CHAPTER II

(On to the Solution of integro-differential equations)
CHAPTER - II

2.1 THE ITERATIVE METHOD SUGGESTED TO SOLVE THE INTEGRO DIFFERENTIAL EQUATION FOR MANY-BODY DISTRIBUTION FUNCTIONS

In the previous chapter, we noted that the statistical mechanical theory of the liquid state starts from integro-differential equation connecting the distribution function and the inter-molecular potential energy. However, this equation could not be solved because it is coupled with the distribution function of the higher order. Kirkwood suggested the superposition approximation to get an approximate solution of the equation. However, this result which is known as Born-Green-Yvon equation is correct only up to certain density. The starting point of our investigation is not the equation connecting the pair distribution with the triple-order distribution function - as in the case of the derivation of the BGY equation. But the basic equation (Eqn. 1.37a) of the previous chapter concerning the h-particle distribution function is considered. The equation can be written as,

$$kT \frac{\partial}{\partial \hat{\mathbf{r}}_i} \ln n_h(\hat{\mathbf{r}}_h) = - \frac{\partial}{\partial \hat{\mathbf{r}}_i} \phi(\hat{\mathbf{r}}_h) - \int \frac{\partial}{\partial \hat{\mathbf{r}}_i} \phi_i, h, \frac{n_{hh}(\hat{\mathbf{r}}_{hh})}{n_h(\hat{\mathbf{r}}_h)} d\hat{\mathbf{r}}_{hh} \cdots (2.1.1)$$

We may interpret the equation as follows. The mean force acting on a molecule at $\hat{\mathbf{r}}_i$ when the second molecule is situated at $\hat{\mathbf{r}}_h$ is compounded of the force,

$$- \frac{\partial}{\partial \hat{\mathbf{r}}_i} (\phi \hat{\mathbf{r}}_h)$$

due to the second molecule and the force due to all the other molecules. Since the probability of finding a third molecule
in the volume element $d\mathbf{r}_{i+h+1}$ is $n_{i+h+1}/n_{i}$, the force due to all the other molecules is given by,

$$-\int \frac{n_{i+h+1}}{n_{i}} \frac{\partial}{\partial \mathbf{r}_{i}} \phi (\mathbf{r}_{i}, \mathbf{r}_{i+h+1}) d\mathbf{r}_{i+h+1}$$

The resultant force must be equal to $\frac{kT}{\mathcal{N}_{i}} \frac{\partial}{\partial \mathbf{r}_{i}} n_{i}(\mathbf{r}_{i})$.

A number of independent derivations of this equation exist. One of them is by Born & Green, who derived this equation by reducing the Liouville equation step by step. Since we want to avoid the superposition approximation we cannot hope to reduce the set of integro-differential equation (2.1.1) to a single equation as done by Born Green & Yvon. We shall have to consider the entire set of equations simultaneously.

We multiply both sides of the equation (2.1.1) by

$$\frac{\mathbf{r}_{i+h}}{\mathbf{r}_{i}} = \frac{\mathbf{r}_{i}-\mathbf{r}_{i-h}}{\mathbf{r}_{i}}$$

which reduces the equation in the following form,

$$kT \frac{\partial}{\partial \mathbf{r}_{i}} n_{i}(\mathbf{r}_{i}) = -\frac{\partial}{\partial \mathbf{r}_{i}} \phi (\mathbf{r}_{i}) - 2\pi \int_{0}^{\infty} \left| \frac{\mathbf{r}_{i+h}+\mathbf{r}_{i+h+1}}{\mathbf{r}_{i}} \right| \frac{\partial}{\partial \mathbf{r}_{i}} \phi (\mathbf{r}_{i+h+1}) + \frac{n_{i+h+1}}{n_{i}} \left( \frac{n^{2}_{i+h}+n^{2}_{i+h+1}-n^{2}_{i}}{2n^{2}_{i+h}} \right) n_{i+h+1} d\mathbf{r}_{i}$$

This equation expresses the usual assumption in all theories of molecular assemblies that the potential energy function of an assembly of molecules is the sum of individual pairs (Chapter III).

This assumption is not wholly correct (Chap. III) However, for the present purpose we apply this additivity rule.
Integrating equation (2.1.2) with respect to $x_{ih}$, we get,

$$n_h = n^h \exp \left( - \frac{1}{KT} \right) \left\{ \phi(\tau^h) + 2\pi \int_0^\infty \int_0^\infty \frac{\partial f_i, h+1}{\partial x_{ih}} \right\}$$

$$\chi_{h+1} \frac{R(\tau^i_{ih}, \tau^i_{ih+1}, \tau^h_{ih+1})}{n^h} d\tau_{ih} d\tau_{ih+1} d\tau_{i, h+1} \ldots (2.1.3)$$

Where,

$$\chi_{h+1} = \frac{n_{h+1}}{n_h}$$

$$R = \left( \frac{2}{\tau_{ih}^2 + \tau_{ih+1}^2 - \tau_{ih+1}^2} \right) / \tau_{ih}$$

$$\phi(\tau^h) = \sum_{j=1}^h \phi_{ij} + \sum_{j=2}^h \sum_{k=j+1}^h \phi_{jk}$$

and $n^h$ is an integration constant.

If for the function $\chi_h$ we choose an approximate function which is accurate to the $K$-th order of approximation and call this as $\chi^K_h$, then the expression for $n_h$ correct to the $K$-th approximation is given by,

$$n^K_h = n^h \exp \left( - \frac{1}{KT} \right) \left\{ \phi(\tau^K_h) + 2\pi \int_0^\infty \int_0^\infty \frac{\partial f_i, h+1}{\partial x_{ih}} \right\}$$

$$\chi^K_{h+1} \frac{R(\tau^i_{ih}, \tau^i_{ih+1}, \tau^h_{ih+1})}{n^h} d\tau_{ih} d\tau_{ih+1} d\tau_{i, h+1} \ldots (2.1.4)$$

Similarly, the expression for $n^K_{h+1}$ correct up to $K$-th approximation can be written as,

$$n^K_{h+1} = n^{h+1} \exp \left( - \frac{1}{KT} \right) \left\{ \phi(\tau^K_{ih+1}) + 2\pi \int_0^\infty \int_0^\infty \frac{\partial f_i, h+2}{\partial x_{ih+1}} \right\}$$

$$R(\tau^i_{ih+1}, \tau^i_{ih+2}, \tau^{h+1}_{ih+2}) d\tau_{ih+1} d\tau_{ih+2} d\tau_{i, h+2} \ldots (2.1.5)$$
Taking \( \lambda_{h+1}^K \) as the function representing \( \lambda_{h+1} \) correct to the \( K \)-th approximation, the function \( \lambda_{h+1}^{K+1} \) representing \( K+1 \)-th correct approximation can be easily found out from the equation (2.1.4) and (2.1.5).

Then,
\[
\lambda_{h+1}^{K+1} = \text{Exp} - \frac{2\pi}{K+1} \left\{ \frac{\partial}{\partial \tau_{i,h+1}} \lambda_{h+1}^K \mathcal{R}(\tau_{i,h+1}, \tau_{h+1}, \tau_{i,h+1}) d\tau_{i,h+1} d\tau_{h+1} d\tau_{i,h+1} - \frac{\partial}{\partial \tau_{i,h+2}} \lambda_{h+2}^K \mathcal{R}(\tau_{i,h+2}, \tau_{h+1}, \tau_{i,h+2}) d\tau_{i,h+2} d\tau_{h+1} d\tau_{i,h+2} \right\} \quad (2.1.6)
\]
We may repeat the procedure to find out \( \lambda_{h+2}^K, \lambda_{h+2}^{K+2} \) and from these values \( n_h \) can be determined to any desired degree of approximation. Now,
\[
\lambda_{h+1}^K = \frac{n_{h+1}^K}{n_h^K} \quad \ldots (2.1.7)
\]
So,
\[
\lambda_{h+1}^{K+1} = \frac{n_{h+1}^{K+1}}{n_h^{K+1}}
\]
\[
= \lambda_{h+1}^K \text{Exp} - \frac{2\pi}{K+1} \left\{ \frac{\partial}{\partial \tau_{i,h+1}} \lambda_{h+1}^K \mathcal{R} d\tau_{i,h+1} d\tau_{h+1} d\tau_{i,h+1} - \frac{\partial}{\partial \tau_{i,h+2}} \lambda_{h+2}^K \mathcal{R} d\tau_{i,h+2} d\tau_{h+1} d\tau_{i,h+2} \right\}
\]
\[
= \lambda_{h+1}^K \text{Exp} - \Delta_h^K \quad \ldots (2.1.8)
\]
Where,
\[
\Delta_h^K = \frac{2\pi}{K+1} \left\{ \frac{\partial}{\partial \tau_{i,h+1}} \lambda_{h+1}^K \mathcal{R} d\tau_{i,h+1} d\tau_{h+1} d\tau_{i,h+1} - \frac{\partial}{\partial \tau_{i,h+2}} \lambda_{h+2}^K \mathcal{R} d\tau_{i,h+2} d\tau_{h+1} d\tau_{i,h+2} \right\}
\]
Therefore,
\[
n_{h+1}^{K+1} = n_h^K \text{Exp} - \Delta_h^K \quad ; \quad n_h^K = n_h^{K-1} \text{Exp} - [\Delta_h^{K-1} + \Delta_h^K]
\]
So,
\[
n_h^K = n_h^0 \text{Exp} - [\Delta_h^0 + \Delta_h^1 + \Delta_h^2 + \cdots] \quad \ldots (2.1.8a)
\]
Convergence of this process is assured by the convergence of the term (within bracket of (2.1.8) and by the approach of
to zero with the increase of $K$. Therefore, if we want to use the vector, the first task to be performed is to find out a suitable zeroth approximation which will ensure the convergence of the series (2.1.8).

### 2.2 Iteration Based on the Zeroth Approximation Suggested by Imperfect Gas Theory

The mathematical step described by the equation (2.1.2) to (2.1.8) describes a general iteration procedure. The actual calculation can be done by choosing a suitable form of zeroth iteration. The most obvious zeroth approximation is suggested from imperfect gas theory, where we neglected all but the binary collisions. Since, the integral terms in the r.h.s. of (2.1.1) is due to the higher order iteration we neglect this. So, the zeroth iteration is:

\[ n^0_h = n^h \exp - \Phi (\tilde{\gamma}^h) \]  \hspace{1cm} (2.2.1)

So,

\[ X^0_{h+1} = n \exp - \frac{1}{kT} \left[ \Phi (\tilde{\gamma}^{h+1}) - \Phi (\tilde{\gamma}^h) \right] \]  \hspace{1cm} (2.2.2)

We shall choose this expression as the zeroth order for the present calculation.

One may proceed through the following successive stages. For the first iteration, we have,

\[ n^1_h = n^0_h \exp - \Delta^0_h \]  \hspace{1cm} (2.2.3)

where,

\[ \Delta^0_h = \frac{2\pi N}{kT} \int \int \int \frac{1}{\delta \tau^i_{h+1}} \Phi (\tilde{\gamma}^{h+1}) \times \exp - \frac{1}{kT} \left\{ \Phi (\tilde{\gamma}^{h+1}) - \Phi (\tilde{\gamma}^h) \right\} \times \]  \hspace{1cm} (2.2.4)
Again for the second iteration, we have,
\[ n_h^2 = n_h^1 \exp - \Delta_h^1 \] \hspace{1cm} \ldots (2.2.5)

Where,
\[ \Delta_h^1 = \frac{2\pi N}{kT} \int \cdots \int A_i \exp - \sum \sum \Phi_{ij} \left[ -\frac{1}{2} \alpha p \sum \frac{2m}{2!} \cdots \right] \] \hspace{1cm} \ldots (2.2.6)

and,
\[ \alpha = \frac{2\pi n}{kT} \]
\[ \beta = \Delta_{h+1} - \Delta_h \]
\[ A_i = \frac{\delta}{\delta r_{i,h+1}} \Phi_{i,h+1} R \] \hspace{1cm} \ldots (2.2.7)

For the third iteration, our result is,
\[ n_h^3 = n_h^2 \exp - (-1)^n \sum \sum n_{h-2} \alpha^{n+1} \] \hspace{1cm} \ldots (2.2.8)

where,
\[ \Delta_h^2 = (-1)^n \sum \sum \gamma_{h-2} \alpha^{n+1} \]
and,
\[ \gamma_h = \int \cdots \int A_i e^{-\frac{1}{kT} \sum \sum \Phi_{ij} (-\frac{1}{2}) \sum \sum \frac{2m}{2!} \cdots} \] \hspace{1cm} \ldots (2.2.9)

Similarly, for the fourth iteration, we have,
\[ n_h^4 = n_h^3 \exp - \Delta_h^3 \] \hspace{1cm} \ldots (2.2.10)

where,
\[ \Delta_h^3 = (-1)^n \sum \sum \delta_h^{n-2} \alpha^{n+1} \] \hspace{1cm} \ldots (2.2.11)

and,
\[ \delta_h^{n-2} = \int \cdots \int A_i \left[ e^{\frac{-1}{kT} \sum \sum \Phi_{ij} (-\frac{1}{2}) \sum \sum \frac{2m}{2!} \cdots} \right] \] \hspace{1cm} \ldots (2.2.12)
where,

\[ A_{n+1-l} = \sum p^{n-2m} q^{m} \left\{ (-1)^{m} \right\} \]

and,

\[ \Omega = \gamma_{h+1}^{o} - \gamma_{h}^{o} \quad ; \quad m = 0 - \infty \]

and for the fifth iteration we have the following expression,

\[ \eta_{h}^{5} = \eta_{h}^{4} \exp \Delta_{h}^{4} \]

where,

\[ \Delta_{h}^{4} = -\int_{0}^{\infty} A_{h} \sum (-1)^{n} a^{n+2} \left\{ (-1)^{m} p^{n-2m} q^{m} \right\} \]

\[ \times \left\{ (-1)^{n-2m} S x + (-1)^{m} n^{m} S y \right\} d\gamma_{l}^{m} \cdots d\gamma_{n}^{m} \]

Where,

\[ S = \left( \gamma_{h+1}^{o} - \gamma_{h}^{o} \right) \]

\[ X = \sum p^{n-2m} q^{m} \left\{ (-1)^{m} \right\} \]

\[ Y = \sum \left\{ p^{n+1-3m} \Omega^{m} \left\{ (-1)^{m} - A_{n+1-l}^{m} \Omega \right\} \right\} \]

The higher iteration expressions can be constructed similarly.

According to our criterion for a satisfactory theory of the liquids, equation of state in the suitable limiting case should be identical with that of imperfect gases. And hence the virial coefficients of our theory must be identical with those obtained by the cluster integral theory.

For the calculation of the equation of state we need the value of \( \eta_{2}(\gamma) \). We summarise below the explicit results for \( \eta_{2}(\gamma) \) up to fourth order. They can be written down immediately from the corresponding expressions of \( \eta_{h} \). In the following expressions we have retained terms only up to \( \frac{1}{(kT)^{n}} \).
where \( n \) is the order of approximation.

\[
\eta_2^1 = \eta_2^0 \exp - \Delta_2^0
\]

\[
= \eta_2^0 \left\{ 1 - \Delta_2^0 \right\}
\]

Correct to the coefficient of \( \frac{1}{kT} \).

\[
\eta_2^2 = \eta_2^1 \exp - \Delta_2^1
\]

\[
= \eta_2^0 \left\{ 1 - \Delta_2^0 \right\} \left\{ 1 - \Delta_2^1 \right\}
\]

\[
= \eta_2^0 \left\{ 1 - \Delta_2^0 - \Delta_2^1 + \Delta_2^0 \Delta_2^1 + \frac{(\Delta_2^0)^2}{2!} + \frac{(\Delta_2^1)^2}{2!} \right\}
\]

Correct up to the coefficient of \( \frac{1}{(kT)^2} \).

Where,

\[
\Delta_2^0 = \frac{2\pi N \frac{\partial}{\partial \lambda_{13}}}{kT} \phi_{13} \exp - \frac{1}{kT} \left\{ \phi(\lambda_{13}^3) - \phi(\lambda_{13}^2) \right\} \times
\]

\[
\frac{\lambda_{13}^2 + \lambda_{23}^2 - \lambda_{34}^2}{2 \lambda_{13}^2} \cdot \lambda_{34} \, d\lambda_{23} \, d\lambda_{34} \, d\lambda_{14}
\]

\[
\Delta_2^1 = \frac{2\pi N \frac{\partial}{\partial \lambda_{14}}}{kT} \phi_{14} \exp - \frac{1}{kT} \left\{ \phi(\lambda_{14}^4) - \phi(\lambda_{14}^3) \right\} \times
\]

\[
\frac{\lambda_{14}^2 + \lambda_{24}^2 - \lambda_{35}^2}{2 \lambda_{14}^2} \cdot \lambda_{35} \, d\lambda_{24} \, d\lambda_{35} \, d\lambda_{14}
\]

\[
\Delta_2^2 = \frac{2\pi N \frac{\partial}{\partial \lambda_{15}}}{kT} \phi_{15} \exp - \frac{1}{kT} \left\{ \phi(\lambda_{15}^5) - \phi(\lambda_{15}^4) \right\} \times
\]

\[
\frac{\lambda_{15}^2 + \lambda_{25}^2 - \lambda_{36}^2}{2 \lambda_{15}^2} \cdot \lambda_{36} \, d\lambda_{25} \, d\lambda_{36} \, d\lambda_{15}
\]
Similarly,

$$n_2^A = n_2^0 \exp -\Delta \alpha^3$$

$$= n_2^0 \left\{ 1 - \Delta^2 \right\} \left\{ 1 - \Delta^2 \right\} \left\{ 1 - \Delta^2 \right\} \left\{ 1 - \Delta^2 \right\}$$

$$= n_2^0 \left\{ 1 - \Delta^2 - \Delta^2 - \Delta^2 - \Delta^2 \right\} + \Delta^2 \Delta^2 + \Delta^2 \Delta^2 +$$

$$\frac{(\Delta^2)^4}{4!} - \frac{(\Delta^2)^4}{4!} - \frac{(\Delta^2)^4}{4!} - \frac{(\Delta^2)^4}{4!} \}$$

$$\ldots (2.2.20)$$

2.3 **SECOND ITERATIVE APPROACH FOR THE EVALUATION OF MULTIPLE DISTRIBUTION FUNCTIONS - DEVELOPMENT VALID FOR LIQUID PHASE**

In article (2.2) we have developed a very powerful iterative method for the solution of the set of integro-differential equation (2.1.1), and found that the resulting theory tallies with the one obtained from the cluster integral formulations.

The agreement of the two assures us the general identity of the basis of these two formulations and affirms our faith in the equation (2.1.1). However, the agreement of the final development also point out that we have find another method of development of equation (2.1.1) so that the validity of the development may not be restricted to the imperfect gas as is the case with cluster integral development.

Any theory of liquid state should predict a damped periodic radial distribution function. The zeroth approximation chosen in the previous chapter was chosen in such a way that provided an agreement with ideal gases in the limit. This approximation chosen did not have any periodic nature. The final development also indicated no periodicity, hence this development yields
branch of the functions representing the multiple distribution functions which are periodic in nature.

Again, the zeroeth approximation of the previous chapter itself yielded the second virial coefficient correctly, therefore, the starting point itself correctly took into account the binary interactions. Further, any periodicity in the radial distribution function can not arise only from binary interaction, but it be the result of ternary interactions. Thus if we want to construct a satisfactory development of the liquid phase, we must start from the expression which is correct to ternary interactions.

The most convenient result we possess for this purpose is the Green's solution of the Born Green equation, a solution correct to ternary interactions. We have sketched the Greens solution of the present thesis. Their result is,

\[ n_2(r) \simeq n^2 \exp - \phi(r)/kT \left\{ 1 + f(r) \right\} \]  

\[ \ldots (2.3.1) \]

Where \( f(r) \) is given by the equation,

\[ n^2 f(r) = \frac{1}{(2\pi)^{3/2}} \int_{-\infty}^{+\infty} \frac{\epsilon \beta^2(s) e^{i\tau s}}{\lambda - \epsilon \beta(s)} ds \]  

\[ \ldots (2.3.2) \]

In the above, the various quantities are defined as follows,

\[ \lambda^{-1} = (2\pi)^{3/2} n \]  

\[ \ldots (2.3.3) \]

\[ n\beta(r) = \frac{1}{(2\pi)^{3/2}} \int_{-\infty}^{+\infty} S \alpha(s) e^{i\tau s} ds \]  

\[ \lambda^{-1} = (2\pi)^{3/2} n \]  

\[ \ldots (2.3.4) \]

\[ \alpha(r) = e^{-\phi(r)/kT} - 1 \]  

\[ \ldots (2.3.5) \]
and $\epsilon$ determined by the relation,

$$(\epsilon - 1) \int_{-\infty}^{\infty} \alpha(\tau) \tau^2 d\tau = \int_{-\infty}^{\infty} f(\tau) \alpha(\tau) \tau^2 d\tau$$

$$(2.3.6)$$

For further development, Green assumes that there is an analytic function $\beta(z)$ which reduces to $\beta(\tau)$ when $z = \tau$ is real. The most general solution of the equation (2.1.1) is then given by the relation (2.3.2) to which as Rushbrook and Scoins have pointed out, must be added,

$$[ A \exp(i\pi Z_K) + B \exp(-i\pi Z_K) ] \frac{1}{\tau}$$

$$(2.3.7)$$

The path of integration in (2.3.2) may follow any course from positive infinity to negative infinity in the complex plane. $Z_K$ in (2.3.7) is any root of the transcendental equation,

$$\beta(z) = \frac{\lambda}{\xi}$$

$$(2.3.8)$$

The additional term may be obtained from (2.3.2) by deforming the path of integration to enclose the singular point $Z_K$.

The precise path of integration for liquid state may be determined by the boundary condition,

$$f(\tau) \approx 0(\tau^{-3}) \quad \text{as, } \tau \rightarrow \infty$$

$$(2.3.9)$$

This condition follows from the condition,

$$\int (\eta_2^{(12)} - \eta^2) d\eta$$

should converge. The boundary condition (2.3.9) excludes the possibility of the terms in (2.3.9). These terms, which are indicative of periodicity, are not excluded if we omit the
condition (2.3.9). Thus, if we choose suitable boundary conditions the long range periodic terms are retained, and the resulting theory should be an approximate theory of solid. Vlasov also had introduced similar ideas.

Thus Green's solution appears to be a very approximate general result valid not only for liquids but also for imperfect gases. In fact, it was shown that one could obtain a development for (2.3.2) which should also be approximately valid for gases. Thus, we may reasonably hope, if we could devise an iterative process starting from Green's result, we could possibly build a theory valid for the whole range of behaviour for the molecular assembly. We shall now try to construct such a method.

Construction of the Zeroeth Order Approximation

The Green's expression discussed above gives only the approximate expression for \( \tau^2(\vec{r}) \). In order to set up an iterative method we should be in a possession of an approximate expression for the general \( \tau^2(\vec{r}^h) \), which we could subsequently use as our zeroeth approximation. To construct this we generalise Green's procedure to a certain extent as below:

We recognised that \( \tau^2(\vec{r}^h) \) are functions only of relative coordinates, i.e.,

\[
\tau^2(\vec{r}_i, \vec{r}_2) = \tau^2(\vec{r}_{12}) \quad \ldots (2.3.10)
\]

Multiplication of (2.2.10) by,

\[
\left| \begin{array}{c}
\vec{r}_{ih} \\
\vec{r}_{ih}
\end{array} \right| = \left| \begin{array}{c}
\vec{r}_i - \vec{r}_h \\
\vec{r}_{ih}
\end{array} \right| \quad \ldots (2.3.11)
\]
We obtain,
\[ \kappa T \frac{\partial}{\partial \tau_{ih}} \ln n_h(\vec{r}_h) = -\frac{1}{\delta \tau_{ih}} \phi(\vec{r}_h) - \int \frac{1}{\delta \tau_{ih}} \phi_{i,h+1} X \]
\[ \frac{n_{h+1}}{n_h} \left( \frac{\tau_{ih}}{\tau_{ih}} \right) \left( \frac{\tau_{ih}}{\tau_{ih}} \right) \left( \frac{\tau_{ih}}{\tau_{ih}} \right) d\tau_{h+1} \ldots (2.3.12) \]

Assuming,
\[ \phi(\vec{r}_h) = \sum_{j=1}^{N} \Phi_{ij} + \sum_{j=1}^{N} \sum_{k=1}^{N} \Phi_{jk} \ldots (2.3.13) \]

We obtain, by noting that \( n_h \to n^H \) asymptotically,
\[ n_h(\vec{r}_h) = n^H \exp \left\{ \phi(\vec{r}_h) - 2 \pi \int \frac{1}{\delta \tau_{ih}} \phi_{i,h+1} \frac{n_{h+1}}{n_h} \left( \frac{\tau_{ih}}{\tau_{ih}} \right) \right\} \]
\[ \left( \frac{\tau_{ih+1} - \tau_{ih}}{2 \tau_{ih}} \right) \cdot n_{h,h+1} d\tau_{h+1} d\tau_{h} \ldots (2.3.14) \]

Further introducing the factor \( \epsilon_k \) in an analogous way with Green's method and neglecting second order terms, we obtain,
\[ n_h(\vec{r}_h) = n^H \exp - \{ \phi(\vec{r}_h) + f_h(\vec{r}_h) \} \ldots (2.3.15) \]

and neglecting three or more factors of \( f_h(\vec{r}_h) \) or \( f_h(\vec{r}_h+1) \).

We obtain,
\[ \kappa f_h(\vec{r}_h) = 2 \pi \int \left\{ \left\{ t+\tau \right\} f_h(t+\tau) + \epsilon_k \alpha_h(t+\tau) \right\} d\tau \ldots (2.3.16) \]

Further introducing the factor \( \epsilon_k \) in an analogous way with Green's method and neglecting second order terms, we obtain,
\[ \kappa f_h(\vec{r}_h) = 2 \pi \int \left\{ \left\{ t+\tau \right\} f_h(t+\tau) + \epsilon_k \alpha_h(t+\tau) \right\} d\tau \ldots (2.3.17) \]
The solution of which is,
\[ \eta \{ f(h) + \epsilon \alpha_h \} = \frac{1}{(2\pi)^{\nu_2}} \int_{-\infty}^{\infty} \epsilon \beta_n(s) e^{i \eta s} ds \quad \cdots (2.3.20) \]
with,
\[ S(\beta_n(s)) = i \int \eta \alpha_n(\eta') e^{-i \eta s} d\eta' \quad \cdots (2.3.21) \]
We shall use the result (2.3.18) for further iterations.

**Method of iteration**

If we write,
\[ \eta^o_n - \eta^h_n \exp - \frac{1}{kT} \left\{ \phi(\eta^h_n) + f^o(h) \right\} \quad \cdots (2.3.22) \]
Then,
\[ \frac{\eta_{n+1}}{\eta^o_n} = \eta_n \exp - \frac{1}{kT} \left\{ \phi(\eta^h_{n+1}) - \phi(\eta^h_n) \right\} + \Delta f^o_{(h+1)} \quad \cdots (2.3.23) \]
We now choose the zeroth approximation as the expression given by (2.3.20) and note,
\[ \Delta f^o_{(h+1)} = f^o_{(h+1)} - f^o_{(h)} \quad \cdots (2.3.24) \]
\[ f^o_{(h)} = f^0_{(h,h+1)} + \sum_{i<h} f^0_{(h+1)}(i) + f^0_{(i+1,h+1)} \]
\[ f^o_{(h+1)} = \frac{1}{(2\pi)^{\nu_2}} \int_{\eta_{h+1} = -\infty}^{\infty} \frac{\epsilon(\eta_{h+1}) \beta^2(\eta_{h+1}) \Theta(\eta_{h+1})}{\lambda - \epsilon(\eta_{h+1})} d\eta_{h+1} \quad \cdots (2.3.25) \]
We can now proceed with further iterations.

Consequently \( \eta_2(\eta) \) to our approximation is simply \( \eta_2(\eta) \) calculated by Green's procedure. Further the assumption that \( \phi(\eta) \) is spherically symmetric is implicit in Green's derivation. When such is not the case \( \eta_2(\eta) \) even in our zeroth approximation may differ considerably from Green's solution.
Now, from BGY equation,
\[ n_h^0 (x^h) = n_h \exp \left( -\frac{1}{kT} \left\{ \phi (x^h) + f_h^0 (x^h) \right\} \right) \] \hspace{1cm} (2.3.26)

with \( f_h^0 \) given in equation (2.3.24)

Then,
\[ n_h^1 (x^h) = n_h \exp \left( -\frac{1}{kT} \left\{ \phi (x^h) + f_h' (x^h) \right\} \right) \] \hspace{1cm} (2.3.27)

Where,
\[ f_h' = -2\pi n \iint \frac{\delta}{\delta \tau_{i,h+1}} \Phi_{i,h+1} \exp \left( -\frac{1}{kT} \left\{ \phi (x^h) + f_h^0 \right\} \right) \times \left( \frac{\tau_{i,h+1} + \tau_{i,h+1} - \tau_{i,h}^2}{2 \tau_{i,h}^2} \right) \tau_{i,h+1} d\tau_{i,h} d\tau_{i,h+1} d\tau_{i,h+1} \]
\[ = f_h^0 + \Delta' f (x^h) \] \hspace{1cm} (2.3.28)

Where,
\[ \Delta' f (x^h) = -2\pi n \iint \frac{\delta}{\delta \tau_{i,h+1}} \Phi_{i,h+1} \exp \left( -\frac{1}{kT} \left\{ \phi (x^h) + f_h^0 \right\} \right) \times \left( \frac{\tau_{i,h+1} + \tau_{i,h+1} - \tau_{i,h}^2}{2 \tau_{i,h}^2} \right) \tau_{i,h+1} d\tau_{i,h} d\tau_{i,h+1} d\tau_{i,h+1} \] \hspace{1cm} (2.3.29)

We can also compute \( f_h^2 (x^h) \) to second order iteration as,
\[ f_h^2 = 2\pi n \iint \frac{\delta}{\delta \tau_{i,h+1}} \Phi_{i,h+1} \exp \left( -\frac{1}{kT} \left\{ \phi (x^h) + f_h' \right\} \right) \times \left( \frac{\tau_{i,h+1} + \tau_{i,h+1} - \tau_{i,h}^2}{2 \tau_{i,h}^2} \right) \tau_{i,h+1} d\tau_{i,h} d\tau_{i,h+1} d\tau_{i,h+1} \]
\[ = f_h' (x^h) + \Delta f_h^2 (x^h) \] \hspace{1cm} (2.3.30)
Where,
\[ \Delta f_h^2 (\tau^h) = 2\pi n \iint \frac{1}{\delta \tau_{i,hi}^2} \phi_{i,hi} \exp \left( \frac{1}{kT} \left[ \phi(\tau^h + \tau_{i,hi}^2) - \phi(\tau^h) - \phi(\tau_{i,hi}^2) \right] \right) \]
\[ \left( \frac{\tau_{ih}^2 + \tau_{i,hi}^2 - \tau_{ih}^2}{2\tau_{ih}^2} \right) \tau_{h,hi} d\tau_{ih} d\tau_{i,hi} d\tau_{h,hi} \ldots (2.3.30a) \]

For the third order iteration,
\[ \Delta f_h^3 (\tau^h) = -2\pi n \iint \frac{1}{\delta \tau_{i,hi}^2} \phi_{i,hi} \exp \left( \frac{1}{kT} \left[ \phi(\tau^h + \tau_{i,hi}^2) - \phi(\tau^h) + \phi(\tau_{i,hi}^2) \right] \right) \]
\[ \left( \frac{\tau_{ih}^2 + \tau_{i,hi}^2 - \tau_{ih}^2}{2\tau_{ih}^2} \right) \tau_{h,hi} d\tau_{ih} d\tau_{i,hi} d\tau_{h,hi} \ldots (2.3.31) \]

And \( \Delta f_h^3 (\tau^h) \) is as in the expression (2.3.32).

Of course we can proceed further and compute \( f_{ih}^3 (\tau^h) \) and so on, but the computational difficulties will increase steeply. However, we may remember that the Green's solution already taken into account the ternary iterations and may be a pretty good approximations. Computations of \( \Delta' (\tau^h) \) will take into account the quarternary interaction as well as the five molecular interactions. It is doubtful therefore we may ever need \( \Delta f_h^3 (\tau^h) \) and higher terms for our study. However, if we need interaction terms involving six or more molecules, we may proceed by straightforward application of our result.

The pair distribution function according to Green's solution is given by,
\[ n_2(\tau_{12}) = n^2 \exp - \phi(\tau_{12})/kT \left[ 1 + f(\tau_{12}) \right] \ldots (2.3.32) \]

where,
\[ f(\tau_{12}) = \frac{1}{(2\pi)^{1/2}} \tau_{12} \int_0^\infty \frac{\epsilon^2 S \beta^2(s) e^{i\epsilon s}}{\lambda - \epsilon^2 \beta^2(s)} ds \ldots (2.3.33) \]
With,
\[ \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} S\alpha(s) \, ds = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{+\infty} j(\alpha) \, ds \] \( \cdots (2.3.34) \)

In Green treatment \( \varepsilon \) was taken to be the average value of \( f(\tau) \). Consequently the equation (2.3.23) yield,
\[ f^{0}_{(h+1)} = f^{0}_{h,h+1} + \sum_{i<h} f^{0}_{i,h} + f^{0}_{i,h+1} \]
\[ = \frac{1}{(2\pi)^{1/2}} \left( \frac{1}{\tau_{h,h+1}} \int_{-\infty}^{\infty} \frac{\varepsilon^2 \beta^2(s) e^{i\eta s}}{\lambda - \varepsilon \beta(s)} \, ds + \sum_{i<h} \frac{1}{\tau_{i,h}} \int_{-\infty}^{\infty} \frac{\varepsilon^2 \beta^2(s) e^{i\eta s}}{\lambda - \varepsilon \beta(s)} \, ds \right) \] \( \cdots (2.3.35) \)

Consequently,
\[ f^{0}_{(h)} = f^{0}_{h,h+1} + \sum_{i<h} f^{0}_{i,h} + f^{0}_{i,h+1} \]
\[ \frac{1}{(2\pi)^{1/2}} \left( \frac{1}{\tau_{h,h+1}} \int_{-\infty}^{\infty} \frac{\varepsilon^2 \beta^2(s) e^{i\eta s}}{\lambda - \varepsilon \beta(s)} \, ds + \sum_{i<h} \frac{1}{\tau_{i,h}} \int_{-\infty}^{\infty} \frac{\varepsilon^2 \beta^2(s) e^{i\eta s}}{\lambda - \varepsilon \beta(s)} \, ds \right) \] \( \cdots (2.3.36) \)

and thus;
\[ \Delta^{0}_{h} = -2\pi n \left[ \phi^{0}_{h,h+1} \exp \left( -\frac{1}{kT} \right) \left[ \phi^{0}_{h,h+1} \right] \right] + \frac{1}{(2\pi)^{1/2}} \left( \frac{1}{\tau_{h,h+1}} \int_{-\infty}^{\infty} \frac{\varepsilon^2 \beta^2(s) e^{i\eta s}}{\lambda - \varepsilon \beta(s)} \, ds + \sum_{i<h} \frac{1}{\tau_{i,h}} \int_{-\infty}^{\infty} \frac{\varepsilon^2 \beta^2(s) e^{i\eta s}}{\lambda - \varepsilon \beta(s)} \, ds \right) \] \( \cdots (2.3.37) \)
Similarly from the equation (2.3.16),

\[
\int_{(h)}^2 = -2\alpha \int_0^\infty \frac{\partial}{\partial \tau_{i,h+1}} \Phi_{i,h+1} \exp \left( \frac{1}{kT} \int \left\{ \phi (\xi_{h+1}^2) - \phi (\xi_h^2) \right\} \right) + \frac{1}{(2\pi)^2} \left( f(h') - f(h) \right) \left( \int \frac{\tau_{i,h+1}^2 + \tau_{i,h+1} - \tau_{i,h+1}^2}{2 \tau_{i,h+1}^2} \right) \int d\tau_{i,h+1} d\tau_{i,h+1} d\tau_{i,h+1}
\]

\[
\int_{(h)}^2 = -2\alpha \int_0^\infty \frac{\partial}{\partial \tau_{i,h+1}} \Phi_{i,h+1} \exp \left( \frac{1}{kT} \int \left\{ \phi (\xi_{h+1}^2) - \phi (\xi_h^2) \right\} \right) + \frac{1}{(2\pi)^2} \left( f(h') - f(h) \right) \left( \int \frac{\tau_{i,h+1}^2 + \tau_{i,h+1} - \tau_{i,h+1}^2}{2 \tau_{i,h+1}^2} \right) \int d\tau_{i,h+1} d\tau_{i,h+1} d\tau_{i,h+1}
\]

We may note here that the integral equation (2.3.33) above has singularity whenever,

\[
\beta(s) = \frac{\lambda}{\xi}
\]

This equation may have real or complex roots. Green suggested that the temperature at which the complex roots starts occurring may be taken to be the temperature at which the liquid state begins to exist.

The above conclusion has been doubted by some authors. They argue that (2.3.33) has singularities which occur perhaps only as singularities of the equation (2.1.1). These singularities may be entirely due to the various approximations implicit.
in deriving the equation (2.3.33) and may not be shown in the exact theory.

In fact, Zimm\(^{113}\) argued that discontinuities in equation of state are noticeable if superposition hypothesis is taken into account, and that the anomalous region whose existence have been asserted by Mayer school is not noticeable, when superposition hypothesis is assumed.

2.4. INTEGRO-DIFFERENTIAL EQUATION FOR LIQUID ALLOYS

In the introduction (sec. 1.11) the general statistical mechanics of fluid mixtures have been given. This theory can be extended in the case of liquid alloys. Unfortunately, the idealised picture of liquid alloys rest on some shaky foundations. The pseudo-potentials in alloys are weak enough when there is a large difference in valency or perhaps, in electronegativity between solvent and solute to justify the use of the Second-order perturbation theory. There are alloy system in which it fails completely and the near free electron model must be abandoned. The distribution functions which describe the structure in such alloys to be so different from those of rigid sphere liquids that a description in terms of chemical bonds between the neighbouring atoms may be required, Pauling (1938, 1947, 1960)\(^{114}\) and Warken & Burry (1953)\(^{115}\) assumed that the metallic bond is as same as the chemical bond for molecules except that the number of valency electrons for each metallic bond is considerably less than for the single bond of a molecule.
To derive the integro-differential equation for binary alloy system we consider two different kinds of molecules of total number $N$ occupying a total volume $V$.

Let $N_1$ and $N_2$ be the number of molecules of the 1st and 2nd kind respectively; $m_1$ and $m_2$ be the molecular masses. We follow the procedure suggested by Yang to develop the equations of motion at equilibrium which is actually a generalized version of Born-Green's equation. If these $N (= N_1 + N_2)$ molecules one can choose any $n_1$ of the first kind and any $n_2$ of the second kind. The distribution function $\eta_{n_1n_2}$ is defined such that $\eta_{n_1n_2} dx_{n_1} dx_{n_2}$ is the probability of finding the volume element $dx_{n_1} \ldots dx_{n_2}$ occupied by any $n_1$ molecules of first kind and the volume element $dx_{n_1} \ldots dx_{n_2}$ by any $n_2$ molecule of the second kind simultaneously at time $t$.

Equation (1.125) (Ch. I) gives the relation between $\eta_{n_1n_2}$ and $\eta_{n_1n_2}$. The exact properties of $\eta_{n_1n_2}$ is necessary to determine the fundamental quantities given in equations (1.126) and (1.127). On account of the resultant compactness of notation, we shall restrict our attention initially to the elementary class of binary alloys. Generalizations to description of less regular alloys will be suggested by specialized theory which is not included in this description.

The mean correlation function may be constructed from $\eta_{n_1n_2}$ and $\eta_{n_1n_2}$ in a way which shows that it is rigorously the pair correlation function acting between a partially coupled particle
and another particle in a fluid composed of \( N-2 \) particles - all are identical with the second. In fact, the alloy is equivalent in all thermodynamic respect to this single component fluid with a single somewhat modified particle.

The mean correlation function is a straight arithmetic mean, since there are essentially equal numbers of atoms numbered 2, \( \ldots \), \( N \); we may also take \( g_m(\mathbf{r}_i, \lambda) \) to be the average of all pair correlation functions between atom 1 and each of 2, \( \ldots \), \( N \) in turn. This latter average may be written as,

\[
g_m(\mathbf{r}_{10}, \lambda) = \frac{\gamma_0^2}{(N-1)Z_N(\lambda)} \sum_{i=2}^{N} \int \cdots \int d^3 \mathbf{r}_i \cdots d^3 \mathbf{r}_N \delta(\mathbf{r}_i - \mathbf{r}_0) \times \exp\left[ -\frac{\Phi_N(\mathbf{r}_1, \ldots, \mathbf{r}_N; \lambda)}{kT} \right]
\]

\[
\hat{Z}_N(\lambda) = \int \cdots \int d^3 \mathbf{r}_1 \cdots d^3 \mathbf{r}_N \exp\left[ -\frac{\Phi_N(\mathbf{r}_1, \ldots, \mathbf{r}_N; \lambda)}{kT} \right]
\]

Expressions for distribution functions of binary mixtures with the composed of species \( \alpha \) and \( \beta \) in the light of iterations:

Although exact theories for liquid mixtures are not available, the emphasis in this area is on relating the properties of mixtures to those of the pure components - since it is the changes which occur on mixing which are of primary interest. In a widely studied approach, the one fluid model, the properties of a binary mixture are taken to be those of a hypothetical pure liquid. It is usual to assume that this hypothetical fluid and the two pure components have conformal intermolecular potentials, and so satisfy the principle of corresponding states. The intermolecular potential for the hypothetical fluid
is calculated as some composition-dependent average of the potentials for the pure component and for the unlike interaction.

So, in the light of above discussions, we may have different expressions for distribution functions of alloy system on consideration of different iterations (Vide Section 2.2):

For Zeroeth iteration (for h = 2),
\[ n_{\alpha\beta}^{(2)} = n_{\alpha\beta}^2 \exp - \phi^{\alpha\beta}(h^2) \]

For the first iteration (for h = 2),
\[ n_{\alpha\beta} \equiv n_{\alpha\beta}^0 \exp - \Delta_h^0 \]

Where,
\[ \Delta_h^0 = \frac{2\pi N}{kT} \int \int \frac{\partial}{\partial \eta_{ih}} \phi_{i,j} \exp - \frac{1}{kT} \left\{ \phi^{\alpha\beta}(h^{h+1}) \right\} R d\eta_{ih} d\eta_{i,h+1} \]

For the second iteration (for h = 2),
\[ n_{\alpha\beta}^2 = n_{\alpha\beta}^1 \exp - \Delta_h^1 \]

Where,
\[ \Delta_h^1 = \frac{2\pi N}{kT} \int \int A_i \exp - \sum \sum \phi_{ij} \left[ 1 - a \Phi + \frac{a^2 \Phi^2}{2} - \ldots \right] \times \]
\[ d\eta_{ih} d\eta_{i,h+1} d\eta_{i,h+1} \]
\[ \phi = \frac{2\pi N}{kT} ; \quad A_i = \frac{\partial}{\partial \eta_{ih}} \phi_{i,h+1} R \]

For the third iteration (for h = 2),
\[ n_{\alpha\beta}^3 = n_{\alpha\beta}^2 \exp - \left( -1 \right)^n \sum n_{h}^{n-2} \alpha^{n+1} \]
\[ = n_{\alpha\beta}^2 \exp - \Delta_h^2 \]
Where,
\[ \Delta h = (-1)^n \sum \gamma_n \alpha^{n+1} \]

\( \delta, \gamma_n = \int_A \exp \left\{-\frac{1}{k} \sum \phi_{ij} (\alpha^0 - \alpha_0^0) \right\} \alpha^{n-1} \alpha^{n+1} \]

\( \delta, \alpha^0 = \beta_{h+1} - \beta_h \)

\( \delta, \beta_{h+1}^k = \frac{1}{k!} \int_4 \cdots \int_A \exp \left\{-\frac{1}{k} \sum \phi_{ij} (\alpha^0 - \alpha_0^0) \right\} \alpha^{n+1} \)

For the fourth iteration (for \( h = 2 \)),
\[ n_{\alpha^0}^4 = n_{\alpha^0}^3 \exp - \Delta h^3 \]

where,
\[ \Delta h = (-1)^n \sum \delta_n \alpha^{n+1} \]

\( \delta, \gamma_n = \int_A \left[ p^n - 3m \Omega (-1)^m A_{m+1} \right] \alpha^{n+1} \alpha^{n+1} \)

For the fifth iteration (for \( h = 2 \)),
\[ n_{\alpha^0}^5 = n_{\alpha^0}^4 \exp - \Delta h^4 \]

where,
\[ \Delta h = \left\{-\int \cdots \int_A \sum (-1)^n \alpha^{n+2} \left\{-(-1)^m p^{n-2-4m} S \right\} + (-1)^{n+2} \right\} \alpha^{n+1} \alpha^{n+1} \]

where,
\[ S = (Y_{h+1} - Y_0) \]
\[ X = \sum \left[ p^{n-2m} \Omega \left\{-(-1)^m \right\} A_{m+1} \right] \]
\[ Y = \sum \left[ p^{n+3m} \Omega \left\{-(-1)^m \right\} A_{m+1} \right] \]

Iterations of higher order may likewise be constructed.