frac{nv}{1-nv}e^{\beta h})e^{-\beta\{U(r)+h\}}}$$

$$= nve^{-\beta U(r)} - \frac{nve^{-\beta U(r)}}{1-nv+nve^{-\beta U(r)}}$$

$$\simeq nv\{1-\beta U(r)\} - \frac{nv\{1-\beta U(r)\}}{1-nv\beta U(r)} \tag{3.74}$$

$$= nv\{1-\beta U(r)\}\{\frac{-nv\beta U(r)}{1-nv\beta U(r)}\}$$

$$= -n^2v^2\{1-\beta U(r)\}\beta U(r)\{1+nv\beta U(r)\}$$

or $$\delta(r) \cong -n^2v^2\beta U(r) \tag{3.75}$$

In the above derivation, because U(r) is a very small negative quantity when r is very large, so $|\beta U(r)|^2 << |\beta U(r)|$ has been used in the derivation. Therefore, for very large r, $\delta(r)$ is proportional to the pair potential function U(r).

Note, $\delta(r)$ is a positive quantity for large r. This is equivalent to $<\mu(r)> \, > \, <\mu(r)>^o$ for large r. The physical explaination for why $\delta(r) > 0$ is as follows: For large r, we expect that $<\mu_i> = <\mu_i>^o$. Substituting this into the right hand side of eq.(2.27), we have

$$<\mu_i> = \frac{<\mu_i>^o + <\mu_i\Delta>^{oo} + <\mu_i\Delta^2>^{oo}/2! + ..}{1 + <\Delta>^{oo} + <\Delta^2>^{oo}/2! + ...}$$

where we use the double superscript zero on the average, $< >^{oo}$, for $< >^o$ being calculated by assuming $<\mu_i> = <\mu_i>^o$. From eqs.(2.30) and (2.31), we find $<\Delta>^{oo} = 0$, and $<\mu_i\Delta>^{oo} = 0$

Thus, $$<\mu_i> \underset{r\to\infty}{=} \frac{<\mu_i>^o + <\mu_i\Delta^2>^{oo}/2! + ...}{1 + <\Delta^2>^{oo}/2! + ...}$$

$$\cong <\mu_i>^o + <\mu_i\Delta^2>^{oo}/2! - <\mu_i>^o<\Delta^2>^{oo}/2!$$

By eq.(1.9), we have

$$\Delta^2 = (-\frac{\beta}{2})^2 \sum_{j\neq k\neq 0} \sum_{l\neq m\neq 0} U_{jk}U_{lm}(\mu_j-<\mu_j>)(\mu_k-<\mu_k>)(\mu_l-<\mu_l>)(\mu_m-<\mu_m>)$$

$$<\mu_i\Delta^2>^o = <\mu_i>^o \frac{\beta^2}{4} \sum_{\substack{j\neq k\neq 0\\ i\neq j\\ i\neq k}} \sum_{\substack{l\neq m\neq 0\\ i\neq l\\ i\neq m}} \frac{\Sigma(..)\tilde{P}_o}{\Sigma\tilde{P}_o} + \frac{\beta^2}{4}\{ [\sum_{\substack{j\neq k\neq 0\\ i=j\\ i\neq k}} \sum_{\substack{l\neq m\neq 0\\ i\neq l\\ i\neq m}} + ...] \frac{\Sigma\mu_i(..)\tilde{P}_o}{\Sigma\tilde{P}_o}\}$$

and

$$<\mu_i>^o<\Delta^2>^o = <\mu_i>^o \frac{\beta^2}{4} \sum_{\substack{j\neq k\neq 0\\ i\neq j\\ i\neq k}} \sum_{\substack{l\neq m\neq 0\\ i\neq l\\ i\neq m}} \frac{\Sigma(..)\tilde{P}_o}{\Sigma\tilde{P}_o}$$

$<u_i\Delta^2>^o - <\mu_i>^o<\Delta^2>^o$ is a positive,

and so $<\mu_i\Delta^2>^{oo} - <\mu_i>^o<\Delta^2>^{oo}$ is a positive, too.

For large r, higher order terms in Δ should give a negligible contributions. Thus, for $r \to \infty$, we have

$<\mu_i> > <\mu_i>^o$

Therefore, when the fluctuation Δ is considered, the particles are likely to move around and have more opportunity to switch their positions from the dense portions (near the central particle) to the dilute portion (far away from the central particle).

E. Approximate Solution of $\Pi(r)$ for Small r

In the last section, we find $\delta(r)$, for very large r, decreases proportionally to the pair potential function from positive quantity to zero. We expect $\delta(r)$, for small r, will start from the negative, so that the sum of $\delta(r)$ will be zero. Here we will solve $\Pi(r)$ in eq. (3.37) for small r, and for a special types of potential and $\sigma \doteq 0$.

For the moment, we consider a general potential U(r). Using the kernel in eq.(3.40), we rewrite

$$K_I(x,r) = N(x + r) - N(\sigma) \qquad \text{when } |x - r| < \sigma$$

$$K_{II}(x,r) = N(x + r) - N(|x-r|) \quad \text{when } |x - r| \geq \sigma \qquad (3.76)$$

where we define

$$N(x) \equiv \int^x \xi U(\xi) d\xi \qquad (3.77)$$

we also define $M(\sigma) \equiv \int_{r-\sigma}^{r+\sigma} N(|x-r|)dx$ (3.78)

By the above definitions, we can write eq.(3.37) as

$$\Pi(r) = \lambda \int_{\sigma}^{r-\sigma} \Pi(x)K_{II}(x,r)dx + \lambda \int_{r-\sigma}^{r+\sigma} \Pi(x)K_{I}(x,r)dx + \lambda \int_{r+\sigma}^{\infty} \Pi(x)K_{II}(x,r)dx$$

$$= \lambda \int_{\sigma}^{r-\sigma} \Pi(x)\{N(x+r) - N(r-x)\}dx + \lambda \int_{r-\sigma}^{r+\sigma} \Pi(x)\{N(x+r) - N(\sigma)\}dx$$

$$+ \lambda \int_{r+\sigma}^{\infty} \Pi(x) \{N(x+r) - N(x-r)\}dx$$

$$= \lambda \int_{\sigma}^{\infty} \Pi(x)N(x+r)dx - \lambda \int_{\sigma}^{r-\sigma} \Pi(x)N(r-x)dx - \lambda \int_{r-\sigma}^{r+\sigma} \Pi(x)N(\sigma)dx$$

$$- \lambda \int_{r+\sigma}^{\infty} \Pi(x)N(x-r)dx$$

$$= \lambda \int_{\sigma}^{\infty} \Pi(x)\{N(x+r) - N(|x-r|)\}dx - \lambda \int_{r-\sigma}^{r+\sigma} \Pi(x)N(\sigma)dx$$

$$+ \lambda \int_{r-\sigma}^{r+\sigma} \Pi(x)N(x-r)dx$$

or $\Pi(r) = \lambda \int_{\sigma}^{\infty} \Pi(x)\{N(x+r)-N(|x-r|)\}dx - 2\sigma\lambda N(\sigma)\Pi(r) + \lambda\Pi(r)M(\sigma)$ (3.79)

Here we also assume $\Pi(r)$ is almost constant in the region $r-\sigma$ to $r+\sigma$. Rearrange eq.(3.79), we have

$$\Pi(r) = \eta \int_{\sigma}^{\infty} \Pi(x)\{N(x+r) - N(|x-r|)\}dx \quad (3.80)$$

where $\eta = \dfrac{\lambda}{1+2\sigma\lambda N(\sigma)-\lambda M(\sigma)}$ (3.81)

So far, we have not assumed that r is small yet. Notice, the equation is independent of the behavior of $N(|\xi|)$ for $|\xi| < \sigma$, i.e. of $U(\xi)$ for $\xi < \sigma$

Eq.(3.80) can be written in two parts,

$$\Pi(r) = \eta \int_\sigma^r \Pi(x)\{N(x+r) - N(r-x)\}dx + \eta \int_r^\infty \Pi(x)\{N(x+r) - N(x-r)\}dx \tag{3.82}$$

By Leibniz's formula, we differentiate $\Pi(r)$,

$$\frac{d\Pi(r)}{dr} = \eta \int_\sigma^r \Pi(x)\{\frac{\partial N(x+r)}{\partial r} - \frac{\partial N(r-x)}{\partial r}\} dx + \eta \int_r^\infty \Pi(x)\{\frac{\partial N(x+r)}{\partial r} - \frac{\partial N(x-r)}{\partial r}\}dx$$

$$+ \eta\Pi(r)\{N(2r) - N(0)\} - \eta\Pi(r)\{N(2r) - N(0)\} \tag{3.83}$$

By eq.(3.77),

$$\frac{\partial}{\partial r} \{N(x+r)\} = (x+r)U(x+r) \tag{3.84}$$

$$\frac{\partial}{\partial r} \{N(r-x)\} = (r-x)U(r-x) \tag{3.85}$$

$$\frac{\partial}{\partial r} \{N(x-r)\} = - (x-r)U(x-r) = (r-x)U(r-x) = \frac{\partial}{\partial r}\{N(r-x)\} \tag{3.86}$$

The last equation is due to $U(r) = U(-r)$, which means that the pair potential depends only the absolute distance between two particles, then

$$\frac{d\Pi(r)}{dr} = \eta \int_\sigma^\infty \Pi(x)\{(x+r)U(x+r) + (x-r)U(x-r)\}dx \tag{3.87}$$

Note, this is an equation for general potential for all r. No Approximation has been used except $\Pi(r) \cong \Pi(x)$ in the region $|r-x| \leq \sigma$.

Now, we will use the special potential in eq.(3.41) to solve the above equation for $\Pi(r)$ as follows: For a special case, assume

$$\sigma = 0 \tag{3.88}$$

And write eq.(3.87) in two parts, the lower limit σ is replaced by 0.

$$\frac{d\Pi(r)}{dr} = \eta\int_0^r \Pi(x)\{Ae^{-\mu(x+r)} - Ae^{-\mu(r-x)}\}dx + \eta\int_r^\infty \Pi(x)\{Ae^{-\mu(x+r)} + Ae^{-\mu(x-r)}\}dx$$

or $$\frac{d\Pi(r)}{dr} = -2\eta Ae^{-\mu r}\int_0^r \Pi(x)\sinh \mu x dx + 2\eta A \cosh \mu r\int_r^\infty \Pi(x)e^{-\mu x}dx \quad (3.89)$$

This is an equation for $\sigma \approx 0$ and all r. We may rewrite this as

$$\frac{d\Pi(r)}{dr} = -2\eta Ae^{-\mu r}\int_0^r \Pi(x)\sinh \mu x dx + 2\eta A \cosh \mu r\{\int_0^\infty \Pi(x)e^{-\mu x}dx - \int_0^r \Pi(x)e^{-\mu x}dx\}$$

For very small r, i.e. $r \approx 0$, the integral $\int_0^r$ will be negligible, so

$$\frac{d\Pi(r)}{dr} = 2\eta A(\cosh \mu r) \int_0^\infty \Pi(x)e^{-\mu x}dx \qquad \text{for } r \doteq 0 \quad (3.90)$$

or $$\frac{d\Pi(r)}{dr} = 2\eta AB(\cosh \mu r) \qquad \text{for } r \doteq 0 \quad (3.91)$$

where $$B \equiv \int_0^\infty \Pi(x)e^{-\mu x}dx = \text{a constant} \quad (3.92)$$

The solution of eq.(3.91), using the condition $\Pi(0) = 0$, is

$$\Pi(r) = \frac{2\eta AB}{\mu} \sinh \mu r \qquad (\text{for } \sigma \approx 0,\ r \approx 0) \quad (3.93)$$

or $$\delta(r) = \frac{2\eta AB}{\mu} \frac{\sinh \mu r}{r} \qquad (\text{for } \sigma \approx 0,\ r \approx 0) \quad (3.94)$$

From this equation, we see the behavior of $\delta(r)$. Because A is a negative constant. If B is a positive, $\delta(r)$ will be negative for small r, the region between large r and small r is unknown. As $\delta(r)$ is negative for small r and $\delta(r)$ is positive for large r, we may expect to find a satisfaction of the condition that

$$\sum_{i=1} \delta_i = 0 \quad (3.95)$$

Later on, we will show how to find B. We will reconsider $\Pi(r)$ for very large r for the case when μ is very small in the next section.

F. Reconsideration of $\Pi(r)$ for Very Large r with $\mu \simeq 0$

When $\mu \doteq 0$, we have a long and weak interation between two particles. We will use the results we have got before to reconsider $\Pi(r)$ for very large r.

Still assuming $\sigma \simeq 0$, we can use $\Pi(r)$ in eq.(3.71) in the integral $\int_r^\infty$ of eq.(3.89) i.e.

$$\frac{d\Pi(r)}{dr} = -2\eta A e^{-\mu r} \int_0^r \Pi(x) \sinh \mu x dx + 2\eta A \cosh \mu r \int_r^\infty \delta_o e^{-2\mu x} dx$$

$$= -2\eta A e^{-\mu r} \int_0^r \Pi(x) \sinh \mu x dx + \frac{\eta A \delta_o}{2u} (e^{-\mu r} + e^{-3\mu r}) \qquad (3.96)$$

For the case of very large r with $\mu \simeq 0$, the integral in the first term will be proportional to r as the integrand approaches a constant, and we have $\mu \simeq 0$ in the denominator of the second term. Therefore

$$\frac{d\Pi(r)}{dr} \cong \frac{\eta A \delta_o}{2\mu} e^{-\mu r} \qquad (\text{for } r \to \infty,\ \mu \simeq 0) \qquad (3.97)$$

The solution of this equation requiring condition $\Pi(\infty) = 0$, is

$$\Pi(r) = \frac{-\eta A}{2\mu^2} \delta_o e^{-\mu r} \qquad (\text{for } r \to \infty,\ \mu \simeq 0) \qquad (3.98)$$

Choosing $-\eta A/2\mu^2 = 1 \qquad (A < 0) \qquad (3.99)$

Then $\Pi(r) = \delta_o e^{-\mu r} \qquad (\text{for } r \to \infty,\ \mu \simeq 0) \qquad (3.100)$

This is the same equation as eq.(3.71). Now we will discuss the assumptions made in these two cases. In the former, we assume $(2U_o\sigma^3/3 - 2\sigma^2 A) \ll 2A\sigma/\mu$, eq.(3.53) and $\mu^2 \gg 2\nu A$, eq.(3.68). And now we assume $-\eta A/2\mu^2 = 1$ and $\mu \simeq 0$. When $\mu \simeq 0$, the former assumption can also be applied, but we have to select $2\nu A$ even being smaller than μ^2. By such assumptions, we may decide those constants A, μ, U_0 in the special potential function in eq.(3.41).

This argument can also be applied to the case where $\sigma \neq 0$ as follows:

Assuming $\sigma \neq 0$, we devide eq.(3.87) in three regions, i.e.

$$\frac{d\Pi(r)}{dr} = \eta\{\int_\sigma^{r-\sigma} + \int_{r-\sigma}^{r+\sigma} + \int_{r+\sigma}^{\infty}\}\{\Pi(x)[(x+r)U(x+r) + (x-r)U(x-r)]\} \, dx \quad (3.101)$$

We will use a special potential, eq.(3.41), for the above equation,

$$\begin{aligned}\frac{d\Pi(r)}{dr} &= \eta\int_\sigma^{r-\sigma}\Pi(x)\{Ae^{-\mu(x+r)} - Ae^{-\mu(r-x)}\}dx \\ &\quad + \eta\Pi(r)\{\int_{r-\sigma}^{r} A[e^{-\mu(x+r)} - e^{-\mu(r-x)}] \, dx \\ &\qquad + \int_r^{r+\sigma} A[e^{-\mu(x+r)} + e^{-\mu(x-r)}] \, dx\} \\ &\quad + \eta\int_{r+\sigma}^{\infty}\Pi(x)\{Ae^{-\mu(x+r)} + Ae^{-\mu(x-r)}\}dx \end{aligned} \quad (3.102)$$

where $\Pi(r)$ is assumed constant in the region $r-\sigma$ to $r+\sigma$.

$$\begin{aligned}\text{or } \frac{d\Pi(r)}{dr} &= -2\eta Ae^{-\mu r}\int_\sigma^{r-\sigma}\Pi(x)(\sinh \mu x)\,dx \\ &\quad + \frac{2\eta A}{\mu}(\sinh \mu\sigma)\Pi(r)e^{-2\mu r} \\ &\quad + 2\eta A(\cosh \mu r)\int_{r+\sigma}^{\infty}\Pi(x)e^{-\mu x}dx \qquad \text{(for all r)}\end{aligned} \quad (3.103)$$

For the case of very large r, $\Pi(r) = \delta_0 e^{-\mu r}$ in eq.(3.71) can be applied in the second term and the last integral. Then

$$\frac{d\Pi(r)}{dr} = -2\eta A e^{-\mu r}\int_{\sigma}^{r-\sigma}\Pi(x)(\sinh\ \mu x)dx + \frac{2\eta A}{\mu}(\sinh\ \mu\sigma)\delta_o e^{-3\mu r}$$
$$+\frac{\eta A}{2\mu}\delta_o(e^{-\mu r} + e^{-3\mu r}) \qquad (\text{for } r \to \infty) \qquad (3.104)$$

For the case of very large r with $\mu \doteq 0$, eq.(3.104) becomes

$$\frac{d\Pi(r)}{dr} \cong \frac{\eta A}{2\mu}\delta_o e^{-\mu r} \qquad (\text{for } r \to \infty,\ \mu \simeq 0) \qquad (3.105)$$

The solution of this equation with the condition $\Pi(\infty) = 0$, is

$$\Pi(r) = \frac{\eta A}{-2\mu^2}\delta_o\ e^{-\mu r} \qquad (\text{for } r \to \infty,\ \mu \simeq 0) \qquad (3.106)$$

By the same assumption $-\eta A/2\mu^2 = 1$ as eq.(3.99), we have

$$\Pi(r) = \delta_o\ e^{-\mu r} \qquad (\text{for } r \to \infty,\ \mu \simeq 0) \qquad (3.107)$$

This is the same result as in eqs.(3.71) and (3.100). So, for large r, we have derived the same expression for $\Pi(r)$ from two very different approaches.

G. Determination of B and r_o

Here we still use the special potential function in eq.(3.41) with $\mu \simeq 0$. We have already defined B in eq.(3.92). In the previous sections, we have derived $\delta(r)$ for very special cases as r is very large and r is very small. We have no idea how $\delta(r)$ will be in the region between these two cases. So we may approximately find a point r_o as the match point for $\delta(r)$ as $r \to 0$ and $r \to \infty$.

For the moment, in general case, we denote

$$\Pi(r) = \overset{<}{\Pi}(r) \quad \text{or} \quad \delta(r) = \overset{<}{\delta}(r) \quad \text{for } r < r_o$$
$$\Pi(r) = \overset{>}{\Pi}(r) \quad \text{or} \quad \delta(r) = \overset{>}{\delta}(r) \quad \text{for } r > r_o \qquad (3.108)$$

For the special potential, eq.(3.41), we assume that $\mu \doteq 0$ and have the result as in eqs.(3.94) and (3.70) as

$$\delta(r) = \frac{2\eta AB}{\mu} \frac{\sinh \mu r}{r} \equiv \delta^{<}(r), \text{ for } r < r_0$$
$$\delta(r) = \delta_0 \frac{e^{-\mu r}}{r} \equiv \delta^{>}(r) \qquad \text{for } r > r_0 \tag{3.109}$$

This has to satisfy the condition,

$$\sum_{i=1} \delta_i = 0 \qquad \text{eq.(3.95)}$$

i.e. $$\int_0^{r_0} \delta^{<}(r) 4\pi r^2 dr + \int_{r_0}^{\infty} \delta^{>}(r) 4\pi r^2 dr = 0 \tag{3.110}$$

We write that $\delta(r)$ is negative before r_0 and $\delta(r)$ is positive after r_0. So far, we know when r is very small, $\delta(r)$ goes downward to negative, then it might go up slowly or oscillatingly to the positive and connect with $\delta(r)$ for very large r. So eq.(3.110) is an approximate equation. Substituting eq.(3.109) into eq.(3.110), we find

$$B = \frac{\delta_0 (\mu r_0 + 1) e^{-\mu r_0}}{-\frac{2\eta A}{\mu} (\mu r_0 \cosh \mu r_0 - \sinh \mu r_0)} \tag{3.111}$$

In the same way, we can use eq.(3.92) to find B as

$$B = \int_0^{r_0} x \delta^{<}(x) e^{-\mu x} dx + \int_{r_0}^{\infty} x \delta^{>}(x) e^{-\mu x} dx \tag{3.112}$$

Using eq.(3.109) for $\delta^{<}(x)$ and $\delta^{>}(x)$ in eq.(3.112), we have

$$B = \frac{(\delta_0 / 2\mu) e^{-2\mu r_0}}{1 - \frac{\eta A}{\mu} \left(r_0 + \frac{e^{-2\mu r_0}}{2\mu} - \frac{1}{2\mu}\right)} \tag{3.113}$$

Therefore, in principle, we can solve for B and r_0 by eqs.(3.111) and (3.113). We next discuss the sign of B:

In eq.(3.111), because $A < 0$ and

$\mu r_0 \cosh\mu r_0 - \sinh\mu r_0 = \mu r_0 \sinh(\mu r_0)\mathcal{L}(\mu r_0) \geqslant 0$

So, B is a positive constant.

Instead, we may derive the sign of B by refering to eq.(3.113).

In eq.(3.113), because $A < 0$ and

$$r_0 + \frac{e^{-2\mu r_0}}{2\mu} - \frac{1}{2\mu} = r_0 + \frac{1}{2\mu}\left\{1-2\mu r_0 + \frac{(-2\mu r_0)^2}{2} - \dots\right\} - \frac{1}{2\mu}$$

$$\cong \mu r_0^2 = \text{a positive}$$

Therefore B is a positive constant for $\mu \cong 0$

Again, it is important to have B as a positive constant. So that, by eq.(3.94), $\delta(r)$ will start downward to r_0 at where $\delta(r)$, eq.(3.70), will decrease exponentially from the positive and approach zero very rapidly. Certainly $\delta(r)$ will satisfy $\sum_i \delta_i = 0$, as B and r_0 are found from this condition.

H. Condensation when $\Delta \neq 0$

Here we don't prove the condensation when $\Delta \neq 0$ in our model. We just like to mention that the construction of rigourous theory of condensation has been attempted by many authors, but not quite successfully yet. Kac, Uhlenbeck and Hemmer[22,23] constructed an exact one-dimensional gas model with the pair potential $U(x) = -\alpha_0 \exp(-\gamma x)$ for $x \geqslant \delta$, (δ is used here as one dimensional hard core distance), and showed the phase transition in the limit $\gamma \rightarrow 0$. For the finite γ, they found no phase transition. Unfortunately, their method is very hard to generalize to more than one dimensional system or to other kinds of pair potential.

When $\Delta \neq 0$, in order to see the condensation in our model, we have to calculate $<\mu_i>$ very rigorously. Because $<\mu_i> = <\mu_i>^o + \delta_i$, so we may find a very exact function for $\delta(r)$. Even though we can not use this $\delta(r)$ to check the condensation for our model, we still can use it in the following chapter to construct an integral equation governing the radial distribution function for high density. When we have solved this equation, we can use this radial distribution function to calculate the pressure p by using eq.(1.2). From the curve of p vs n, if there is a plateau (or discontinuity), we then have a condensation in our model. The condensation theory is now beyond mathematical power, but it can be done by the numerical calculation through present high speed computers.

CHAPTER IV

INTEGRAL EQUATION OF THE RADIAL DISTRIBUTION FUNCTION

In Chapter I, it was assumed, following Cohn, that when $\Delta = 0$, $<\mu_i> = <\mu_i>^0$, from which he derived the integral equation governing the radial distribution function, eq.(1.23). The numerical results turned out very good for low density[9,13]. But when the density increases, Δ can not be neglected. We have to consider the difference $\delta(r)$ between $<\mu(r)>$ and $<\mu(r)>^0$, where r is the distance of a cell from the central particle. In this Chapter, we will show the construction of the integral equation for $\Delta \neq 0$ and its linearized solution for a general potential. The solution for special potential is also discussed.

A. The Integral Equation

In the original derivation of Cohn's integral equation, $<\mu_i> = n v \rho(r) = <\mu_i>^0$ was assumed. Here we will derive a modified Cohn's integral equation by adding $\delta(r)$ to $<\mu_i>^0$ so that his equation can be used for much higher density.

We rewrite: $<\mu_i> = <\mu_i>^0 + \delta_i$ eq.(2.34) (4.1)

and $<\mu_i> = n v \rho(r)$ eq.(1.13) (4.2)

$$<\mu_i>^0 = \frac{z e^{-\beta<\phi_i>}}{1+z e^{-\beta<\phi_i>}} \quad \text{eq.(1.14)} \tag{4.3}$$

Substituting eqs.(4.2) and (4.3) into eq.(4.1), we have

$$n v \rho(r) = \frac{z e^{-\beta\phi(r)}}{1+z e^{-\beta\phi(r)}} + \delta(r) \tag{4.4}$$

where $\phi(r) \equiv \langle\phi_i\rangle$, the bracket < > and subscript are omitted,

$$\text{or}\quad \phi(r) = -\frac{1}{\beta}\ln\frac{\{nv\rho(r) - \delta(r)\}}{z\{1-nv\rho(r) + \delta(r)\}} \tag{4.5}$$

From eq.(1.15), we have $z = \xi_o e^{\beta h}$ and $nv = \xi_o/(1+\xi_o)$, then eq.(4.5) becomes,

$$\phi(r) = h + \frac{1}{\beta}\ln\frac{(1+\xi_o) - \xi_o\{\rho(r) - (1+\xi_o)\tilde{\delta}(r)\}}{\rho(r) - (1+\xi_o)\tilde{\delta}(r)} \tag{4.6}$$

where we define $\tilde{\delta}(r) \equiv \delta(r)/\xi_o$ (4.7)

Eq. (4.6) is an exact equation for $\phi(r)$. So it can be connected directly with eq.(1.21), which is also an exact equation for $\phi(r)$. Hence, an integral equation can be written as

$$\frac{r}{\beta}\ln\frac{(1+\xi_o) - \xi_o\{\rho(r) - (1+\xi_o)\tilde{\delta}(r)\}}{\rho(r) - (1+\xi_o)\tilde{\delta}(r)} = rU^o(r) + 2\pi n\int_\sigma^\infty x\rho(x)K(x,r)\,dx \tag{4.8}$$

This is a modified Cohn's integral equation, $K(x,r)$ is defined in eq.(1.25) and $U^o(r) = U(r)-h$ as in (1.24). Note, this is an exact integral equation for general cases. $U(r)$ stands for the general type of pair potential. To the extent that $\delta(r)$ could be derived exactly, this equation can be applied to all dense systems. Here $\delta(r)$ is found as in Chapter III by calculating the fluctuation terms, i.e. $\langle x_i e^{\Delta}\rangle^o/\langle e^{\Delta}\rangle^o$ as in eq.(3.29), a special potential function is used to solve for $\delta(r)$.

B. Linearized Solution for $\rho(r)$

Here we will consider a linearized solution for $\rho(r)$ in eq.(4.8).

We write $\rho(r) = 1 + \omega(r)$ (4.9)

where $\omega(r)$ is not necessary smaller than 1 as was assumed before in eq.(1.27). Then eq.(4.8) becomes

$$\frac{r}{\beta}\ \ln\ \frac{1-\xi_o\{\omega(r)-(1+\xi_o)\tilde{\delta}(r)\}}{1+\omega(r)-(1+\xi_o)\tilde{\delta}(r)} = rU^{o}(r)+2\pi n\int_{\sigma}^{\infty}x\rho(x)K(x,r)\,dx \qquad (4.10)$$

Here we will make an assumption to solve the above equation. It is just a mathematical assumption, no sufficiently physical interpretation.

Assume $\{\omega(r)-(1+\xi_o)\tilde{\delta}(r)\} \ll 1$ and $\xi_o \leq 1$ (4.11)

Then $(1+\xi_o)\{\omega(r)-(1+\xi_o)\tilde{\delta}(r)\} \cong -\beta U^{o}(r) - \frac{2\pi n\beta}{r}\int_{\sigma}^{\infty} x\{1+\omega(x)\}K(x,r)\,dx$

$$\text{or } \omega(r) = (1+\xi_o)\tilde{\delta}(r) - \frac{\beta}{1+\xi_o}\,U^{o}(r) - \frac{2\pi n\beta}{1+\xi_o}\,\frac{1}{r}\int_{\sigma}^{\infty} x\{1+\omega(x)\}K(x,r)\,dx \qquad (4.12)$$

This equation has been linearized. By Fredholm's method[24], to O(n), we get

$$\omega(r) = (1+\xi_o)\tilde{\delta}(r) - \frac{\beta}{1+\xi_o}\,U^{o}(r) - \frac{2\pi n\beta}{1+\xi_o}\,\frac{1}{r}\int_{\sigma}^{\infty}xK(x,r)\,dx$$
$$- 2\pi n\beta\frac{1}{r}\int_{\sigma}^{\infty}x\tilde{\delta}(x)K(x,r)\,dx + \frac{2\pi n\beta^2}{(1+\xi_o)^2}\ \frac{1}{r}\int_{\sigma}^{\infty}xU^{o}(x)K(x,r)\,dx \qquad (4.13)$$

Define,

$$I_1(r) \equiv \frac{1}{r}\int_{\sigma}^{\infty}xK(x,r)\,dx \qquad (4.14)$$
$$I_2(r) \equiv \frac{1}{r}\int_{\sigma}^{\infty}xU^{o}(x)K(x,r)\,dx \qquad (4.15)$$
$$I_3(r) \equiv \frac{1}{r}\int_{\sigma}^{\infty}x\tilde{\delta}(x)K(x,r)\,dx \qquad (4.16)$$

By eqs.(4.13) to (4.16), and eq.(4.9), we have

$$\rho(r) = 1 + (1+\xi_o)\tilde{\delta}(r) - \frac{\beta}{1+\xi_o}\,U^{o}(r) - \frac{2\pi n\beta}{1+\xi_o}\,I_1(r) + \frac{2\pi n\beta^2}{(1+\xi_o)^2}I_2(r) - 2\pi n\beta I_3(r) \qquad (4.17)$$

This is the general solution for all kinds of pair potential. $I_1(r)$ and $I_2(r)$ can be calculated easily and have been carried out before by using Buckingham potential[9]. As for $I_3(r)$, we first devide the kernel into three regions. By eq.(4.16)

$$I_3(r) = \frac{1}{r}\int_{\sigma}^{r-\sigma} x\tilde{\delta}(x)K_{II}^{<}(x,r)\,dx + \frac{1}{r}\,\tilde{\delta}(r)\int_{r-\sigma}^{r+\sigma} xK_I(x,r)\,dx$$
$$+\frac{1}{r}\int_{r+\sigma}^{\infty} x\tilde{\delta}(x)K_{II}^{>}(x,r)\,dx \qquad (4.18)$$

where K_I and K_{II} are defined in eq.(3.40). K_I is for $|x-r| < \sigma$, K_{II} is for $|x-r| \geq \sigma$. Also we denote $K_{II} \equiv K_{II}^{<}$ for $x < r$ and $K_{II} \equiv K_{II}^{>}$ for $x > r$. $\tilde{\delta}(r)$ in the region $r - \sigma$ to $r + \sigma$ is considered almost constant.

Next, we denote $\tilde{\delta}(r) \equiv \tilde{\delta}^{<}(r)$ for $r<r_o$ and $\tilde{\delta}(r)\equiv\tilde{\delta}^{>}(r)$ for $r>r_o$ and apply these for $\delta(r)$ of eq.(4.18). It depends on the position of r and whether $r < r_o$ or $r > r_o$. In general, we can write

(a) For r very small,

$$I_3(r) \cong \frac{1}{r}\int_{\sigma}^{r-\sigma} x\tilde{\delta}^{<}(x)K_{II}^{<}(x,r)\,dx + \frac{1}{r}\,\tilde{\delta}^{<}(r)\int_{r-\sigma}^{r+\sigma} xK_I(x,r)\,dx$$
$$+\frac{1}{r}\left\{\int_{r+\sigma}^{r_o} x\tilde{\delta}^{<}(x)K_{II}^{>}(x,r)\,dx + \int_{r_o}^{\infty} x\tilde{\delta}^{>}(x)K_{II}^{>}(x,r)\,dx\right\} \qquad (4.19)$$

(b) For r very large,

$$I_3(r) \cong \frac{1}{r}\left\{\int_{\sigma}^{r_o} x\tilde{\delta}^{<}(x)K_{II}^{<}(x,r)\,dx + \int_{r_o}^{r-\sigma} x\tilde{\delta}^{>}K_{II}^{<}(x,r)\,dx\right\}$$
$$+\frac{1}{r}\,\tilde{\delta}^{>}(r)\int_{r-\sigma}^{r+\sigma} xK_I(x,r)\,dx + \frac{1}{r}\int_{r+\sigma}^{\infty} x\tilde{\delta}^{>}(x)K_{II}^{>}(x,r)\,dx \qquad (4.20)$$

Note, eqs.(4.19) and (4.20) can be used for all kinds of pair potential. If the special potential as in eq.(3.41) is used, by eqs.(3.109) and (4.7), we have

$$\tilde{\delta}(r) = \tilde{\delta}^{<}(r) = \frac{2nAB}{\mu\xi_0}\frac{\sinh \mu r}{r} \qquad \text{for } r < r_0$$
$$\hat{\delta}(r) = \hat{\delta}^{>}(r) = \frac{\delta_0}{\xi_0}\frac{e^{-\mu r}}{r} \qquad \text{for } r > r_0 \qquad (4.21)$$

Using these two equations and the proper kernels in eqs.(4.19) and (4.20), we can find $I_3(r)$. Then, by eq. (4.17), we will get $\rho(r)$ for all r.

C. Limitations

Here we will try to see the validity of eq.(4.8) for a system whose density is so high that $\xi_0 \to \infty$. From eq.(1.15), $\xi_0 = nv/(1-nv)$, $\xi_0 = 0$ for $nv = 0$, $0 < \xi_0 < 1$ for $0 < nv < 1/2$, $\xi_0 = 1$ for $nv = 1/2$, $1 < \xi_0 < \infty$ for $\frac{1}{2} < nv < 1$, then $\xi_0 \to \infty$ for $nv = 1$. So assume

$$\xi_0 >> 1 \qquad (4.22)$$

Then eq.(4.8) becomes

$$\frac{r}{\beta} \ln \frac{\xi_0\{1-\rho(r)[1-\delta(r)/\rho(r)]\}}{\rho(r)[1-\delta(r)/\rho(r)]} = rU^0(r)+2\pi n\int_\sigma^\infty x\rho(x)K(x,r)dx \qquad (4.23)$$

Since $\delta(r)/\rho(r) << 1$ for $r \to \infty$, then the left hand side has a term $\ln\{1-\rho(r)\}$. Because $\rho(r)$ is larger than or equal to 1, so it is a negative infinite which is no meaning at all. So eq.(4.8) is not good for $\xi_0 >> 1$, i.e. $nv = 1$. As for the case of $\xi_0 > 1$, i.e. $nv > 1/2$, it is hard to judge from eq.(4.8). But for the case $\xi_0 \le 1$, i.e. $nv \le 1/2$, the theory can be applied very well, according to the calculations having carried out before[9,13]. This agrees with the original assumptions that neighboring cells are not simultaneously occupied in deriving Cohn's integral equation.

CHAPTER V

CONCLUSION

The original Cohn's integral equation, eq.(1.23), and its modified form, eq.(4.8), are different from the others, such as B-G-Y-K, HNC and PY integral equations, eqs.(1.30) to (1.34). The method used in our derivation is not exact, yet it makes it possible to avoid the use of Kirkwood's supperposition approximation[4], which is used in the B-G-Y-K integral equation for the system of not high density, and also to avoid the use of the very complicated method of cluster diagram[16], which is used in HNC equation for the system of high density.

For sufficiently small number density (how small it is, see Cohn's original paper), the original Cohn's integral equation, eq.(1.23), applies very well to the first order of ξ_0. This is due to his assumptions that neighboring cells are not simultaneously occupied and $\Delta \cong 0$. In this paper, we extend his theory for high density by deriving the difference $\delta(r)$ between $<\mu(r)>$ and $<\mu(r)>^0$ for the case when $\Delta \neq 0$.

The equation governing $\delta(r)$ is derived in two forms: eqs.(2.38) and (3.33). The first one, eq.(2.38), is derived up to the first order of Δ, using the relation of the product of cell occupation numbers (if Δ=0), eq.(2.28), to calculate $<\Delta>^0$, $<\mu_i\Delta>^0$ etc. The second one, eq.(3.33), is derived up to all the orders of Δ, using Einstein's formula of the probability of fluctuation to calculate $<e^{\Delta}>^0$, which has all the orders of Δ. We use the second form to find the solution of $\delta(r)$ for very large r and for very small r, by using a special potential function, eq.(3.41). For very small r, $\delta(r)$ starts downward in the negative direction, and for very large r, $\delta(r)$ starts from some positive quantity and decreases exponentially to zero. For the region between very large r and very small r, even though we have no idea how $\delta(r)$ behaves, we can approximately use the condition that the sum of $\delta(r)$ in all the regions vanishes to find a point r_0, at where $\delta(r)$ for very large r and for very small r match. Unfortunately, due to the special construction of the kernel, K(x,r) in eq.(1.25), we have to use a special potential to solve for $\delta(r)$ analytically. More effort is needed to derive $\delta(r)$ analytically for all kinds of potential function.

The right hand side of Cohn's integral equation, eq.(1.23) is derived exactly, but not the left hand side of his equation. If we could calculate $\langle\mu_i\rangle$ as accurately as possible, then it would be a very perfect and exact integral equation governing the radial distribution function. In general, we can find $\langle\mu(r)\rangle$ by adding $\delta(r)$ to $\langle\mu(r)\rangle^0$ and derive the modified Cohn's integral equation as in eq.(4.8), which would be an exact integral equation for general cases, if $\delta(r)$ could be found exactly for the general potential. We show in the last chapter how to linearize the integral equation and get an analytically solvable solution for $\rho(r)$.

The fluctuation Δ plays a very important role in the dense system. When $\Delta = 0$, we have proved that the average of the product of several cell occupation numbers is equal to the product of several average cell occupation number. There is no correlation between them. We also are able to prove that no condensation exists in the system when $\Delta = 0$. When the density of the system increases, we can not neglect the fluctuation, $\Delta \neq 0$, there exists the possibility of condensation if the density of the fluids is high enough for its occurrence. The proof of the condensation for dense system is still beyond our power of mathematics, except the case of nearest neighbor interaction in one dimensional model[22,25] and two dimensional Ising model[26], as the spontaneous maganetization of a two-dimensional Ising model was calculated by Yang[27]. Certainly in the future, we hope that the work on one and two dimensional models can be applied to the three dimensional model of the real system.

Here, we like to mention that in Chapter III, the Einstein's formula of the probability of fluctuation being used to calculate the average $< >^{o}$ to all the orders of Δ is the main key to derive an integral equation governing $\delta(r)$. We can solve $\delta(r)$ for general pair potential $U(r)$ only when r is very large. When r is small, to solve $\delta(r)$ for general potential is still hard to do, so $\delta(r)$ is solved for the special potential only. Even using the special potential, we are still hard to solve for $\delta(r)$ in the middle region of r. We point out these difficult works here so that the overcoming of these difficulties might be carried out some day in the future.

The method used in developing Cohn's integral equation, eq.(1.23) has the same technique previously applied by Cohn to the theory of electrolytes[28], in which he considered a positive (or a negative) ion in a single occupied cell only. But when the density increases, one positive ion and one negative ion might bound together in one cell, so the chemical bound and the neighboring cells being simultaneously occupied have to be consided. We may construct a probability of distribution for some positive (or negative) ions in a single occupied cell and some bound ions in double occupied cell, and find the average cell occupation number. Then, by the same procedures as in this paper, we might be able to apply Cohn's theory for the binding problems in the theory of electrolytes. This is an another way to extend Cohn's theory for high density.

APPENDIX

A. Derivation of Total Potential Energy $\phi(r)$

The potential energy $\phi(r)$ of a particle at point P, with distance r from the central particle O, arises from two kinds:

(1) $\phi'(r)$, the potential energy on P due to all particles except the central particle O.

(2) U(r), the pair potential between P and the central particle O.

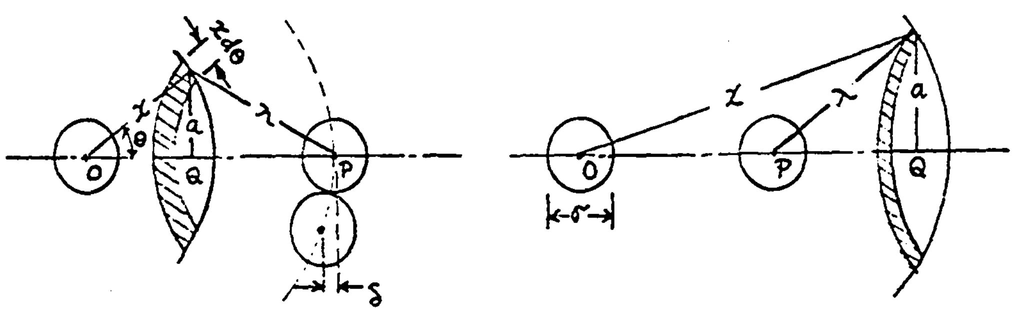
Therefore, we may write

$$\phi'(r) = \phi(r) - U(r) \tag{A.1}$$

The contributions to $\phi'(r)$ at P come from two categories (See Fig. A.1) :

OP = r
QP = c
OQ = b

OP = r
PQ = b



(a) When $x \leq r$ (b) When $x \geq r$

Fig. A.1, Contribution of particles Interaction at P.

(a) Particles in the region $x \leq r$, $x \geq \sigma$. See Fig. A.1(a).

We define

$a = x \sin \theta$

$$d\tau = 2\pi(x \sin\theta)(x d\theta)(dx)$$

$$dc = (x d\theta)\sin\theta \tag{A.2}$$

$$\lambda = [r^2 + x^2 - 2rx\cos\theta]^{\frac{1}{2}} = [x^2 - r^2 - 2cr]^{\frac{1}{2}}$$

When $x \geq \sigma$, and $r - x \geq \sigma$, we have

$$\begin{aligned}\phi'(r) &= \int_{volume} n(x)\, U(\lambda)\, d\tau \\ &= 2\pi\int_{x=\sigma}^{r-\sigma} x\, n(x)\, dx \int_{\theta=0}^{\pi} U(\lambda)\, x \sin\theta\, d\theta \\ &= 2\pi\int_{\sigma}^{r-\sigma} x\, n(x)\, dx \int_{r-x}^{r+x} U(\lambda)\, dc \end{aligned} \tag{A.3a}$$

When $r - x \leq \sigma$, $r>x$, we have, (by the same form as above)

$$\phi'(r) = 2\pi\int_{r-\sigma}^{r} x\, n(x)\, dx \int_{\delta}^{r+x} U(\lambda)\, dc \tag{A.3b}$$

where

$$\delta = \frac{\sigma^2 - x^2 + r^2}{2r} \tag{A.3b'}$$

Therefore, the contributions to $\phi'(r)$ from all particles in the region $x \leq r$, $x \geq \sigma$ is the sum of eqs. (A.3a) and (A.3b), i.e.

$$\phi'(r) = 2\pi\int_{\sigma}^{r-\sigma} x\, n(x)\, dx \int_{r-x}^{r+x} U(\lambda)\, dc + 2\pi\int_{r-\sigma}^{r} x\, n(x)\, dx \int_{\delta}^{r+x} U(\lambda)\, dc \tag{A.4}$$

(b) Particles in the region $x \geq r$, $x \geq \sigma$. See Fig. A.1 (b).

By the same procedure as in (a), when $x \geq \sigma$, $x - r \geq \sigma$, we have

$$\phi'(r) = 2\pi\int_{r+\sigma}^{\infty} x\, n(x)\, dx \int_{-(x+r)}^{x-r} U(\lambda)\, db \tag{A.5a}$$

When $x - r \leq \sigma$, $x > r$, we have

$$\phi'(r) = 2\pi\int_{r}^{r+\sigma} x\, n(x)\, dx \int_{-(x+r)}^{-\delta} U(\lambda)\, db \tag{A.5b}$$

Therefore, the contributions to $\phi'(r)$ from all particles in the region $x \geq r$, $x \geq \sigma$ is the sum of eqs. (A.5a) and (A.5b), i.e.

$$\phi'(r) = 2\pi\int_{r+\sigma}^{\infty} xn(x)\,dx \int_{-(x+r)}^{x-r} U(\lambda)\,db + 2\pi\int_{r}^{r+\sigma} xn(x)\,dx \int_{-(x+r)}^{-\delta} U(\lambda)\,db \tag{A.6}$$

The sum of eqs. (A.4) and (A.6) is equal to $\phi'(r)$ in eq. (A.1), therefore, after changing variables and use $n(x) = n\rho(x)$, we have

$$\phi(r) = U(r) + 2\pi n \int_{\sigma}^{\infty} x\rho(x)\,dx \int_{r-x}^{r+x} U(\lambda)\,dc + 2\pi n\int_{r-\sigma}^{r+\sigma} x\rho(x)\,dx\int_{\delta}^{r-x} U(\lambda)\,dc \tag{A.7}$$

Changing the variables by letting $y=x^2-r^2+2cr$ and $\xi=y^{\frac{1}{2}}$, we have

$$\int_{r-x}^{r+x} U(\lambda)\,dc = \frac{1}{2r}\int_{(x-r)^2}^{(x+r)^2} U(y^{\frac{1}{2}})\,dy = \frac{1}{r}\int_{|x-r|}^{x+y} \xi U(\xi)\,d\xi \tag{A.8}$$

$$\int_{\delta}^{r-x} U(\lambda)\,dc = \frac{1}{r}\int_{\sigma}^{|x-r|} \xi U(\xi)\,d\xi \tag{A.9}$$

Define the function $G(x,r)$ as in eq.(1.26), we can write eq.(A.7) as

$$\phi(r) = U(r)+\frac{2\pi n}{r}\left\{\int_{\sigma}^{\infty} x\rho(x)\,dx \int_{|x-r|}^{x+r} \xi U(\xi)\,d\xi+\int_{0}^{\infty} x\rho(x)\,dx \int_{\sigma}^{|x-r|} G(x,r)\,\xi U(\xi)\,d\xi\right\} \tag{A.10}$$

Using the kernal $K(x,r)$ in eq.(1.25) and changing $\int_0^{\infty}$ to $\int_{\sigma}^{\infty}$ on the second term in eq.(A.10), we finally have eq.(1.21).

B. Calculation of $\mathcal{L}^{-1}\delta_i$

$$\mathcal{L}\delta_i = \coth \delta_i - \frac{1}{\delta_i} \tag{B. 1}$$

$$= \left(\frac{1}{\delta_i} + \frac{\delta_i}{3} - \frac{\delta_i^{\ 3}}{45} + \ldots\right) - \frac{1}{\delta_i}$$

$$\text{or } \mathcal{L}\delta_i \cong \frac{\delta_i}{3} - \frac{\delta_i^{\ 3}}{45} \tag{B.2}$$

$$\text{Because } \mathcal{L}^{-1}(\mathcal{L}\delta_i) = \mathcal{L}(\mathcal{L}^{-1}\delta_i) = \delta_i \tag{B.3}$$

and by eq.(B.2), $\mathcal{L}(\mathcal{L}^{-1}\delta_i) = \frac{(\mathcal{L}^{-1}\delta_i)}{3} - \frac{(\mathcal{L}^{-1}\delta_i)^3}{45}$

So $\frac{(\mathcal{L}^{-1}\delta_i)}{3} - \frac{(\mathcal{L}^{-1}\delta_i)^3}{45} = \delta_i$

$$\text{or } (\mathcal{L}^{-1}\delta_i)^3 - 15(\mathcal{L}^{-1}\delta_i) + 45\,\delta_i = 0 \tag{B.4}$$

Assume $(\mathcal{L}^{-1}\delta_i)$ has the form as

$$\mathcal{L}^{-1}\delta_i = A_1\delta_i + A_2\delta_i^{\ 2} + A_3\delta_i^{\ 3} + \ldots \tag{B.5}$$

where A_1, A_2, A_3 are the constants to be found.

Substituting eq.(B.5) into (B.4), we have, to $0(\delta_i^{\ 3})$,

$$(A_1^{\ 3}\delta_i^{\ 3} + \ldots) - 15(A_1\delta_i + A_2\delta_i^{\ 2} + A_3\delta_i^{\ 3}) + 45\,\delta_i = 0$$

$$\text{or } \delta_i(-15A_1+45) + \delta_i^{\ 2}(-15A_2) + \delta_i^{\ 3}(A_1^{\ 3}-15A_3) = 0 \tag{B.6}$$

Because $\delta_i \neq 0$, so the coefficients of δ_i's should be zero. i.e.

$$-15A_1 + 45 = 0, \qquad A_1 = 3$$

$$-15A_2 = 0, \qquad A_2 = 0 \tag{B.7}$$

$$A_1^{\ 3} - 15A_3 = 0, \qquad A_3 = \frac{27}{15} = \frac{9}{5}$$

By eqs.(B.5) and (B.7), we have

$$\mathcal{L}^{-1}\delta_i = 3\delta_i + \frac{9}{5}\delta_i^{\,3} + \ldots \tag{B.8}$$

The second term can be neglected (as δ_i is the order of zero), So $\mathcal{L}^{-1}\delta_i = 3\,\delta_i$ is used to the left hand side of eq.(3.33).

C. Integrations of $K_I(x,r)$ and $K_{II}(x,r)$ in the Region $|r-x|<\sigma$ for Very Large r

$$\int_{r-\sigma}^{r+\sigma} K_I(x,r)\,dx = \int_{r-\sigma}^{r+\sigma} dx\{\int_\sigma^{x+r} \xi U(\xi)\,d\xi\} \qquad \text{by eq.(3.40)}$$

$$= \int_{r-\sigma}^{r+\sigma} dx\{A \int_\sigma^{x+r} e^{-\mu\xi} d\xi\} \qquad \text{by eq.(3.41)}$$

$$= \frac{A}{\mu^2}\{e^{-\mu(2r+\sigma)} - e^{-\mu(2r-\sigma)} + 2\mu\sigma e^{-\mu\sigma}\} \tag{C.1}$$

$$= (2A\sigma/\mu)e^{-\mu\sigma} \quad (\text{if } r \to \infty) \qquad \text{eq.(3.44)}$$

$$\int_{|r-x|<\sigma} K_{II}(x,r)\,dx = \int_{r-\sigma}^{r} dx\{\int_{r-x}^{x+r} \xi U(\xi)\,d\xi\} + \int_r^{r+\sigma} dx\{\int_{x-r}^{x+r} \xi U(\xi)\,d\xi\} \text{ by eq.(3.40)}$$

$$= \int_{r-\sigma}^{r} dx\{U_0 \int_{r-x}^{\sigma} \xi d\xi + A\int_\sigma^{x+r} e^{-\mu\xi} d\xi\}$$

$$+ \int_r^{r+\sigma} dx\{U_0 \int_{x-r}^{\sigma} \xi d\xi + A\int_\sigma^{x+r} e^{-\mu\xi} d\xi\} \quad \text{by eq.(3.41)}$$

$$= 2U_0\sigma^3/3 + \frac{A}{\mu^2}\{e^{-\mu(2r+\sigma)} - e^{-\mu(2r-\sigma)} + 2\mu\sigma e^{-\mu\sigma}\} \tag{C.2}$$

$$= 2U_0\sigma^3/3 + (2A\sigma/\mu)e^{-\mu\sigma} \quad (\text{if } r \to \infty) \qquad (\text{eq.3.45})$$

D. Derivation of $\rho(r) = e^{-\beta U(r)}$ as $r \to \infty$

Here we will first derive the relation between the radial distribution function and the potential of mean force[4,10]. Let us consider two particles, 1 and 2, with a fixed distance r apart. The mean force, $\langle F_2 \rangle^{1,2}$, exerted on particle 2 due to all the other particles is

$$\langle F_2 \rangle^{1,2} = \frac{\int_V - \nabla_2 V_P \, e^{-\beta V_P} \, d\underline{r}_3 \ldots d\underline{r}_N}{\int_V e^{-\beta V_P} \, d\underline{r}_3 \ldots d\underline{r}_N} \tag{D. 1}$$

where V_P is the total potential energy. We will define the potential of mean force, $W(\underline{r}_1,\underline{r}_2)$, in such a way that

$$\langle F_2 \rangle^{1,2} \equiv - \nabla_2 W(\underline{r}_1,\underline{r}_2) = -\nabla_2 W(r) \tag{D.2}$$

The radial distribution function $\rho(r)$ of particle 1 (central particle) being fixed and particle 2 being with distance r from particle 1 is

$$\rho(r) = \frac{V \int_V e^{-\beta V_P} \, d\underline{r}_3 \ldots d\underline{r}_N}{\int_V e^{-\beta V_P} \, d\underline{r}_2 \ldots d\underline{r}_N} \tag{D.3}$$

Then, eq.(D.1) may be written as

$$\begin{aligned}
\langle F_2 \rangle^{1,2} &= \frac{\int_V (-\nabla_2 V_P) \, e^{-\beta V_P} \, d\underline{r}_3 \ldots d\underline{r}_N}{\int_V e^{-\beta V_P} \, d\underline{r}_2 \ldots d\underline{r}_N} \cdot \frac{\int_V e^{-\beta V_P} \, d\underline{r}_2 \ldots d\underline{r}_N}{\int_V e^{-\beta V_P} \, d\underline{r}_3 \ldots d\underline{r}_N} \\
&= \frac{\nabla_2}{\beta} \left\{ \frac{\int_V e^{-\beta V_P} \, d\underline{r}_3 \ldots d\underline{r}_N}{\int_V e^{-\beta V_P} \, d\underline{r}_2 \ldots d\underline{r}_N} \right\} / \left\{ \frac{\int_V e^{-\beta V_P} \, d\underline{r}_3 \ldots d\underline{r}_N}{\int_V e^{-\beta V_P} \, d\underline{r}_2 \ldots d\underline{r}_N} \right\} \\
&= \frac{\nabla_2}{\beta} \left\{ \frac{\rho(r)}{V} \right\} / \left\{ \frac{\rho(r)}{V} \right\} \\
&= \frac{1}{\beta} \nabla_2 \ln \rho(r)
\end{aligned} \tag{D.4}$$

By eqs.(D.2) and (D.4), we have

$$-\nabla_2 W(\underline{r}_1,\underline{r}_2) = \frac{1}{\beta} \nabla_2 \ln \rho(r)$$

or $\ln \rho(r) = -\beta W(r) + C$ (C is a constant) (D.5)

Because $\rho(r) \to 1$ and $W(r) \to 0$ as $r \to \infty$, so $C = 0$. Then

$$\rho(r) = e^{-\beta W(r)} \qquad \text{(D.6)}$$

When r is very large, the potential of mean force approaches the pair potential function, i.e. $W(r) \to U(r)$ as $r \to \infty$, because it is in the low density limit when r is very large. Therefore

$$\rho(r) \cong e^{-\beta U(r)} \qquad \text{for } r \to \infty \qquad \text{eq.(3.64)}$$

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