CHAPTER III

(On the way to Calculate intermolecular potential energy)
3.1 INTRODUCTION

The present chapter consists of two parts - the first is the result of our investigations for the calculation of the effective intermolecular potential energy functions with which the liquid metal molecules actually interact when they form a part of the assembly in the liquid state of aggregation. We thought that this investigation is necessary because at least in liquids actually existing interaction potential may not be the same as the pair potential with which two molecule pairs interact in an isolated state. This is because the rest of the molecules may exert considerable influence on the pair considered and this influence may be sufficient to alter the nature of the interaction curve. The original integro-differential equation (1.37a) connecting the distribution function with the potential energy function was approximated and the radial distribution function was calculated assuming the potential energy to be known.

In this present chapter we follow exactly reversed chain of arguments. This means we assume that the distribution functions are known functions \( g(r) \) \( Known \) and the interaction potentials are calculated from the integro-differential equation. Actually, the distribution function can be calculated from the X-ray diffraction data (Chapter I, Sec. 1.11). So, we have used the X-ray diffraction results to obtain detailed informations on the potential energy functions existing in the liquid state.
The second part (Part II) of the present Chapter tries to formulate expressions for the reduced distribution functions (RDF). Getting an analytical expression of the intermolecular potential energy in the first part (Part I) of the Chapter (Chapter III), we put this in the expressions of Chapter II and get the desired values of the reduced distribution functions (RDF). We have considered the expressions for \( h=2 \). We have written expressions for the reduced distribution functions up to the fourth order approximations, with the hope that the expressions for the reduced distribution functions (RDF) on consideration of higher order approximations (beyond fourth order) may likewise be constructed. The chapter concludes with different relations interconnecting distribution functions and potential energy functions (Hypernated chain approximation (HNC), Percus-Yevick equation (PY), Born-Green Yvon (BGY) equation) to show that these three equations can be correlated with certain closer approximations.
3.2 PRELIMINARY COMMENTS

In the Chapter-II of this thesis the integro-differential equation of the statistical mechanical theory has been developed. The iterative procedure can be employed to get the radial distribution function to any desired degree of accuracy. This can be employed to study the liquid metals also. Unfortunately, in actual applications we are handicapped by the almost complete lack of our knowledge about the intermolecular forces. Ab initio, quantitative calculations of these forces are very much complicated and compels a worker in this field to rely almost entirely on the empirical relations given in Chapter I (Page 4). In developing the statistical mechanical formalism, we are forced to use the additivity assumptions. Because the many-body interactions are not known, the total interaction potential for a system of \( N \) - Particles can be expanded as the sum of 2, 3 and \( n \)-body potentials.

\[
\phi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \frac{1}{2} \sum_{i \neq j} \sum_{j=1}^{N} \phi_{ij} + \frac{1}{3!} \sum_{i \neq j, j \neq k} \sum_{k=1}^{N} \phi_{ijk} + \ldots
\]

where, \( \phi_{ij} = \phi_{12}(\vec{r}_1, \vec{r}_2); \phi_{ijk} = \phi_{123}(\vec{r}_1, \vec{r}_2, \vec{r}_3) \) and so on.

Much statistical mechanical theory would still be applicable
at least in certain density ranges, if,

\[ \phi = \frac{1}{2} \sum_{i \neq j} \sum_{j \neq l} \phi_{ij} \]  

... (3.2.2)

\( \phi \) Effect are related to the bare two-body potential in simple way, equation (3.2.1) can be written as:

\[ \phi = \frac{1}{2!} \sum_{i \neq j} \sum_{j \neq l} \left( \phi_{ij} + \frac{2!}{3!} \sum_{k \neq l, j} \phi_{ijk} + \cdots + \frac{2!}{N!} \sum_{k \neq l, j} \sum_{l \neq j} \phi_{ijkl} + \cdots \right) \]

Thus, \( \phi_{ij} \) Effect

\[ \phi_{ij} = \phi_{ij} \left\{ 1 + \frac{1}{3} \sum_{k \neq l, j} \left( \phi_{ijk}/\phi_{ij} \right) + \cdots \right\} \]  

... (3.2.3)

For a given configuration (\( \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n \)) a static distribution of the \( N \)-molecules, the factor multiplying the bare two-body potential \( \phi_{ij} \) will depend, in addition to \( \mathbf{r_i} \) and \( \mathbf{r_j} \), on all the other (\( N-2 \)) \( \mathbf{r}_k \). For a crystal the \( K \) summation \( \sum_{k=i,j}^N \phi_{ijk} \) is carried over all the lattice points except the chosen pair \( ij \). If we neglect the vibration this defines,

\[ \phi_{ij} \text{ effect} = \phi_{ij} \text{ effect} \left( \mathbf{r}_i, \mathbf{r}_j, \{ \mu \} \right) \]  

... (3.2.4)

where \( \{ \mu \} \) symbolizes dependence on some bulk properties of the solid.

For a liquid, we may obtain \( \phi_{ij} \text{ effect} \) by averaging the sum over all (\( \mathbf{r}_1, \ldots, \mathbf{r}_N \)) while keeping \( \mathbf{r}_1, \mathbf{r}_j \) fixed, i.e.,

\[ \phi_{ij} \text{ effect} = \phi_{ij} + \frac{1}{3} \left( \sum_{k=l,j}^N \phi_{ijk} \right) + \cdots \]  

... (3.2.5)
will depend on the density $\rho$ of the liquid as well as on
\[ r_{ij} = r_i - r_j, \quad \langle \rangle_k \text{ denotes the statistical averaging over } k. \]
One thus obtains a density dependent pair potential,
\[ \phi_{ij}^{\text{effect}} = \phi_{ij}^{\text{effect}}(r_{ij}; \rho) \quad \ldots \quad (3.2.6) \]

Now, let us consider a solution with $n_a$ solvent molecules $a$ and $n_b$ solute molecules $b$. Distribution of the non-pairwise potential into effective pair potential depends on the type of pairing ($aa$, $bb$, $ab$). Care must be taken to avoid counting some of the interaction twice. For arbitrary distribution,
\[
\phi = \frac{1}{2!} \sum_{i<j}^{n_a} \phi_{ij}^{aa} + \frac{1}{2!} \sum_{m>n}^{n_c} \sum_{n_c}^{c} \phi_{mn}^{cc} + \frac{1}{2!} \sum_{i+m}^{n_a} \sum_{m}^{c} \phi_{im}^{ab} + \frac{1}{3!} \sum_{i<j<k}^{n_a} \phi_{ijk}^{aaa} + \frac{1}{3!} \sum_{m<n}^{n_a} \sum_{n}^{c} \phi_{mn}^{abc} + \frac{1}{3!} \sum_{i<j}^{n_a} \sum_{m}^{c} \phi_{ijk}^{abc} + \ldots + \text{higher terms} \quad (3.2.7)
\]

Again, we define,
\[
\phi = \frac{1}{2!} \sum_{i<j}^{n_a} \phi_{ij}^{aa} \quad \text{effect} + \frac{1}{2!} \sum_{m<n}^{n_c} \sum_{n}^{c} \phi_{mn}^{bc} \quad \text{effect} + \sum_{i+m}^{n_a} \sum_{m}^{c} \phi_{im}^{ab} \quad \text{effect} \quad \ldots (3.2.8)
\]

Definition now becomes ambiguous. The environment of a given pair contains some $a$ and some $b$ molecules. It would be desirable to define the $\phi$ effect as the effective potential of a pair immersed in a medium of a given bulk composition, i.e., $x_a + x_b = 1$,
\[
\text{where, } \quad x_a = \frac{n_a}{n_a + n_b} \quad \& \quad x_b = \frac{n_b}{n_a + n_b}
\]
This may be possible if \( a \) and \( b \) are quite similar and local concentration effects are neglected. So,

\[
\phi^{ab}_{ij} \text{ Effect } = \phi^{ab}_{ij} \text{ Effect } (\kappa \rho ; \chi_a) \quad \ldots (3.2.9)
\]

a composition as well as density dependent potential after suitable statistical averaging. However, there still remains the problem of how many \( \phi_{ijm}^{aab} \) terms are attributable to \( \phi_{ijab} \) effect and how many to \( \phi_{imab} \) effect.

In a dilute solution of \( b \) in \( a \), the situation is simple. The environment of the \('bb\) pair is essentially all \( a \). The same is true for \('ab\) or an \('a\) pair. Consistent to this picture: all the \( \phi_{ijm}^{aab} \) terms are assigned to the \( \phi_{im}^{ab} \) pair, \( \phi_{imn}^{ab} \) to \( \phi_{mn}^{bb} \) and so on.

\[
\phi = \frac{1}{2!} \sum_{i,j} \left\{ \phi_{ij}^{aa} + \frac{1}{3} \sum_{k \neq i,j} \phi_{ijk}^{aaa} + \ldots \right\} + \sum_{i,m} \left\{ \phi_{im}^{ab} + \frac{1}{2!} \sum_{j \neq i} \phi_{imj}^{aba} + \ldots \right\} + \frac{1}{2} \sum \{ \cdot \} \quad \ldots (3.2.10)
\]

In dilute solutions, the \( \phi^{bbb} \) and \( \phi^{bb} \) terms are negligible. Thus, in dilute solution the effective pair potential becomes:

(1) Between two solvent molecules:

\[
\phi_{ij}^{aa} \text{ Effect } = \phi_{ij}^{aa} \left[ \frac{1}{2} \sum_{\kappa \rho} \kappa \rho \right] B_{aa} (\kappa_{ij} ; \rho) \quad \ldots (3.2.10a)
\]
where,
\[ B(a_a) (\mathbf{r}_{ij}, \rho) = 1 + \frac{1}{3} \left\langle \sum_k \phi_{ijk} \right\rangle + \cdots \]

(2) Between one solvent and one solute molecule:
\[ \phi_{im}(\text{sol.}) = \phi_{im} B(a_b) (\mathbf{r}_{im}, \rho) \]
where,
\[ B(a_b) (\mathbf{r}_{im}, \rho) = 1 + \frac{1}{2} \left\langle \sum \phi_{imj} / \phi_{im} \right\rangle + \cdots \]

(3) Between two solute molecules:
\[ \phi_{mn} \text{ Effect} = \phi_{mn} B(a_a) (\mathbf{r}_{mn}, \rho) \]
where,
\[ B(a_a) (\mathbf{r}_{mn}, \rho) = 1 + \left\langle \sum \phi_{mnj} / \phi_{mn} \right\rangle + \cdots \]

In a dilute solution only 'a' molecules are round in a relatively small region. In this case difference between \[\sum_{a}^m \text{ and } \sum_{b}^N \] is negligible. So, we can write:
\[ \phi_{ij}(\text{sol.}) = \phi_{ij} \text{ Effect (pure liquid)} \]
except when \( i \) and \( j \) are near a 'b' molecule. Now, let us express the effective potentials in terms of the distribution function.

\[ \phi_{aa} (\mathbf{r}_{ij}, \rho) = \phi_{aa} (\mathbf{r}_{ij}) + \frac{1}{3} \int \phi_{aa} (\mathbf{r}_{ij}, \mathbf{r}_{ik}) d \mathbf{r}_k \]

\[ g^{[3]} (\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) \]

The \[ \rho (\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = \rho g^{[3]} (\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) \] is the
unsymmetrical distribution function giving the probability density for finding any one molecule at \( \vec{r}_k \) while two definite molecules are kept at \( \vec{r}_1, \vec{r}_j \).

We know that the total average energy,

\[
E = \frac{3}{2} N k T + \langle \phi(\vec{r}_1, \cdots, \vec{r}_N) \rangle
\]

\[
\langle \phi \rangle = \frac{1}{2!} \rho^2 v \int_0^\infty \phi_{aa}(\tau_{12}) \mathcal{g}(\tau_{12}) 4\pi \tau_{12}^2 d\tau_{12} +
\]

\[
\frac{1}{3!} \rho^3 \iiiint \phi_{aaa} \mathcal{g}^{(3)} \, d^3 \tau_1 \, d^3 \tau_2 \, d^3 \tau_3
\]

Then,

\[
\langle \phi \rangle = \frac{1}{2!} \rho^2 v \int_0^\infty \phi_{aa}^{\text{eff}}(\tau_{12}) \mathcal{g}(\tau_{12}) 4\pi \tau_{12}^2 d\tau_{12}
\]

Since, the symmetrical correlation factor \( \mathcal{g}^{(3)} \) equals to,

\[
\mathcal{g}^{(3)}(\tau_1, \tau_2, \tau_3) = \mathcal{g}^{(2)}(\tau_{12}) \mathcal{g}^{(3)}(\tau_1, \tau_2)
\]

Here,

\( V = \) total volume.

3.2.1

The effective intermolecular potential energy as shown above can be calculated from the experimental X-ray scattering data and the integro-differential equation. Johnson, Hutchinson and March, and Sengupta and Guha first calculated the intermolecular potential energy for liquid metals from their radial distribution function which can be obtained from the X-ray scattering technique. Sengupta and Guha have made similar studies for non-metallic liquid systems including the electrolyte solutions. Guha and Chatterjee made the calculation for the potential energy functions for Tl and In and effect of the...
secondary interactions have been calculated. These methods of determination of potential energy functions have been criticized by Housemann and Bagchi because of the non-reliability of the experimental scattered beam intensity at short ranges.

In Chapter II, we have suggested a method to solve iteratively the original integro-differential equation. This equation along with the X-ray scattering can be used to find the force laws. The purpose is to find out an analytical expression for the effective potential energy function as all the thermodynamical and physico-chemical properties of the liquid metals and alloys can be calculated from radial distribution function g(r) and the potential energy function, so the involvement of this analytical expression for the potential energy with g(r) can be used for different purposes.

3.3. THE ITERATIVE SCHEME FOR CALCULATION OF $\phi(r)$ FROM KNOWN $g^{12'}(r)$

For our purpose, we begin with the set of integro-differential equation (cf. equation 1.37 a, Chapter I):

$$kT \frac{\partial}{\partial \bar{n}_i} \left( \ln \bar{n}_i \bar{\phi}(\bar{\rho}_h) \right) = \frac{\partial}{\partial \bar{n}_i} \bar{\phi}(\bar{\rho}_h) - \int \frac{\partial}{\partial \bar{n}_i} \bar{\phi}(\bar{\rho}_i, \bar{n}_{h+1}) \times \frac{\bar{n}_i^{h+1}(\bar{\rho}_{h+1})}{\bar{n}_i^{h}(\bar{\rho}_h)} d\bar{n}_i^{h+1} \quad \ldots(3.3.1)$$

Which is an exact set of coupled equations relating distribution functions of different order with potential energy expression. The use of superposition approximation decouples
the above set. Putting $h=2$ in the above equation and after some mathematical manipulation, it is reduced to BGY equation (cf. Article 1.7, Chapter - I).

March and his fellow workers evaluated the potential energy function by inverting the BGY equation itself for liquid metals and Argon. Such a technique invariably faces criticism due to the peculiarities seen in the results which may arise from the inherent approximation used to derive BGY equation, and may not stand for actual intermolecular interactions persistent in a given molecule pair forming a part of the ensemble.

This provokes us to create an iterative method starting from equation (3.3.1) itself. Integration of equation (3.3.1) with respect to $r_i$ results,

$$k_T \left[ n^h \left( \frac{h^h}{h^h} \right) \right] = -\phi \left( \frac{h^h}{h^h} \right) \int \frac{\partial}{\partial r_i} \left[ \phi \left( \frac{h^h}{h^h} \right) \right] \times$$

$$\frac{n^{h+1} \left( \frac{h^{h+1}}{h^{h+1}} \right)}{n^h \left( \frac{h^h}{h^h} \right)} \frac{d\frac{h^h}{h^h}}{d\frac{h^h}{h^h}} \quad \ldots (3.3.2)$$

where $n^h$ is from integration by applying the condition as,

$$\phi \left( \frac{h^h}{h^h} \right) \rightarrow 0 \quad , \quad n^h \left( \frac{h^h}{h^h} \right) \rightarrow h^h$$

Let us write,

$$\frac{n^{h+1} \left( \frac{h^{h+1}}{h^{h+1}} \right)}{n^h \left( \frac{h^h}{h^h} \right)} = \lambda^{h+1}$$

This equation defines $\lambda^{h+1}$ correctly when the correct expressions for $n^h \left( \frac{h^h}{h^h} \right)$ and $n^{h+1} \left( \frac{h^{h+1}}{h^{h+1}} \right)$ are known. We are handicapped as we know only $n^2(r)$ correctly from experiment.
We find that the knowledge of \( \lambda^3 \) depends on the knowledge of \( n^3(\vec{r}^3) \) which is not given. This is why a special iterative method is to be welcomed as each step of iteration from a given \( h \) needs the knowledge for the function with exponent \( h+1 \). For successful iterative procedure we should first decide a first order approximate function which would be close enough to the final result so that iteration becomes meaningful. This can be obtained from the equation (3.3.2) itself by neglecting the integral part. The equation (3.3.2) can be written as,

\[
\phi(\vec{r}^h) = -kT \ln \left[ \frac{n^h(\vec{r}^h)}{n^h} \right] + \int \delta_{\vec{r}_i} \left[ \phi(\vec{r}_{i,h+1}) \right] \lambda_{h+1} \, d\vec{r}_{h+1} \, d\vec{r}_i \quad \ldots (3.3.4)
\]

Omitting the integral part, the first order approximation to \( \phi(\vec{r}^h) \) becomes,

\[
\phi_0(\vec{r}^h) = -kT \ln \left[ \frac{n^h(\vec{r}^h)}{n^h} \right] \quad \ldots (3.3.5)
\]

likewise for \( (h+1) \) molecules, the first approximation to \( \phi(\vec{r}^{h+1}) \) is,

\[
\phi_0(\vec{r}^{h+1}) = -kT \ln \left[ \frac{n^{h+1}(\vec{r}^{h+1})}{n^{h+1}} \right] \quad \ldots (3.3.6)
\]

Therefore,

\[
\lambda^{h+1} = \exp \left[ -\phi_0(\vec{r}^{h+1})/kT + \phi_0(\vec{r}^h)/kT \right] \quad \ldots (3.3.7)
\]

Thus to this approximation,

\[
\phi_0(\vec{r}^2) = -kT \ln \left[ \frac{n^2(\vec{r}^2)}{n^2} \right] \quad \ldots (3.3.8)
\]
Here, we substitute \( n'(r)/n \) by \( g'(r) \) - a quantity which can be easily obtained from X-ray diffraction data. But for the successive iteration a knowledge of \( n'(r)_{-3} \) is necessary. But this is not an experimentally determined quantity. Directly from equation (3.3.4) for \( h=3 \), we may have to the first approximation,

\[
\phi_o(\tau^3) = -kT \ln \left[ \frac{n'(\tau^3)/n^3}{n'_{-3}/n_{-3}} \right] \quad \ldots (3.3.9)
\]

It is easily understood from equation (3.3.4) that in general \( \phi(\tau^h) \) is not additive. But to the first order approximation we may accept \( \phi_o(\tau^3) \) to be additive, i.e.,

\[
\phi(\tau^3) = \sum_{j>i=1}^3 \phi(\tau_{ij}) \quad \ldots (3.3.10)
\]

Therefore, to this assumption, the first approximate value to \( \lambda_{3}^{'} \) is,

\[
\lambda_{0}^{'} = n \exp \left[ -\left\{ \sum_{j>i=1}^3 \phi_o(\tau_{ij}) - \phi_o(\tau_{12}) \right\} / kT \right] \quad \ldots (3.3.11)
\]

and generally, the first approximation to \( \lambda_{h+1}^{'} \) is,

\[
\lambda_{0}^{'} = n \exp \left[ -\sum_{j>i=1}^{h+1} \phi_o(\tau_{ij}) / kT + \sum_{j>i=1}^{h} \phi_o(\tau_{ij}) / kT \right] \quad \ldots (3.3.12)
\]

One thing to note at this point is that the assumption of additive at this stage is not critical, because any error introduced at this stage automatically gets corrected as iteration proceeds.
Therefore, the second approximation to $\phi(\vec{r}^h)$ is,

$$\phi_1(\vec{r}^h) = \frac{h}{j} \Phi_0(\vec{r}_{ij}) - \int \frac{\partial}{\partial \vec{r}_i} \left[ \Phi(\vec{r}_{ih+1}) \right] \lambda_0 \vec{r}_{h+1} \vec{r}_i$$

$$= \alpha_0 h' + \alpha_1 h' \quad \ldots (3.3.13)$$

and the second approximation to $\phi(\vec{r})$ is,

$$\phi_1(\vec{r}) = -kT \ln g^2(\vec{r}) - \int \frac{\partial}{\partial \vec{r}_i} \left[ \Phi_0(\vec{r}_{13}) \right] \lambda_0 \vec{r}_3 \vec{r}_i$$

$$= \alpha_0 2^2 + \alpha_1 2^2 \quad \ldots (3.3.14)$$

where,

$$\alpha_0 h' = \sum_{j>i} \Phi_0(\vec{r}_{ij})$$

$$\alpha_1 h' = -\int \frac{\partial}{\partial \vec{r}_i} \left[ \Phi_0(\vec{r}_{ih+1}) \right] \lambda_0 \vec{r}_{h+1} \vec{r}_i$$

$$\alpha_0 2^2 = -kT \ln g^2(\vec{r}) \quad \text{(experimentally determined)}$$

and,

$$\alpha_1 2^2 = -\int \frac{\partial}{\partial \vec{r}_i} \left[ \Phi_0(\vec{r}_{13}) \right] \lambda_0 \vec{r}_3 \vec{r}_i$$

$$= -\int \frac{\partial}{\partial \vec{r}_i} \alpha_0 \vec{r}_3 \vec{r}_i \quad \ldots (3.3.16)$$

Therefore, the third approximation to $\phi(\vec{r}^h)$ is,

$$\phi_2(\vec{r}^h) = \alpha_0 h' - \int \frac{\partial}{\partial \vec{r}_i} \Phi_1(\vec{r}_{ih+1}) \lambda_0 \vec{r}_{h+1} \vec{r}_i$$

$$= \alpha_0 h' - \int \frac{\partial}{\partial \vec{r}_i} (\alpha_0 2^2 + \alpha_1 2^2) \lambda_0 \vec{r}_{h+1} \vec{r}_i$$

$$= \alpha_0 h' + \alpha_1 h' + \alpha_2 h' \quad \ldots (3.3.17)$$

where,

$$\alpha_2 h' = -\int \frac{\partial}{\partial \vec{r}_i} (\alpha_1 2^2) \lambda_0 \vec{r}_{h+1} \vec{r}_i \quad \ldots (3.3.18)$$
Further refinement requires the following,

\[
\phi_3 \left( \tau^h \right) = \alpha_0^h + \alpha_1^h + \alpha_2^h + \alpha_3^h \\
\phi_4 \left( \tau^h \right) = \alpha_0^h + \alpha_1^h + \alpha_2^h + \alpha_3^h + \alpha_4^h \\
\phi_\gamma \left( \tau^h \right) = \alpha_0^h + \alpha_1^h + \ldots + \alpha_\gamma^h 
\]

... (3.3.19)

\( \alpha_\gamma^h \) may be found by successive iteration.

More explicitly,

\[
\alpha_\gamma^h = - \int \int \frac{\partial}{\partial \tau_i} \alpha_\gamma^h \lambda_i \lambda_{h+1} \ d\tau_{h+1} \ d\tau_i 
\]

... (3.3.20)

It is to note that two factors restrict the above process of calculations. The first is the accuracy necessary for the determination of the \( n^h(\tau) \) and \( n^{h+1}(\tau^{h+1}) \) functions from which we start our calculations. Second factor is the trouble in evaluating the integral in each iterative step which amounts intensive labour at each successive step.

3.3.1 EXPRESSIONS FOR POTENTIAL ENERGIES OF BINARY MIXTURES WITH THE COMPOSED OF SPECIES \( \alpha \) & \( \beta \) IN THE LIGHT OF ITERATION

Exact theories for liquid mixtures are not available. 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 potential for the pure component and for the unlike interactions.
Keeping above discussions in mind we venture to write the following expressions:

The set of integro-differential equation for the binary mixtures relating distribution function and potential energy, is,

\[ kT \frac{\delta}{\delta \mathbf{r}_i} \ln n_{\alpha \beta}^{\prime \prime} (\mathbf{r}_i) = - \frac{\delta}{\delta \mathbf{r}_i} \phi^{\prime \prime} (\mathbf{r}_i) - \int \frac{\delta}{\delta \mathbf{r}_i} \phi^{\prime \prime} (\mathbf{r}_i, h) \times \frac{n_{\alpha \beta}^{h+1} (\mathbf{r}_i, h)}{n_{\alpha \beta}^{h} (\mathbf{r}_i, h)} \, d\mathbf{r}_i. \]

Integration of above equation with respect to \( \mathbf{r}_i \) results,

\[ kT \ln \frac{n_{\alpha \beta}^{h+1} (\mathbf{r}_i, h)}{n_{\alpha \beta}^{h} (\mathbf{r}_i, h)} = - \phi^{\prime \prime} (\mathbf{r}_i) - \int \frac{\delta}{\delta \mathbf{r}_i} \phi^{\prime \prime} (\mathbf{r}_i, h) \times \frac{n_{\alpha \beta}^{h+1} (\mathbf{r}_i, h)}{n_{\alpha \beta}^{h} (\mathbf{r}_i, h)} \, d\mathbf{r}_i. \]

Umitting integral part, the first order approximation to \( \phi^{\prime \prime} (\mathbf{r}_i) \) becomes,

\[ \phi^{\prime \prime}_0 (\mathbf{r}_i) = - kT \ln \frac{n_{\alpha \beta}^{h+1} (\mathbf{r}_i, h)}{n_{\alpha \beta}^{h} (\mathbf{r}_i, h)}, \]

Above equation, for number of molecules interacting equal to \( h=2 \), stands as,

\[ \phi^{\prime \prime}_0 (\mathbf{r}_i) = - kT \ln \frac{n_{\alpha \beta}^{2} (\mathbf{r}_i)}{n_{\alpha \beta}^{0} (\mathbf{r}_i)} = - kT \ln n_{\alpha \beta}^{0} (\mathbf{r}_i) \]

3.4 ACTUAL CALCULATION OF \( \phi (\mathbf{r}) \) FROM X-RAY DATA

Our interest rests in finding out the intermolecular potential energy, i.e., \( \phi (\mathbf{r}_{12}) \). Therefore, we have to start from the function \( n^{\prime \prime} (\mathbf{r}_{12}) \) which we take as to be
experimentally known. However, in each step of iteration, the
triplet distribution function $n'(r^3)$ is to be replaced by
an approximation. Hence, right at the start of calculation we
may assume superposition approximation, i.e.

$$n'(r^3) = \frac{n(\mathbf{r}_{12}) n(\mathbf{r}_{13}) n(\mathbf{r}_{23})}{n^3} \quad \ldots (3.4.1)$$

and a generalisation of the relation for $n'^{(h)}(r^h)$ whenever
$h > 3$. We have already referred that the assumptions at the
first stage are not critical provided they are closer to the
actual value because the method of iteration is a self-correcting
process. The function $n'^{(2)}(r^2)$ is connected with $g'^{(2)}(r)$ —
the radial distribution function. This $g'^{(2)}(r)$ can be computed
from X-ray diffraction data. Zernicke and Prince suggested
an expression relating the intensity of total coherent scattering
$I_{eu}(z)$ to $g'^{(2)}(r)$.

The relevant relation is,

$$I_{eu}(z) = N F^2(z) \left[ I - \int_0^\infty \left[ 1 - \frac{1}{2} \hat{g}^2(z) \right] \sin(z \mathbf{r}) \frac{1}{Z^2} 4 \pi Z^2 \mathbf{r} \mathbf{d} \mathbf{r} \right] \quad \ldots (3.4.2)$$

$I_{eu}(z)$ which is the total coherent intensity can be calculated
from the reduced intensity $i(Z)$ which is again the structurally
sensitive part of $I_{eu}(z)$. The required relation is,

$$i(Z) = I_{eu}(Z) - \sum_i F_i^2(Z) \quad \ldots (3.4.3)$$

Where $\sum_i F_i^2(Z)$ is the part of the scattering ascribable to
independent atoms and the sum is over Stoichiometric units.
The BGY equation can be written as thus.

\[ \phi(\mathbf{r}_{12}) = -kT \ln g'_{2}(\mathbf{r}_{12}) + \frac{4\pi}{\lambda} \int g'_{2}(s) \frac{d}{ds} \phi(s) \, ds \times \left( \mathbf{r}_{12} \cdot \mathbf{s} \right) \times \left[ g'_{2}(x) - 1 \right] \, dx \]  
\[ \ldots (3.4.6) \]
where, \[ \tau = \tau_1 - \tau_2 , \quad S = \tau_1 - \tau_3 , \quad t = \tau_2 - \tau_3 \quad \text{and} \quad x = \tau + \tau' \]

The Green's solution for \( g''(x) \) of BGY equation (3.4.6) which is applicable to liquid state was obtained by writing \( g''(x) \) approximately as,

\[
g''(x) \approx \exp \left[ -\frac{\phi(x)}{kT} \right] \left[ 1 + f(x) \right]
\]

\[
\approx 1 + \xi' \alpha(x) + f(x)
\]

where, \[ \alpha(x) = \exp \left[ -\frac{\phi(x)}{kT} \right] - 1 \]

and,

\[
f(x) = \frac{\exp[x]}{x^2} \int \frac{\phi'(s)}{s^2} \frac{d}{dx} \int \frac{1}{s^2 - t^2} \times
\]

\[\times \left[ g''(x) - 1 \right] \, dx \]

Green observed that \( f(x) \) is a quantity much smaller than unity. As \( \alpha'(x) \) and \( \alpha(x) \) are both negligible for small \( x \), so that when multiplied by these factors \( f(x) \) may be replaced by \( \xi' - 1 \), its average value in the neighbourhood of the origin. \( \xi' \) varies both with density and temperature. \( \xi' \) equals unity at low density and at high temperature. It is possible to get an explicit expression for \( \xi' \) in terms of density and temperature. From this, it becomes evident that its value may deviate quite largely from unity even at low temperature. On the other hand, it may be considered practically constant with respect to density \(^{119}, \, ^{120}\); substituting equation (3.4.7) in (3.4.8), \( t \, f(x) \)

becomes,

\[
\alpha \, f(x) = 2\pi \exp \left[ (t + \tau') \left( f(t + \tau') + \xi' \alpha(t + \tau') \right) \right] \, dt \, \xi' \alpha'(s) \, ds
\]

\[\ldots(3.4.9)\]
With the help of Fourier transformation, the above equation can be solved. Hence, we write,

\[ ZG(Z) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \hat{\phi}(\zeta) \sin(\zeta \omega) d\zeta \]  \hspace{1cm} \ldots(3.4.10)

\[ Z\beta(Z) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \hat{\phi}(\zeta) \sin(\zeta \omega) d\zeta \]  \hspace{1cm} \ldots(3.4.11)

So that equation (3.4.9) becomes,

\[ \lambda'G(Z) = \left[ G(Z) + \epsilon'\beta(Z) \right] \epsilon'\beta(Z) \]  \hspace{1cm} \ldots(3.4.12)

in which

\[ \lambda' = \frac{1}{\sqrt{(2\pi)^{3/2} \pi}} \]  \hspace{1cm} \ldots(3.4.13)

So, by Fourier inversion theorem,

\[ \hat{\phi}(\zeta) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{\epsilon^2 Z\beta(Z) \sin(Z \omega) \lambda' - \epsilon'\beta(Z)}{\lambda' - \epsilon'\beta(Z)} d\omega \]  \hspace{1cm} \ldots(3.4.13a)

Which is the general solution of equation (3.4.9). We get from equations (3.4.2) and (3.4.7),

\[ I_{\epsilon\omega}(Z) = NF^2(Z) \left[ 1 + 4\pi n/Z \right] \epsilon'\beta(Z) + G(Z) \]  \hspace{1cm} \ldots(3.4.14)
This we obtain when the Fourier transforms of $\mathcal{A}(\vec{r})$ and $f(\vec{r})$ are incorporated, and $E(z)$ is expressed in terms of $(\beta(z))$ from equation (3.4.12). As $I_{\text{eq}}(z)$ is known experimentally, $(\beta(z))$ can be calculated from the knowledge of $\varepsilon'$. Determination of $\varepsilon'$ for any type of interaction is in general quite difficult. For practical purpose one can put $\varepsilon' = 1$. We have accepted it as unity for our calculation at this stage of approximation. Hence, from knowing $(\beta(z))$ we can calculate $f(\vec{r})$ and hence the second approximation value of the pair potential $\phi(\vec{r})$, i.e.,

$$\phi(\vec{r}) = \phi_0(\vec{r}) + \alpha_1^{(2)}$$  

\hspace{1cm} ...(3.4.15)

where,

$$\alpha_1^{(2)} = \int (\vec{r} - \vec{s}) \frac{d}{d^3} \phi(\vec{s}) d\vec{s} \times
\int (\vec{s}^2 - \vec{r}^2) [\frac{g'((\vec{s}) - 1)] d\vec{s}$$  

\hspace{1cm} ...(3.4.16)

We have already referred that $f(\vec{r})$ can be evaluated from the intensity data alone. If we want to proceed to calculate the next contribution which arises in the second iterative step, we should only calculate $\alpha_2^{(2)}$ with the help of the formula already given in equation (3.3.18) for $h=2$. Further iterative steps may be carried out in the similar fashion but calculations become more and more difficult in each step of successive iteration.

3.5 WHAT WE HAVE DONE

The present calculation are meant up to the second iteration. We have taken a large no. of liquid metals and alloys at different temperatures and at normal atmospheric
pressure. The X-ray scattering data have been taken for elemental liquid metals Tl\textsuperscript{122}, Cd\textsuperscript{123}, Sn\textsuperscript{123}, In\textsuperscript{124}, Ag\textsuperscript{125}, Cu\textsuperscript{126}, Hg\textsuperscript{124}, Au\textsuperscript{127}, 128, Li\textsuperscript{129}, Na\textsuperscript{129}, K\textsuperscript{129}, Rb\textsuperscript{129}, Cs\textsuperscript{129}, Pb\textsuperscript{130} and Al\textsuperscript{131}, respectively and for alloy like Hg-In\textsuperscript{96}, Hg-Tl\textsuperscript{132}, Au-Sn\textsuperscript{127}, 128, Ag-Sn\textsuperscript{125} and Cu-Sn\textsuperscript{126} respectively.

The calculations are made in a computer in the University Service Instrumentation Centre, University of Kalyani, Kalyani (Nadia), West Bengal.

3.6 RESULTS AND DISCUSSION

We have used the preceding approach to calculate the interaction potential that exists between the liquid metal molecules at different temperatures. We have also determined the peak/trough positions at these temperatures. The latter data gives us - (a) the distance of the closest approach between two liquid metal molecules, and,

b) The distance at which the second and third layer of liquid metal molecules exist surrounding the given molecule.

The Fig. 1 first gives the radial distribution curve of the alkali metals taken from N.S. Gingrich and Le Roy Heaton\textsuperscript{110}. The Fig. 2 shows the first iteration results (for $\phi_0$) and the second iteration results (for $\phi_1$) for the alkali metals (Li, Na, K, Rb, Cs)\textsuperscript{110,134} at their melting temperatures. In the figures 3 to 13 (---) represents the first iteration results (for $\phi_0$) corresponding to the liquid metals Tl\textsuperscript{122} (at 700°C
and 350°C) Cd\textsuperscript{123} (at 650°C and 350°C) Sn\textsuperscript{123} (at 1100°C, and 250°C) In\textsuperscript{124} (at 650°C and 170°C), Ag\textsuperscript{125} (at 961°C), Cu\textsuperscript{126} (at 1083°C), Hg\textsuperscript{124} (at 25°C)\textsuperscript{23}, Pb\textsuperscript{130} (at 350°C), Ga\textsuperscript{133} (at 150°C), and Al\textsuperscript{131} (at 700°C) respectively. In the figures 3 to 13 (.....) show the second iteration results $\phi_i$ for these metals.

Table (3.6.1) and (3.6.2) show the closest distances of approach and the co-ordination number for different metals and alloys (at different % compositions) and the depth of the potentials (as obtained from graphs).

**TABLE - 3.6.1**

<table>
<thead>
<tr>
<th>Metals studied</th>
<th>Temp. (°C)</th>
<th>Closest distances of approach (Å)</th>
<th>Co-ordination No. (Å)</th>
<th>Depth of potential (e.v.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl</td>
<td>700</td>
<td>3.30</td>
<td>8.0</td>
<td>-.07</td>
</tr>
<tr>
<td>&quot;</td>
<td>350</td>
<td>3.31</td>
<td></td>
<td>-.0475</td>
</tr>
<tr>
<td>Cd</td>
<td>650</td>
<td>3</td>
<td>8.3</td>
<td>-.057</td>
</tr>
<tr>
<td>&quot;</td>
<td>350</td>
<td>3.03</td>
<td></td>
<td>-.045</td>
</tr>
<tr>
<td>Sn</td>
<td>1100</td>
<td>3.125</td>
<td></td>
<td>-.08</td>
</tr>
<tr>
<td>&quot;</td>
<td>250</td>
<td>3.126</td>
<td>8.5</td>
<td>-.045</td>
</tr>
<tr>
<td>&quot;</td>
<td>232</td>
<td>3.15</td>
<td></td>
<td>-.06969</td>
</tr>
<tr>
<td>In</td>
<td>650</td>
<td>3.23</td>
<td>8.0</td>
<td>-.059</td>
</tr>
<tr>
<td>&quot;</td>
<td>170</td>
<td>3.24</td>
<td></td>
<td>-.035</td>
</tr>
<tr>
<td>Ag</td>
<td>961</td>
<td>2.8</td>
<td>10.0</td>
<td>-.10489</td>
</tr>
<tr>
<td>Cu</td>
<td>1083</td>
<td>2.4</td>
<td>11.5</td>
<td>-.11607</td>
</tr>
<tr>
<td>Hg</td>
<td>25</td>
<td>2.9</td>
<td>10.0</td>
<td>-.0279</td>
</tr>
<tr>
<td>Au</td>
<td>1063</td>
<td>2.83</td>
<td>8.5</td>
<td>-.19372</td>
</tr>
</tbody>
</table>
### TABLE 3.6.1 contd ...

<table>
<thead>
<tr>
<th>Metals studied</th>
<th>Temp. (°C)</th>
<th>Closest distance of approach (Å)</th>
<th>Co-ordination no. (Å)</th>
<th>Depth of potential (e.v.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>180</td>
<td>3.5</td>
<td>9.5</td>
<td>-0.0391</td>
</tr>
<tr>
<td>Na</td>
<td>114</td>
<td>3.55</td>
<td>9.5</td>
<td>-0.05</td>
</tr>
<tr>
<td>K</td>
<td>70</td>
<td>4.57</td>
<td>9.5</td>
<td>-0.051</td>
</tr>
<tr>
<td>Rb</td>
<td>40</td>
<td>5.2</td>
<td>9.5</td>
<td>-0.036</td>
</tr>
<tr>
<td>Cs</td>
<td>30</td>
<td>5.25</td>
<td>9.0</td>
<td>-0.06</td>
</tr>
<tr>
<td>Pb</td>
<td>3.40</td>
<td>8.0</td>
<td>-</td>
<td>-0.105</td>
</tr>
<tr>
<td>*Ga</td>
<td>150</td>
<td>1.94</td>
<td>-</td>
<td>-0.02</td>
</tr>
<tr>
<td>*Al</td>
<td></td>
<td>2.57</td>
<td>10.6</td>
<td>-0.075</td>
</tr>
</tbody>
</table>

Table 3.6.2 shows the closest distances of approach, depth of potentials at different temperatures for the alloy system Au-Sn, Ag-Sn, Cu-Sn, Hg-Tl, Hg-In.

### TABLE 3.6.2

<table>
<thead>
<tr>
<th>Alloy studied</th>
<th>Composition</th>
<th>Temp. (°C)</th>
<th>Closest distance of approach</th>
<th>Depth of potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-Sn alloy</td>
<td>Pure Sn</td>
<td>232</td>
<td>3.125</td>
<td>-0.06969 e.v.</td>
</tr>
<tr>
<td></td>
<td>Sn (80%)</td>
<td>220</td>
<td>2.94</td>
<td>-0.0493 e.v.</td>
</tr>
<tr>
<td></td>
<td>Sn (67%)</td>
<td>252</td>
<td>2.81</td>
<td>-0.063 e.v.</td>
</tr>
<tr>
<td></td>
<td>Sn (50%)</td>
<td>290</td>
<td>2.0</td>
<td>-0.076 e.v.</td>
</tr>
<tr>
<td></td>
<td>Sn (30%)</td>
<td>500</td>
<td>2.875</td>
<td>-0.10822 e.v.</td>
</tr>
<tr>
<td></td>
<td>Pure Au</td>
<td>1063</td>
<td>2.83</td>
<td>-0.19372 e.v.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Contd...</td>
</tr>
</tbody>
</table>
Table 3.6.2 contd...

<table>
<thead>
<tr>
<th>Alloy Studied</th>
<th>Composition</th>
<th>Temp (°C)</th>
<th>Closest distances of approach (Å)</th>
<th>Depth of potential (e.v.)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ag-Sn alloys</strong></td>
<td>Pure Sn</td>
<td>232</td>
<td>3.125</td>
<td>-.06969 e.v.</td>
</tr>
<tr>
<td></td>
<td>Sn (68.5%)</td>
<td>245</td>
<td>3.08</td>
<td>-.03278 e.v.</td>
</tr>
<tr>
<td></td>
<td>Sn (50%)</td>
<td>400</td>
<td>2.98</td>
<td>-.04811 e.v.</td>
</tr>
<tr>
<td></td>
<td>Sn (36.5%)</td>
<td>750</td>
<td>2.97</td>
<td>-.0728 e.v.</td>
</tr>
<tr>
<td></td>
<td>Sn (36.5%)</td>
<td>750</td>
<td>2.97</td>
<td>-.07995 e.v.</td>
</tr>
<tr>
<td></td>
<td>Sn (18.5%)</td>
<td>910</td>
<td>2.97</td>
<td>-.0893 e.v.</td>
</tr>
<tr>
<td></td>
<td>Pure Ag.</td>
<td>961</td>
<td>2.8</td>
<td>-.10409 e.v.</td>
</tr>
<tr>
<td><strong>Hg-Tl alloy</strong></td>
<td>Pure Hg</td>
<td>25</td>
<td>2.9</td>
<td>-.0279</td>
</tr>
<tr>
<td></td>
<td>Tl (5%)</td>
<td>25</td>
<td>3.0</td>
<td>-.0274</td>
</tr>
<tr>
<td></td>
<td>Tl (8.5%)</td>
<td>25</td>
<td>3.1</td>
<td>-.0189</td>
</tr>
<tr>
<td></td>
<td>Tl (16%)</td>
<td>25</td>
<td>3.11</td>
<td>-.02586</td>
</tr>
<tr>
<td></td>
<td>Tl (28.6%)</td>
<td>25</td>
<td>3.2</td>
<td>-.026</td>
</tr>
<tr>
<td></td>
<td>Tl (40%)</td>
<td>25</td>
<td>3.28</td>
<td>-.0248</td>
</tr>
<tr>
<td><strong>Cu-Sn alloy</strong></td>
<td>Pure Sn</td>
<td>232</td>
<td>3.125</td>
<td>-.06969</td>
</tr>
<tr>
<td></td>
<td>Sn (78%)</td>
<td>480</td>
<td>3.1</td>
<td>-.0494</td>
</tr>
<tr>
<td></td>
<td>Sn (55%)</td>
<td>620</td>
<td>3</td>
<td>-.03192</td>
</tr>
<tr>
<td></td>
<td>Sn (45%)</td>
<td>680</td>
<td>2.73</td>
<td>-.062116</td>
</tr>
<tr>
<td></td>
<td>Sn (35%)</td>
<td>735</td>
<td>2.7</td>
<td>-.0762</td>
</tr>
<tr>
<td></td>
<td>Sn (20%)</td>
<td>850</td>
<td>2.7</td>
<td>-.09</td>
</tr>
<tr>
<td></td>
<td>Pure Cu</td>
<td>1083</td>
<td>2.4</td>
<td>-.116</td>
</tr>
</tbody>
</table>

Contd...
<table>
<thead>
<tr>
<th>Alloy studied</th>
<th>Composition</th>
<th>Temp. (°C)</th>
<th>Closest distances of approach (Å)</th>
<th>Depth of potential (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg-In alloy</td>
<td>Pure Hg</td>
<td>25</td>
<td>2.9</td>
<td>-0.0279</td>
</tr>
<tr>
<td></td>
<td>In (5%)</td>
<td>25</td>
<td>3.06</td>
<td>-0.028156</td>
</tr>
<tr>
<td></td>
<td>In (12%)</td>
<td>25</td>
<td>3</td>
<td>-0.0288</td>
</tr>
<tr>
<td></td>
<td>In (35%)</td>
<td>25</td>
<td>3.09</td>
<td>-0.0287</td>
</tr>
<tr>
<td></td>
<td>In (42%)</td>
<td>25</td>
<td>3.1</td>
<td>-0.028</td>
</tr>
<tr>
<td></td>
<td>In (50%)</td>
<td>25</td>
<td>3.105</td>
<td>-0.0273</td>
</tr>
<tr>
<td></td>
<td>In (62%)</td>
<td>25</td>
<td>3.1</td>
<td>-0.02819</td>
</tr>
<tr>
<td></td>
<td>Pure In</td>
<td>170</td>
<td>3.1</td>
<td>-0.0394</td>
</tr>
</tbody>
</table>

Figures 14 to 18 represent the potential energy functions for the alloys Au-Sn, Ag-Sn, Cu-Sn, Hg-Tl and Hg-In for different compositions and at different temperatures. (---) signifies first iteration results and (----) signifies second iteration results.

Figures 19 to 22 show the change of the closest distance of approach with composition for different alloys. These figures illustrate the deviation from general additivity principle.

The striking features of these potential energy functions are the damped oscillatory nature. This long-range oscillatory nature was noticed by Johnson et al.\textsuperscript{134} and Sengupta et al.\textsuperscript{135} in their previous studies and can be explained by considering the partial screening of the Fermi energy\textsuperscript{142}.  

\textsuperscript{134} Johnson et al.
\textsuperscript{135} Sengupta et al.
\textsuperscript{142} Fermi energy
FIGURE 1

ATOMIC DISTRIBUTIONS OF LIQUID ALKALI METALS NEAR MELTING TEMPERATURES

\[4 \pi r^2 \rho(r)\]

\[r(\text{Å})\]

Li (180°C)
Na (100°C)
K (65°C)
Rb (40°C)
Cs (20°C)
CASE STUDY: Na (at 114°C)

FIG. 2

Potential energy (eV.) vs. r (Å)

(---) for 1st iteration
(----) for 2nd iteration

FIG. 2
CASE STUDY: Li (at 180°C)

Potential energy (eV)

Potential energy (eV)

r(Å)

(—–) for 1st iteration
(—–—–) for 2nd iteration

FIG. 2
CASE STUDY: K (at 70°C)

Potential energy (eV)

r (Å)

(-----) for 1st iteration
(-.-.-.-) for 2nd iteration

FIG. 2
CASE STUDY: Cs (at 30°C)

Potential energy (e.v.)

--- for 1st iteration
----- for 2nd iteration

FIG. 2
FIG. 3

1 is for Tl at 350°C
2 is for Tl at 700°C
1′ & 2′ represent 2nd iteration results
FIG. 4

1 is for Cd at 350°C
2 is for Cd at 650°C
1' & 2' represent 2nd iteration results
CASE STUDY: Sn at 1100°C

1 is for Sn at 1100°C (1st iteration)

V represents 2nd iteration results

1' represents 2nd iteration results

FIG 5
CASE STUDY: Sn at 250°C

Potential energy (e.v.)

r (Å)

1 is for Sn at 250°C (1st iteration)
1' represents 2nd iteration results

FIG. 5
$1$ is for In at $170^\circ C$ 1st iteration
$2$ is for In at $650^\circ C$ 1st iteration
$1'$ & $2'$ represent 2nd iteration results
CASE STUDY: PURE Ag (1234 Å)
(-) for 1st. iteration
(----) for 2nd. iteration

FIG. 7

Potential energy (eV)

r (Å)
CASE STUDY: PURE Cu$(1083^\circ C)$

(- - -) represents 1st iteration

(----) represents 2nd iteration
CASE STUDY: PURE Hg (at 25°C)

For first iteration

For second iteration

Figure 9

Potential energy (eV)

Distance (Å)
CASE STUDY: Pb (350°C)

Potential energy (e.v.)

r(Å)

(—) for 1st iteration
(---) for 2nd iteration

FIG. 10
CASE STUDY: Ga (150°C)

[Derived by Ascarelli from PY theory. Ascarelli - Phys. Rev. 143, 36-47, 1966]

FIG. 11
CASE STUDY: Al (700°C)

Potential energy (eV)

r (Å)

(---) for 1st iteration
(-----) for 2nd iteration

FIG. 12
CASE STUDY: Au-Sn alloys

FIG. 15

1 is for Pure Sn (232°C), 1st iteration
2 is for 80% Sn (220°C), 1 & 2, represent 2nd iteration results

Potential energy (eV)
CASE STUDY: Au-Sn alloys

1st iteration is for 50% Sn (563 Å)
2nd iteration is for 30% Sn (773 Å).

y & 2 represent 2nd iteration results.

FIG 14

Potential energy (eV) vs. r (Å)

1 is for 50% Sn (563 Å)
2 is for 30% Sn (773 Å)

1' & 2' represent 2nd iteration results.
CASE STUDY: Ag-Sn alloys

1 is for 18.5% Sn (1183 Å)
2 is for Pure Ag (1234 Å)
1' & 2' represent 2nd iteration results

FIG. 15
CASE STUDY: Ag - Sn alloys

Potential energy (e.v.)

-0.090 -0.075 -0.05 -0.025 0 0.025 0.05

r (Å)

1 is for 36.5% Sn (1023 Å)
2 is for 25% Sn (1123 Å)
1' & 2' represent 1st iteration results

FIG 15 a
CASE STUDY: Ag - Sn alloys

FIG. 15b

1 is for 68.5% Sn (518 Å)
2 is for 50% Sn (673 Å)
1' & 2', represent 2nd iteration results
CASE STUDY: Cu-Sn alloys

1 is for 55% Sn (893 Å)
2 is for 78% Sn (753 Å)
1' & 2' represent 2nd iteration results

Potential energy (e.v.)

r (Å)

1 is for 55% Sn (893 Å)
2 is for 78% Sn (753 Å)
1' & 2' represent 2nd iteration results

FIG 16
CASE STUDY: Cu-Sn alloy

1 is for 45% Sn (at 953 Å) 1st iteration
2 is for 35% Sn (at 1008 Å)
1' & 2' represent 2nd iteration results
CASE STUDY: Hg-Tl alloys

1 is for Pure Hg (25°C)
2 is for 40% Tl (25°C)

1' & 2' represent 2nd iteration results
CASE STUDY: Hg-Tl alloy

Potential energy (e.v.)

1 is for 5% Tl (25°C)
2 is for 8.5% Tl (25°C)
1' & 2' represent 2nd iteration results

FIG. 17a
CASE STUDY: Hg-Tl alloys

1 is for Tl 28% (25°C) 
2 is for Tl 16% (25°C)

1' & 2' represent 2nd iteration results

FIG. 17.b
CASE STUDY Hg-In alloy

1 is for 12% In
2 is for 5% In
1' & 2' represent 1st iteration res

TEMP. 25°C

FIG 18
CASE STUDY: Hg-In alloys

1 is for 62% In (25°C)
2 is for 50% In (25°C)
1' & 2' represent 2nd iteration results

Fig. 16a
CASE STUDY: Hg-In alloys

1 is for 42% In; 2 is for 35% In; TEMP. 25°C; 1' & 2' represent 1st iteration results

FIG. 18b
Cu - Sn alloys

 FIG. 19
FIG. 20

The diagram illustrates the variation of a parameter (labeled as \( \epsilon \)) measured in Ångströms (Å) as a function of at\% Mg. The graph shows four distinct curves for different alloy systems:
- Pb-Mg
- Sn-Mg
- Al-Mg
- Ag-Mg

Each curve represents a specific alloy system, and the x-axis indicates the at\% content of Mg.
Au - Sn alloys

FIG. 21
Ag - Sn alloys

FIG. 22
3.7 THE PROPOSED ANALYTICAL EXPRESSION FOR EFFECTIVE INTERMOLECULAR POTENTIAL ENERGY

We have shown that the effective intermolecular potential energy function in an assembly of molecules is a complicated temperature dependent damped oscillatory function. We have shown in the page (page no. 110) this temperature dependency arises through the averaging individual pair-potentials with respect to other molecules present in the system. Our results for the potential energy obtained through the iterations are represented in the figures 1 to 18.

In theoretical calculations such numerical tabulations are not very convenient. The damped oscillatory curves show the behavior of a distorted charge distribution around an ion. This may be similar to the Friedel oscillation. So it will be very useful if we can represent the curves by some analytical function.

March et al. thought that \( \Phi (\mathbf{r}) \) may be represented as,

\[
\Phi(\mathbf{r}) = \exp \left[ -\alpha_n |\mathbf{r}| \right] \frac{1}{K^3} \cos (-2K|\mathbf{r}|) \quad \ldots (3.7.1)
\]

Where \( \alpha_n \) and \( K \) are constants. Theoretical justification of the above type of analytical expression is possible. We argue as follows:

Replacing,

\[
\mathbf{g}^2(\mathbf{r}) = \exp \left[ -\Phi(\mathbf{r})/KT \right] U(\mathbf{r}) \quad \ldots (3.7.2)
\]

and,

\[
U(\mathbf{r}) = e^{\mathbf{f}(\mathbf{r})} = 1 + f(\mathbf{r}) \quad \text{neglecting higher orders of } f(\mathbf{r}) \]

which is defined in equation (3.4.8), Green solved the equation.
(3.4.6) and found that \(f(\vec{r})\) is an odd function in \(\vec{r}\) of the form, \(A \vec{r} + B \vec{r}^3 + \ldots\). So, one can expand \(U(\vec{r})\) as follows:
\[
U(\vec{r}) = U(0) \left[ 1 + C \vec{r}^2 + \cdots \right]
\]
\(\ldots (3.7.3)\)

Correspondingly, \(\varphi(\vec{r}) = U(0) \exp \left[ -\phi(\vec{r})/kT \right] \left[ 1 + C \vec{r}^2 + \cdots \right] \)
\(\ldots (3.7.4)\)

For large values of Bogolyubov assumed,
\[
U(\vec{r}) = 1 + \frac{\phi(\vec{r})}{\vec{r}}
\]
\(\ldots (3.7.5)\)

This assumption was made on the basis that \(\phi(\vec{r})\) has a short range character and the values of \(\vec{r}\) exceed the radius of action of intermolecular force. Then as \(\vec{r}\) tends to \(\infty\), \(U(\vec{r})\) tends to unity. With these assumptions Bogolyubov solved eqn. (3.4.6) and found that,
\[
\varphi(\vec{r}) = 1 + \frac{1}{\vec{r}} \sum A_n \exp \left[ -|\alpha_n| \vec{r} \right] \cos \left[ B_n \vec{r} + \delta_n \right]
\]
\(\ldots (3.7.6)\)

Where, \(A_n, B_n\), and \(\delta_n\) are undetermined quantities in this approximation. With equation (3.7.6) and (3.7.2) we get,
\[
\exp \left[ -\phi(\vec{r})/kT \right] U(\vec{r}) = 1 + \frac{1}{\vec{r}} \sum A_n \exp \left[ -|\alpha_n| \vec{r} \right] \cos \left[ B_n \vec{r} + \delta_n \right]
\]
\(\ldots (3.7.7)\)

For large value of \(\vec{r}\), \(\exp \left[ -\phi(\vec{r})/kT \right] \) can be replaced by unity. So the equation (3.7.7) can be written restricting to the first term,
\[
\phi(\vec{r}) = A_i \exp \left[ -|\alpha_i| \vec{r} \right] \cos \left( B_i \vec{r} + \delta_i \right)
\]
\(\ldots (3.7.8)\)
This equation (3.7.8) can be reduced to the equation (3.7.1) if we put the undetermined quantities, \( A_j = \frac{1}{r^3} \), \( B_j = -2K \) and \( \delta_j = 0 \). The replacement of \( A \) by \( \frac{1}{r^3} \) may be justified by the fact that for damped oscillation the amplitude of oscillation should diminish gradually as \( r \) increases.

Torra et al.\(^{139}\) suggested the following expression,

\[
\phi(\frac{r}{\rho}) = \frac{A_{\rho_0}^3}{\rho^3} \exp\left[-\alpha \frac{r}{\rho}\right] \cos\left[2K(B + \frac{r}{\rho})\right] \quad (3.7.9)
\]

of potential energy function for liquid lead metal at 397°C, where, \( A_{\rho_0}^3 \), \( K \), \( \alpha \) and \( B \) are constants. The values of these constants at 397°C are \( A_{\rho_0}^3 = 2.92 \) e.v. \( \frac{A}{\rho} \), \( K = 9.80 \frac{A}{\rho} \), \( B = 1.31 \frac{A}{\rho} \) and \( \alpha = -0.11 \frac{A}{\rho} \). They found that their result agrees well with the experiment.

None of the solutions above fit the calculated results. By trial and error method, we have seen that the potential energy expression for the liquid metals and binary alloys may be represented as:

\[
\phi(\frac{r}{\rho}) = \frac{A}{\rho} \exp\left[-\alpha \frac{r}{\rho}\right] \cos 2K(B + \frac{r}{\rho}) \quad (3.7.10)
\]

as before \( A \), \( \alpha \), \( B \) & \( K \) are the four parameters.

The best values for the 4 parameters of the alkali metals are given in Table (3.7.1). For other metals—Table (3.7.2) shows the result.

Table 3.7.3 gives effective hard sphere diameters of some liquid metals and alloys.
TABLE - 3.7.1 [Considering equation (3.7.9)]

<table>
<thead>
<tr>
<th>A (e.v.)</th>
<th>( \alpha (A^{-1}) )</th>
<th>B (( \AA ))</th>
<th>K (( A^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.081</td>
<td>1.65</td>
<td>1.06</td>
</tr>
<tr>
<td>Na</td>
<td>0.066</td>
<td>2.45</td>
<td>1.05</td>
</tr>
<tr>
<td>K</td>
<td>0.061</td>
<td>2.75</td>
<td>0.86</td>
</tr>
<tr>
<td>Rb</td>
<td>0.053</td>
<td>3.50</td>
<td>0.81</td>
</tr>
<tr>
<td>Cs</td>
<td>0.075</td>
<td>3.10</td>
<td>0.71</td>
</tr>
</tbody>
</table>

TABLE - 3.7.2 [Considering equation (3.7.10)]

<table>
<thead>
<tr>
<th>(Temp. °C)</th>
<th>A (e.v.( \AA / ^{0} \K))</th>
<th>( \alpha (A^{-1}) )</th>
<th>B (( \AA ))</th>
<th>K (( A^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TI</td>
<td>700</td>
<td>0.68</td>
<td>0.37</td>
<td>-1.94</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>0.38</td>
<td>0.2689</td>
<td>-1.94</td>
</tr>
<tr>
<td>Cd</td>
<td>650</td>
<td>0.977</td>
<td>0.5854</td>
<td>-1.94</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>0.4969</td>
<td>0.4216</td>
<td>-1.94</td>
</tr>
<tr>
<td>Sn</td>
<td>1100</td>
<td>2.478</td>
<td>0.7344</td>
<td>-1.94</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>1.259</td>
<td>0.691</td>
<td>-1.94</td>
</tr>
<tr>
<td>In</td>
<td>650</td>
<td>5.704</td>
<td>1.042</td>
<td>-1.94</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>0.7921</td>
<td>0.6023</td>
<td>-1.94</td>
</tr>
</tbody>
</table>

Contd...
<table>
<thead>
<tr>
<th></th>
<th>(Temp. °C)</th>
<th>A (e.v.°K)</th>
<th>α (°K⁻¹)</th>
<th>β (°K⁻¹)</th>
<th>K (°K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Au-Sn Alloys:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure Sn</td>
<td>232</td>
<td>1.26</td>
<td>1.26</td>
<td>-1.93</td>
<td>1.52</td>
</tr>
<tr>
<td>Sn (80%)</td>
<td>220</td>
<td>0.00045</td>
<td>1.145</td>
<td>-1.94</td>
<td>1.524</td>
</tr>
<tr>
<td>Sn (67%)</td>
<td>252</td>
<td>0.00078</td>
<td>2.998</td>
<td>-1.94</td>
<td>1.524</td>
</tr>
<tr>
<td>Sn (50%)</td>
<td>290</td>
<td>0.0019</td>
<td>5.792</td>
<td>-1.94</td>
<td>1.524</td>
</tr>
<tr>
<td>Sn (30%)</td>
<td>500</td>
<td>0.00049</td>
<td>0.07</td>
<td>-1.94</td>
<td>1.524</td>
</tr>
<tr>
<td><strong>Ag-Sn Alloys:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure Sn</td>
<td>232</td>
<td>1.26</td>
<td>0.699</td>
<td>-1.93</td>
<td>1.52</td>
</tr>
<tr>
<td>Sn (68.5%)</td>
<td>245</td>
<td>0.00131</td>
<td>6.186</td>
<td>-1.94</td>
<td>1.524</td>
</tr>
<tr>
<td>Sn (50%)</td>
<td>400</td>
<td>0.00139</td>
<td>0.63</td>
<td>-1.94</td>
<td>1.524</td>
</tr>
<tr>
<td>Sn (36.5%)</td>
<td>800</td>
<td>0.00183</td>
<td>7.27</td>
<td>-1.94</td>
<td>1.524</td>
</tr>
<tr>
<td>Sn (25%)</td>
<td>900</td>
<td>0.000485</td>
<td>0.28</td>
<td>-1.94</td>
<td>1.524</td>
</tr>
<tr>
<td>Sn (18.5%)</td>
<td>960</td>
<td>0.00112</td>
<td>0.54</td>
<td>-1.94</td>
<td>1.524</td>
</tr>
<tr>
<td>Pure Ag</td>
<td>961</td>
<td>0.00082</td>
<td>0.44</td>
<td>-1.94</td>
<td>1.524</td>
</tr>
<tr>
<td><strong>Cu-Sn Alloys:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure Sn</td>
<td>232</td>
<td>1.26</td>
<td>0.699</td>
<td>-1.93</td>
<td>1.52</td>
</tr>
<tr>
<td>Sn (78%)</td>
<td>480</td>
<td>0.00427</td>
<td>0.98</td>
<td>-1.94</td>
<td>1.524</td>
</tr>
<tr>
<td>Sn (55%)</td>
<td>620</td>
<td>0.000193</td>
<td>0.196</td>
<td>-1.94</td>
<td>1.524</td>
</tr>
<tr>
<td>Sn (45%)</td>
<td>680</td>
<td>0.0034</td>
<td>2.09</td>
<td>-1.94</td>
<td>1.524</td>
</tr>
<tr>
<td>Sn (35%)</td>
<td>735</td>
<td>0.00104</td>
<td>0.603</td>
<td>-1.94</td>
<td>1.524</td>
</tr>
<tr>
<td>Sn (20%)</td>
<td>850</td>
<td>0.000489</td>
<td>0.294</td>
<td>-1.94</td>
<td>1.524</td>
</tr>
<tr>
<td>Pure Cu</td>
<td>1083</td>
<td>0.0002915</td>
<td>1.457</td>
<td>-1.94</td>
<td>1.524</td>
</tr>
</tbody>
</table>
### TABLE 3.7.3
(Effective hard sphere diameters of some liquid metals and alloys)

<table>
<thead>
<tr>
<th>Metals/Alloys studied</th>
<th>Temperature (°C)</th>
<th>$R^*(\text{Å}) =$ Minimum distance of approach</th>
<th>$\phi$ effective (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl</td>
<td>700</td>
<td>3.3</td>
<td>3.19</td>
</tr>
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<td></td>
<td>350</td>
<td>3.31</td>
<td>3.23</td>
</tr>
<tr>
<td>Cd</td>
<td>650</td>
<td>3.125</td>
<td>2.09</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>3.126</td>
<td>2.8</td>
</tr>
<tr>
<td>Sn</td>
<td>1100</td>
<td>2.76</td>
<td></td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>650</td>
<td>3.23</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>3.24</td>
<td>3.04</td>
</tr>
<tr>
<td>Li</td>
<td>180</td>
<td>3.15</td>
<td>3.11</td>
</tr>
<tr>
<td>Na</td>
<td>100</td>
<td>3.82</td>
<td>3.65</td>
</tr>
<tr>
<td>K</td>
<td>65</td>
<td>4.64</td>
<td>4.55</td>
</tr>
<tr>
<td>Rb</td>
<td>40</td>
<td>4.97</td>
<td>4.82</td>
</tr>
<tr>
<td>Cs</td>
<td>30</td>
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<td>5.20</td>
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<tr>
<td><strong>Au-Sn Alloys</strong></td>
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<td></td>
</tr>
<tr>
<td>Pure Sn</td>
<td>232</td>
<td>3.125</td>
<td>2.7</td>
</tr>
<tr>
<td>Sn (80%)</td>
<td>220</td>
<td>2.94</td>
<td>2.66</td>
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<tr>
<td>Sn (67%)</td>
<td>252</td>
<td>2.81</td>
<td>2.63</td>
</tr>
<tr>
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<td>2.82</td>
<td>2.63</td>
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<td><strong>Ag-Sn Alloys</strong></td>
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<td></td>
</tr>
<tr>
<td>Pure - Sn</td>
<td>232</td>
<td>3.125</td>
<td>2.7</td>
</tr>
<tr>
<td>Sn (68.5%)</td>
<td>245</td>
<td>3.08</td>
<td>2.81</td>
</tr>
<tr>
<td>Sn (50%)</td>
<td>400</td>
<td>2.96</td>
<td>2.8</td>
</tr>
<tr>
<td>Sn (36.5%)</td>
<td>800</td>
<td>2.97</td>
<td>2.8</td>
</tr>
<tr>
<td>Sn (25%)</td>
<td>900</td>
<td>2.97</td>
<td>2.75</td>
</tr>
<tr>
<td>Sn (18.5%)</td>
<td>960</td>
<td>2.97</td>
<td>2.78</td>
</tr>
<tr>
<td>Pure - Ag</td>
<td>961</td>
<td>2.8</td>
<td>2.75</td>
</tr>
</tbody>
</table>

Contd...
TABLE - 3.7.3
(Effective hard sphere diameters of some liquid metals and alloys)

<table>
<thead>
<tr>
<th>Metals/Alloys studied</th>
<th>Temperature (°C)</th>
<th>$R^*(A^0)$ = Minimum distance of approach</th>
<th>$\sigma$ effective (A°)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cu-Sn Alloys:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure Sn</td>
<td>232</td>
<td>3.125</td>
<td>2.7</td>
</tr>
<tr>
<td>Sn (78%)</td>
<td>480</td>
<td>3.1</td>
<td>2.68</td>
</tr>
<tr>
<td>Sn (55%)</td>
<td>620</td>
<td>3</td>
<td>2.65</td>
</tr>
<tr>
<td>Sn (45%)</td>
<td>680</td>
<td>2.73</td>
<td>2.62</td>
</tr>
<tr>
<td>Sn (35%)</td>
<td>735</td>
<td>2.7</td>
<td>2.59</td>
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<tr>
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<td>850</td>
<td>2.7</td>
<td>2.58</td>
</tr>
<tr>
<td>Pure Cu</td>
<td>1083</td>
<td>2.4</td>
<td>2.37</td>
</tr>
<tr>
<td><strong>Hg-Tl Alloys:</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Pure Hg</td>
<td>25</td>
<td>2.9</td>
<td>2.3</td>
</tr>
<tr>
<td>Tl (5%)</td>
<td>25</td>
<td>3</td>
<td>2.87</td>
</tr>
<tr>
<td>Tl (8.5%)</td>
<td>25</td>
<td>3.1</td>
<td>2.89</td>
</tr>
<tr>
<td>Tl (16%)</td>
<td>25</td>
<td>3.11</td>
<td>2.89</td>
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<td>Tl (28.6%)</td>
<td>25</td>
<td>3.2</td>
<td>2.9</td>
</tr>
<tr>
<td>Tl (40%)</td>
<td>25</td>
<td>3.28</td>
<td>2.97</td>
</tr>
<tr>
<td>Pure Tl</td>
<td>350</td>
<td>3.29</td>
<td>2.97</td>
</tr>
<tr>
<td><strong>Hg-In Alloys:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure Hg</td>
<td>25</td>
<td>2.9</td>
<td>2.3</td>
</tr>
<tr>
<td>In (5%)</td>
<td>25</td>
<td>3.06</td>
<td>2.8</td>
</tr>
<tr>
<td>In (12%)</td>
<td>25</td>
<td>3</td>
<td>2.9</td>
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<td>In (35%)</td>
<td>25</td>
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<td>In (42%)</td>
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<td>In (50%)</td>
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<td>2.81</td>
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<tr>
<td>In (62%)</td>
<td>25</td>
<td>3.11</td>
<td>2.9</td>
</tr>
<tr>
<td>Pure In</td>
<td>170</td>
<td>3.1</td>
<td>2.88</td>
</tr>
</tbody>
</table>
3.8 THE GENERAL INTERPRETATION IN TERMS OF THE INCOMPLETE SCREENING IN LIQUID METALS

Johnson & March\textsuperscript{140} (1963) pointed out that the damped oscillations are clearly coming from the incomplete screening of the metal ions by the conduction electrons. March\textsuperscript{112} considered that the liquid metals consist of ions of charge $Z |e|$ ($|e|$ = the electronic charge) and $N$ conduction electrons. March\textsuperscript{141} assumed:

(1) the conduction electrons form an ideal quantum gas which obeys Fermi-Dirac Statistics & completely degenerate, (2) The ions are point charges and their potential is given by $\frac{Ze}{r}$ if conduction electrons are absent. The basic physical core of the problem is the evaluation of the shielding effect which the modified electron distribution generates the Coulomb potential of the ions. The shielding effect can be calculated according to the semi-classical method which is essentially the Thomas-Fermi method\textsuperscript{142}. If the co-ordinate origin is selected at the ion, then the potential energy of an electron at the point $r$ becomes:

$$\phi(r) = -\frac{Ze^2}{r} + \phi^{(e)}(r) \quad \ldots (3.8.1)$$

Where, $\phi^{(e)}$ is the potential energy produced by the change in the electron distribution. In order to be able to apply this approximation, one must consequently require that $\phi(r)$ is a function that is slowly varying in space. This is equivalent to saying that $\phi(r)$ undergoes only small changes over characteristic lengths (in our case the de Broglie wavelength of electrons at the Fermi surface is $\frac{2\pi}{K_F}$). With this assumption we immediately
obtain the electron density at the point \( r \) (\( p_f = \text{max.} \) momentum, \( k_f = \text{wave no.} \)),

\[
\mathcal{Q}^e(\mathbf{r}) = \frac{8\pi}{3\hbar^3} |\mathbf{p}_f|^3(\mathbf{r})
\]

...(3.8.2)

The Fermi energy must remain constant and therefore,

\[
\varepsilon_F = \frac{\mathbf{p}_f^2(\mathbf{r})}{2m} + \phi(\mathbf{r})
\]

...(3.8.3)

So, from above two equations we obtain Thomas-Fermi equation,

\[
\mathcal{Q}^{(e)}(\mathbf{r}) = \frac{8\pi}{3\hbar^3} (2m)^{3/2} \left[ \varepsilon_F - \phi(\mathbf{r}) \right]^{3/2}
\]

...(3.8.4)

The local change in the electron density (polarization) is, therefore, given by the equation,

\[
\mathcal{Q}^{(e)} (\mathbf{r}) - \mathcal{Q}^{(e)}_0 = \frac{8\pi}{\hbar^3} (2m)^{3/2} \left\{ [\varepsilon_F - \phi(\mathbf{r})]^{3/2} - \varepsilon_F \right\}
\]

...(3.8.5)

As a next step with important consequences for the further calculation we will now linearize this equation. We obtain,

\[
\mathcal{Q}^{(e)} (\mathbf{r}) - \mathcal{Q}^{(e)}_0 = -\frac{4\pi}{\hbar^3} (2m)^{3/2} \varepsilon_F^{1/2} \phi(\mathbf{r})
\]

...(3.8.6)

Introduction into the Poisson equation of electrostatics yields,

\[
\Delta \phi(\mathbf{r}) = 4\pi e^2 \left[ \mathcal{Q}^{(e)}_0 - \mathcal{Q}^{(e)}_0^{(e)} \right]
\]

\[
= 4\pi e^2 \left[ \frac{\hbar^3}{2m} \varepsilon_F^{1/2} \phi(\mathbf{r}) \right]
\]

...(3.8.7)

or, with the abbreviation : \( q_f^2 = \frac{4\pi k_f m e^2}{\hbar^2} \)

...(3.8.8)

We have,

\[
\Delta \phi(\mathbf{r}) = q_f^2 \phi(\mathbf{r})
\]

...(3.8.9)
The following boundary conditions will be employed:

\[
\begin{align*}
\phi(r) &\rightarrow -Ze^2 \quad \text{for} \quad r \rightarrow 0 \\
\phi(r) &\rightarrow 0 \quad \text{for} \quad r \rightarrow \infty
\end{align*}
\]

...(3.6.10)

The solution of (3.8.9) is,

\[
\phi = -\frac{Ze^2}{r} \quad e^{-\gamma r}
\]

...(3.8.11)

This equation first derived by Hott describes the shielding effect of the ion charge by the conduction electrons. The "shielding length" \( \frac{1}{q} \) is of the order of \( 1 \text{Å} \) for "good metals". The close correlation of the preceding analysis to the Debye-Hückel theory for solutions of strong electrolytes is easily recognized.

The introduction of an ion into the ideal Fermi gas will also produce a change of the average kinetic energy of the electrons. It can be calculated by the following method. According to the assumptions — the K.E. of the undisturbed Fermi gas is identical to the zero-point energy so that we can write an equation,

\[
E_{0, \text{kin}} = \frac{3h^2}{10m} \left( \frac{3}{8\pi} \right)^{2/3} \int d\gamma \left[ \phi_o (r) \right]^{5/3}
\]

...(3.8.12)

With the equation in this form we can again locally apply a relation that holds for free electrons. The kinetic energy in the presence of an ion is found to be,

\[
E_{\text{kin}} - E_{0, \text{kin}} = \xi_f \int d\gamma \left[ \phi_o (r) - \phi_o \right] + \frac{5\xi}{\phi_o} \int d\gamma \left[ \phi_o \right]^{5/3}
\]

...(3.8.13)

If \( \left( \phi_o \right) \) is assumed to be a small quantity as discussed above, then the change in the kinetic energy becomes,

\[
E_{\text{kin}} - E_{0, \text{kin}} = \xi_f \int d\gamma \left[ \phi_o (r) - \phi_o \right] + \frac{5\xi}{3\phi_o} \int d\gamma \left[ \phi_o \right]^{5/3} + \frac{1}{3} \left[ \phi_o \right]^{3/2}
\]

...(3.8.14)
The first term on the right side must be identical to zero since
the motion of the charge does not alter the number of conduction
electrons.

With the preceding results one can easily calculate the
effective interaction between two ions 1 and 2 that are immersed
in the Fermi gas of conduction electrons. We point out that,
as a result of the linear equation, the total potential $\Phi$ at
the point $r$ is simply obtained by a superposition of the two
shielded potentials $\phi_1$ and $\phi_2$,

$$\Phi = \phi_1 + \phi_2$$

...(3.8.15)

The interaction energy between two ions at a distance $r$ is
given by the change of the total energy of the metal which is
generated when the 2 ions are moved from infinity to a distance
$r$ from each other. This energy change consists of the following
three contributions:

(1) The interaction of charge $Ze$ of the ion 1 with the shielded
potential of ion 2 is given by,

$$\frac{Z^2 e^2}{r} e^{-\frac{q}{r}}$$

...(3.8.16)

(2) The interaction of the transported charge $-(q^2/4\pi e^2)\phi_1$
around ion 1 with the potential $\phi_2$:

$$-\frac{q^2}{4\pi e^2} \int d\tau \phi_1 \phi_2$$

...(3.8.17)
The change of the kinetic energy as expressed by equation (3.8.14). With equations (3.8.7) and (3.8.9), we obtain the contribution,

\[ \left(\frac{q^2}{4\pi\varepsilon_0^2}\right)^2 \int \frac{\delta F}{\delta \phi_1} \left[ (\phi_1 + \phi_2)^2 - \phi_1^2 - \phi_2^2 \right] = \frac{q^2}{4\pi\varepsilon_0^2} \int d\phi \phi_1 \phi_2 \]

\[ \cdots (3.8.18) \]

The contributions 2 & 3 cancel each other and we obtain the interaction energy of two ions at a distance \( r \),

\[ U(r) = \frac{Z^2 e^2}{\varepsilon_0} e^{-q/r} \]

\[ \cdots (3.8.19) \]

With assumption that we have made, one indeed obtains effective two-body central forces for the interaction between the ions. The forces are simply equal to the electrostatic interaction of a charge \( Ze \) of the ion 1 with the shielded potential of the ion 2. The function above is drawn in Fig. (Curve-1).

![Fig. 23: Pair-potentials of liquid metals for the point ion model.](image)

**Fig.** 23: Pair-potentials of liquid metals for the point ion model.

**Curve 1:** Semi classical theory, curve - 2: wave mechanical theory.

The above interaction potential represents a pure repulsive potential between ions and is, therefore, compatible with the existence of stable liquid metals. One is led to the conclusion that the Thomson-Fermi approximation which corresponds roughly
to geometric optics is not adequate. We are forced to include electron wave diffraction by ions, i.e., we must solve the Schrödinger equation for this problem. In the following we outline the derivation of March and Murray which is essentially a Hartree approximation, i.e., a reduction to the single electron problem with a self-consistent potential.

As in the preceding derivation, the self-consistency is obtained by the introduction of the Poisson equation. The eigen functions of the unperturbed problem are plane waves,

$$\psi_{\alpha,k} = \sqrt{ \frac{\hbar^2}{2m}} e^{-iKr}$$  \hspace{1cm} (3.8.20)

If the corresponding perturbed wave function is denoted by $\psi_k$, then the Schrödinger equation becomes,

$$\Delta \psi_k + \frac{2m}{\hbar^2} \left[ \varepsilon_k - \phi(r) \right] \psi_k = 0$$  \hspace{1cm} (3.8.21)

The formal solution can be written in the form,

$$\psi_k(r) = \sqrt{ \frac{\hbar^2}{2m}} e^{-iKr} - \frac{m}{2\hbar^2} \int dr' G(r,r') \phi(r') \psi_k(r')$$  \hspace{1cm} (3.8.22)

where,

$$G(r,r') = \frac{e^{ik|r-r'|}}{|r-r'|}$$

On the right side of equation we introduce the approximation $\psi_k(r') = \sqrt{ \frac{\hbar^2}{2m}} e^{iKr'}$ and retain only linear terms in $\phi$ as in the preceding derivation, we obtain,

$$\sum \psi_k^* \psi_k = \sum \left\{ \sqrt{ \frac{\hbar^2}{2m}} - \frac{m}{2\hbar^2} \int dr' \phi(r') [G(r,r') e^{ik(r'-r)} + G^*(r,r') e^{-iK(r'-r)}] \right\}$$  \hspace{1cm} (3.8.23)

The summation over $k$ can be replaced by integration. Considering
there are $2V/(2\pi)^3$ states per unit volume in $k$ space, the
electron density therefore becomes,

$$Q^e(\mathbf{r}) = \varepsilon_o - \frac{2m}{(2\pi)^3 \hbar^2} \int d\mathbf{r}' \phi(\mathbf{r}') \int d\mathbf{k} [G(\mathbf{r}, \mathbf{r}') \times e^{ik(\mathbf{r}-\mathbf{r}')} + G^*(\mathbf{r}, \mathbf{r}') e^{-ik(\mathbf{r}-\mathbf{r})}] \quad \ldots (3.8.24)$$

$G$ has spherical symmetry, so that, we can introduce polar co­
ordinates and integrate over the angles,

$$Q^e(\mathbf{r}) = \varepsilon_o - \frac{2m}{(2\pi)^3 \hbar^2} \int d\mathbf{r}' \phi(\mathbf{r}') \times 4\pi \int_0^{2\pi} \frac{\sin(k|\mathbf{r}-\mathbf{r}'|)}{|k|} \frac{2\cos(k|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|^2} \, k^2 \, dk \quad \ldots (3.8.25)$$

Integration for $k$ yields,

$$Q^e(\mathbf{r}) - \varepsilon_o = -\frac{m}{2\pi} \frac{k_F^2}{\hbar^2} \int d\mathbf{r}' \phi(\mathbf{r}') \frac{j_1(2k_F|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|^2} \quad \ldots (3.8.26)$$

where,

$$j_1(\lambda) = \lambda^{-2} (\sin \lambda - \lambda \cos \lambda)$$

is the first order spherical Bessel function with the earlier
assumption, i.e., that $\phi$ is a function which varies slowly in
space. We are now able to replace $\phi(\mathbf{r})$ in the integral by $\phi(\mathbf{r})$.

The integration may now be carried out; the result is again
equal to equation (3.8.5). The preceding calculations is thus
indeed a generalization of the previous method. Introduction
of (3.8.26) into the Poisson equation results in a generalization
of the previous method. Introduction of (3.8.26) into the Poisson
equation results in a generalization of Mott's equation,

$$\Delta \phi(\mathbf{r}) = \frac{me^2}{\hbar^2} \frac{2k_F}{\lambda^2} \int d\mathbf{r}' \phi(\mathbf{r}') \frac{j_1(2k_F|\mathbf{r}-\mathbf{r}'|)}{(\mathbf{r}-\mathbf{r}')^2} \quad \ldots (3.8.27)$$
Numerical solutions of this equation were listed in the form of tables by March and Murray. The interaction potential is then obtained by considerations analogous to those discussed above, details are available in the publication by Corless and March. The result is shown in the curve 2. It is apparent that the basic difficulty with equation (3.8.19) is now indeed solved. The coulomb repulsion is followed by a main minimum followed by secondary maxima and minima of decreasing amplitude which was described by the relation, 

\[ \phi(r) \sim \frac{\cos(2k_F r)}{r^3} \quad \ldots (3.8.20) \]

in the asymptotic limit. This behaviour of a distorted charge distribution around an ion was first pointed by Blandin, Daniel and Friedel. Frequently it is referred to as Friedel oscillation.

The above equation (3.8.20) represents the oscillatory part of the potential energy. So the equation (3.8.5) which is the analytical representation of the calculated potential energy function of the liquid metals and alloys can be explained from the basis of the partial screening of the potential energy function.
PART - II

3.9. EXPRESSIONS FOR RDF ON DIFFERENT DEGREES OF APPROXIMATIONS

In the part-I of this article we have shown how the intermolecular potential energy can be calculated from the experimental intensity data of X-ray scattering. The analytical expressions of the potential energy have also been formulated. In the Chapter-II, we have shown the iterative method of solving the integro-differential equation connecting the radial distribution function (RDF) and the intermolecular potential energy function. Having obtained the analytical expression we can put this in the expressions of Chapter-II and get the desired values of RDF. From Chapter-II, the expression for the RDF have zero approximation for h = 2 is,

\[ \eta_2^0 = n^2 \exp - \phi (\vec{r}^2) \]

\[ \frac{\eta_2^0}{n^2} \exp - \phi (\vec{r}^2) \]

\[ g^0 = \frac{\eta_2^0}{n^2} = \exp - \phi (\vec{r}^2) \]

\[ = \exp - \frac{A_2^0}{\eta_3^3} \exp [\frac{\pi^3}{-\alpha \vec{r}^2}] \cos \left[ 2k (B + \vec{r}) \right] \]

...(3.9.1)

On consideration of first approximation the expression for the RDF (for h = 2) is,

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

\[ \Rightarrow g_2 = \frac{\eta_2}{\eta_2^0} = \exp - \Delta_2^0 \]

...(3.9.2)
where,

$$\Delta_2^0 = \frac{2\pi n}{K_T} \iiint \frac{\partial}{\partial \nu_{13}} \phi_{13} \exp - \frac{1}{k_T} \{ \phi(\nu^2) - \phi(\nu^3) \} \times \frac{\nu_{12}^2 + \nu_{13}^2 - \nu_{23}^2}{2 \nu_{12}^2} \nu_{23} d\nu_{23} d\nu_{13} d\nu_{12}$$

The expression for the RDF on consideration of second approximation for $h = 2$ is:

$$n_2^2 = n_2^1 \exp - \Delta_2^1$$

$$g(n) = \frac{n_2^2}{n_2^1} = \exp - \Delta_2^1$$

(3.9.3)

Where,

$$\Delta_2^1 = \frac{2\pi n}{K_T} \iiint \frac{\partial}{\partial \nu_{14}} \phi_{14} \exp - \frac{1}{k_T} \{ \phi(\nu^2) - \phi(\nu^3) \} \times \frac{\nu_{14}^2 + \nu_{23}^2 - \nu_{34}^2}{2 \nu_{14}^2} \nu_{34} d\nu_{23} d\nu_{34} d\nu_{14}$$

The expression for the RDF on consideration of third approximation for $h = 2$ is:

$$n_2^3 = n_2^2 \exp - \Delta_2^2$$

$$g(n) = \frac{n_2^3}{n_2^2} = \exp - \Delta_2^2$$

(3.9.4)

Where,

$$\Delta_2^2 = \frac{2\pi n}{K_T} \iiint \frac{\partial}{\partial \nu_{15}} \phi_{15} \exp - \frac{1}{k_T} \{ \phi(\nu^2) - \phi(\nu^3) \} \times \frac{\nu_{15}^2 + \nu_{14}^2 - \nu_{45}^2}{2 \nu_{14}^2} \nu_{45} d\nu_{15} d\nu_{14} d\nu_{45}$$
The expression for the RDF on consideration of fourth order approximation for $h = 2$ is,

$$\eta_2^4 = \eta_2^3 \exp(-\Delta_2^3)$$

$$\therefore \mathcal{g}(n) = \frac{\eta_2^4}{\eta_2^3} = \exp(-\Delta^3) \quad \ldots(3.9.5)$$

Where,

$$\Delta_2^3 = \frac{2\pi n}{kT} \int \frac{1}{\delta r_{16}} \phi_{16} \exp \left\{ \frac{1}{kT} \left\{ \phi(r_{16}) - \phi(r_{15}) \right\} \right\} \times$$

$$\frac{r_{16}^2 + r_{15}^2 - r_{56}^2}{2r_{15}^2} \int_0^{r_{56}} \int_0^{r_{15}} \int_0^{r_{16}}$$

we can calculate the RDF from the intermolecular potential parameters, i.e., $A =$ the amplitude, $r_0 =$ position of the first node, $k =$ \text{wave length of the oscillation}, $\beta =$ the phase and $\alpha =$ the attenuation parameter which can be determined from $k_f =$ the diameter of the Fermi sphere.

From the above analysis of Chapter I and II, which are interconnected, the actual calculation of the RDF is not necessary. It is obvious that the calculated results will agree with the X-ray diffraction results. However, the computer simulated results determined from the Monte-Carlo calculations may not agree with our results. This is, we believe, due to the consideration of a particular type of potential energy function (rigid sphere potential, Lennard - Jones potential, etc.) which are phenomenological in nature and represents the bare and density-independent two-body potential.
However, we must not neglect the existing other molecular theories like hypernateo chain approximation (HNC), Percus Yevick equation (PY). Particularly the PY equation solved for rigid spheres by Thiele & Wartheim and later well-represented by Carnahan and Starling equation are very useful for practical calculations and engineering application.

However, the above equations have some limitations and there is a recent revival of the interest in the non-linear integral equation for the pair distribution function of the classical fluids. The three equations namely - the BGY equation, HNC equation & PY equation can be written as,

\[ (1) \quad -kT \nabla_1 g_{(2)}(r_{12}) = g_{(2)}(r_{12}) \nabla_1 \phi(r_{12}) + \rho \int g_{(2)}(r_{12}) g_{(2)}(r_{23}) g_{(2)}(r_{13}) \nabla_1 \phi(r_{13}) d\vec{r}_3 \quad (BGY) \]

\[ (2) \quad g_{(2)}(r_{12}) = \exp \left\{ -\frac{\phi(r_{12})}{kT} + h(r_{12}) - C(r_{12}) \right\} \quad (HNC) \]

\[ (3) \quad g(r_{12}) = \exp \left\{ -\frac{\phi(r_{12})}{kT} \right\} \left[ 1 + h(r_{12}) - C(r_{12}) \right] \quad (PY) \]

Where, \( h(r) \) = total correlation function and \( C(r) \) = direct correlation function.

It is obvious from the above equations that the linearisation of the second exponential of the HNC equation gives rise to the PY equation. Moreover, it can be shown with the help of the Ornstein-Zernike equation and the BGY equation can be reduced
to the HNC equation as follows:

In eqn (1) (i.e., BbY eqn.) we may substitute for $g_{(2)}(\tau_{13})$

$$\nabla_1 \Phi(\tau_{13})$$

from,

$$-kT \nabla_1 g_{(2)}(\tau_{13}) = g_{(2)}(\tau_{13}) \nabla_1 \Phi(\tau_{13}) + \rho \int g_{(3)}(\tau_{134}) \nabla_1 \Phi(\tau_{14}) \, d\tau_4$$

giving,

$$-kT \nabla_1 g_{(2)}(\tau_{12}) = g_{(2)}(\tau_{12}) \nabla_1 \Phi(\tau_{12}) + \rho \int g_{(2)}(\tau_{12}) g_{(2)}(\tau_{23}) \times$$

$$\left[ -\nabla_1 g_{(2)}(\tau_{13}) kT - \rho \int g_{(2)}(\tau_{13}) g_{(2)}(\tau_{34}) g_{(2)}(\tau_{14}) \nabla_1 \Phi(\tau_{14}) \, d\tau_4 \right] \, d\tau_3$$

repeating this process for $g_{(2)}(\tau_{14}) \nabla_1 \Phi(\tau_{14})$ yields,

$$-kT \nabla_1 g_{(2)}(\tau_{12}) = g_{(2)}(\tau_{12}) \nabla_1 \Phi(\tau_{12}) - kT \rho \int g_{(2)}(\tau_{12}) \times$$

$$g_{(2)}(\tau_{23}) \nabla_1 g_{(2)}(\tau_{13}) \, d\tau_3 + kT \rho^2 \int g_{(2)}(\tau_{12}) g_{(2)}(\tau_{23}) \times$$

$$g_{(2)}(\tau_{13}) g_{(2)}(\tau_{34}) \left[ -\nabla_1 g_{(2)}(\tau_{14}) kT - \rho \int g_{(2)}(\tau_{14}) g_{(2)}(\tau_{45}) g_{(2)}(\tau_{15}) \nabla_1 \Phi(\tau_{15}) \, d\tau_5 \right] \, d\tau_4 \, d\tau_3$$

The general expression of this series is,

$$-kT \nabla_1 \ln g_{(2)}(\tau_{12}) = \nabla_1 \Phi(\tau_{12}) + kT \sum_{n=1}^{\infty} (-1)^n \frac{\rho^n}{n!} \times$$

$$\left\{ \cdots \left\{ \nabla_1 g_{(2)}(1, n+2) \right\} g_{(2)}(n+1, n+2) \times$$

$$\prod_{i=3}^{n+2} \left\{ g_{(2)}(1, i) \ g_{(2)}(i-1, i) \right\} \, d\tau_3 \cdots d\tau_{n+2}$$

Each term in the series can be represented by a cluster diagram of a simple closed loop and a complete set of cross links radiating from particle 1.

Abe also establishes a formal solution of the indirect
triplet correlation \( T_3 (r_{123}) \) defined by,
\[
q_3 (r_{123}) = q_{(2)} (r_{12}) q_{(2)} (r_{23}) q_{(2)} (r_{31}) T_3 (r_{123})
\]
in terms of the infinite power series in the density. In practice, however, this solution is only applicable to gaseous systems at low density.

A useful approximate closed form to the infinite series (3.8.26) has been obtained by Abe who sets the factors \( g(1,i) \) equal to unity. The resulting soln is:
\[
- \frac{\Phi(r)}{kT} = \ln g_{(2)} (r) - \frac{1}{(2\pi)^2} \int \frac{[1 - S(K)]^2}{S(K)} e^{ik\cdot r} dk
\]
where
\[
s(k) = \text{structure factor} = 1 + 4\pi \rho \int [g_{(12)} - 1] \frac{r_{12} s(\kappa r_{12})}{K} d\kappa_{12}
\]
which may be very easily shown to be:
\[
- \frac{\Phi(r)}{kT} = \ln g_{(2)} (r) - \left[ h(r) - C(r) \right]
\]
This, interestingly enough, is the HNC approximation.

Thus, it has been shown that the three equations can be correlated with certain closer approximations. It is obvious from the above analysis that BGY equation should be the obvious choice for the zeroth approximation for our iteration procedure.

One of main criticism of the PY & HNC equation is their inability to represent the phase transformation which is obviously an important property to be explained by any theoretical formulation. The most important characteristics of the BGY equation is that it can explain the phase-transformations\(^{155,156}\).
the BGY equation as the zero approximation this important characteristics is preserved and the final result of any desired accuracy can explain the phase transformation.