# CHAPTER III

# THE ZIMAN THEORY OF ALKALI METALLIC LIQUID

## 3.1 INTRODUCTION

Ziman[8] formulated a theory for the d.c. electrical conductivity of liquid monovalent metals and successfully applied his theory to alkali metals with respect to experimental data. For this theory, conduction electron is assumed as a free particle in existence of classical ions. Thus the perturbation technique can be applied to find the interacting matrix element and used it to get the scattering cross section. In addition, a radial distribution function, probability to find another atom from the fixed atom, and a pseudopotential is necessary to the calculation of the electron mean free path. In next sections we will briefly review related topics and finally give the Ziman theory.

## 3.2 STRUCTURE OF LIQUIDS [15]

The structure of liquids can be determined from the X-ray diffraction experiment by analyzes the intensity that scattered by a sample. The instantaneous intensity at the detector is

$$I = |A_0|^2 \int dr e^{i(\Delta \mathbf{q} \cdot \mathbf{r})} \left\langle \sum_{i,j}^{N} \delta(\mathbf{r} + \mathbf{r}_i - \mathbf{r}_j) \right\rangle \qquad (3.2.1)$$

where   $N$ is a number of atoms,

$\mathbf{r}_i$ , $\mathbf{r}_j$  the position vectors of atoms,

$\Delta \mathbf{q}$  the electron momentum transfer and

$A_0$  the amplitude of incident electrical plane wave beam of X-ray.

The quantity $I$ relates to the radial distribution function $g(r)$, excluding $\Delta\mathbf{q} = \mathbf{0}$, shifting the zero of $g(r)$, by

$$I(\Delta\mathbf{q}) = |A_0|^2 N\left\{1 + \rho \int e^{i(\Delta\mathbf{q}\cdot\mathbf{r})}[g(r)-1]d\mathbf{r}\right\} \qquad (3.2.2)$$

where

$$\rho g(r) = \frac{1}{N}\left\langle \sum_{i\neq j}^{N} \delta(\mathbf{r}+\mathbf{r}_i - \mathbf{r}_j)\right\rangle, \qquad (3.2.3)$$

$N$ number of atoms,

and $\rho = N/V$ is the atomic density of volume $V$.

The function $h(r)$, defined by

$$h(r) = g(r) - 1 \qquad (3.2.4)$$

is called the total correlation function.

In the perfect gas, an atom at any region has no effect at all on the uniform distribution of the other atoms, so that

$$g(r) = 1. \qquad (3.2.5)$$

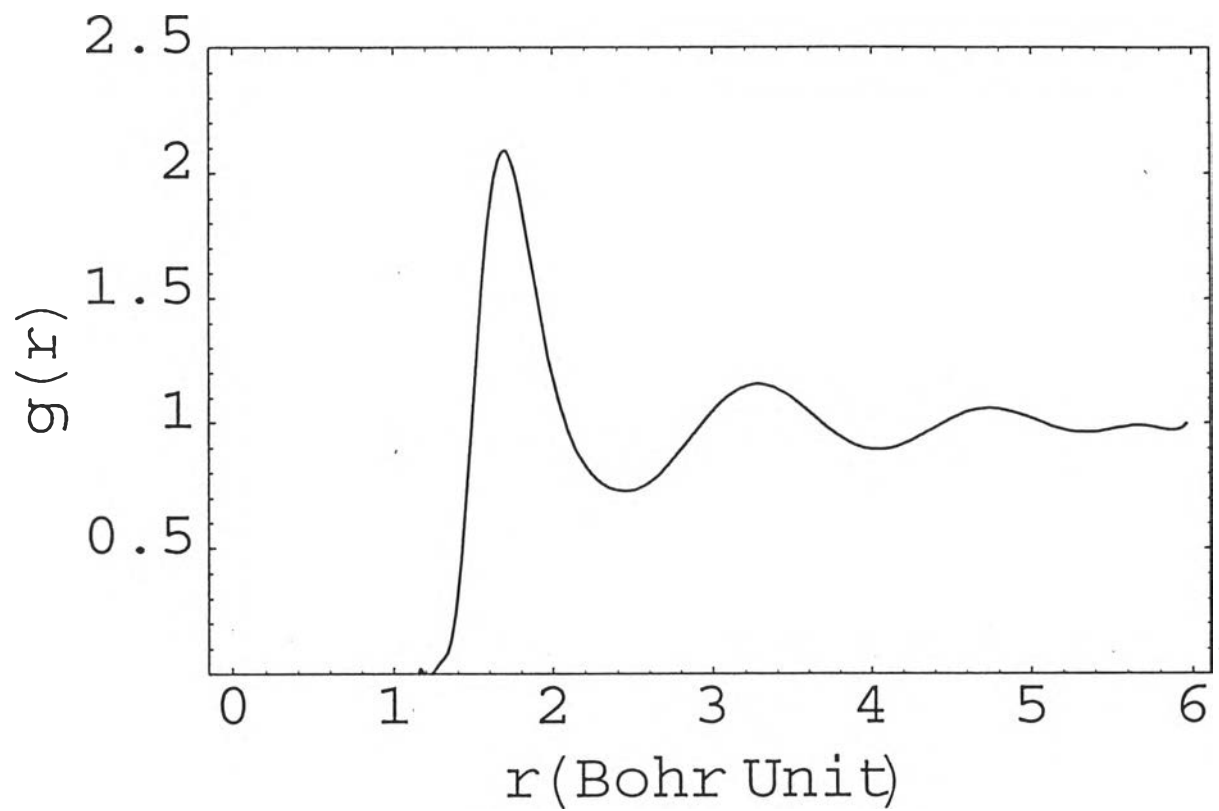A typical $g(r)$ for a liquid is sketched in Fig. 3.1 [9].

Figure 3.1 A radial distribution $g(r)$ measures the probability to find another atom from the fixed atom [9].

From Fig. 3.1 a region where $g(r) = 0$ dues to repulsion of the other atom by the one at the origin. A bump represents a shell of neighbors in the attractive part of the central atoms potential. A few further wiggles represents their neighbors and so on, and an asymptotic value of $g(r) \to 1$ far away.

The function $h(r)$ differs only in that it starts at $-1$ and goes to zero far away. For the perfect gas, substituting Eq. (3.2.5) into (3.2.2), one finds

$$I_{P.G.} = |A_0|^2 N, \tag{3.2.6}$$

where $P.G.$ stands for perfect gas.

This result offers a natural normalization procedure. One can eliminate $A_0$ by defining

$$a(\Delta \mathbf{q}) = \frac{I(\Delta \mathbf{q})}{I(\Delta \mathbf{q})_{P.G.}} = 1 + \rho \int e^{i(\Delta \mathbf{q} \cdot \mathbf{r})} h(r) d\mathbf{r} \tag{3.2.7}$$

$a(\Delta \mathbf{q})$ is called the structure factor.

One cannot expect to be able to measure $g(r)$ for a liquid near the triple point by mean of the X-ray scattering experiments. If one takes Eq. (3.2.7) in the limit as $\Delta \mathbf{q} \to \mathbf{0}$, one sees that

$$a(0) = 1 + \rho \int h(r) d\mathbf{r} \tag{3.2.8}$$

$$= \rho k_B T \kappa_T \tag{3.2.9}$$

where $\kappa_T$ is the isothermal compressibility, infinite at the critical point of a gas-liquid phase transition and $k_B$ is Boltzmann's constant.

## 3.3 THE PSEUDOPOTENTIAL [8]

In a liquid, the conduction electrons behave as if they were free except for a modest field attracted to each ion. This field represents a balance between an electrostatic attraction and the Pauli repulsion exerted by bound states in the core, to which the conduction electrons must be orthogonal with the core electrons. The deep singularity in the electrostatic term inside the ion core is nearly cancelled out by the large kinetic energy associated with the rapid oscillations of the wave function in this region. Thus the net effect is the same as the weak pseudopotential acting on a pseudowave function, which is the same as the real wave function without the rapid oscillations in the core. A function $U_a(\mathbf{r} - \mathbf{R}_i)$ represents the pseudopotential for all electronic states. The total potential field $U(\mathbf{r})$ acting on a conduction electron at $\mathbf{r}$ is the sum of contributions from the ions at their position $\mathbf{R}_i$:

$$U(\mathbf{r}) = \sum_{i=1}^{N} U_a(\mathbf{r} - \mathbf{R}_i) \tag{3.3.1}$$

Note that $\mathbf{R}_i$ is not independent random variables but correlated with each other in a very complicated way.

## 3.4 CORRELATION IN LIQUID [8]

From the previous section, the matrix element of an electron for transitions induced by the total potential of this whole assembly of atoms is

$$U_{\mathbf{k},\mathbf{k}'} = \frac{1}{V} \sum_{j=1}^{N} \int U_a(\mathbf{r} - \mathbf{R}_j) \exp[i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}] d\mathbf{r}$$

$$= \frac{1}{V} \sum_{j=1}^{N} \exp[i(\mathbf{K} \cdot \mathbf{R}_j)] \int U_a(\mathbf{r} - \mathbf{R}_j) \exp[i\mathbf{K} \cdot (\mathbf{r} - \mathbf{R}_j)] d\mathbf{r}$$

$$= U(\mathbf{K}) \frac{1}{N} \sum_{j=1}^{N} \exp\left[i\left(\mathbf{K} \cdot \mathbf{R}_j\right)\right] \qquad (3.4.1)$$

where, $\dfrac{N}{V}$ is atomic concentration. Under the translational invariant assumption, the corresponding Fourier component is

$$U(\mathbf{K}) = \frac{N}{V} \int e^{i(\mathbf{K} \cdot \mathbf{r})} U_a(\mathbf{r}) \, d\mathbf{r} \qquad (3.4.2)$$

and electron momentum transfer $\mathbf{K} = \mathbf{k}' - \mathbf{k}$.

In general, this sum is a rather irregular function of $\mathbf{K}$, of more or less random phase. But one is interested mainly in the mean value of the square modulus of matrix element, which can be expressed in terms of the radial distribution function of atoms in the liquid as described in the previous Chapter. It is shown in the treatises on X-ray diffraction that [16]

$$a(K) = \left| \frac{1}{N} \sum_{j=1}^{N} \exp\left[i\left(\mathbf{K} \cdot \mathbf{R}_j\right)\right] \right|^2 \qquad (3.4.3)$$

$$= 1 + \frac{4\pi N}{V} \int_0^{\infty} [g(R) - 1] \frac{\sin(KR)}{K} R \, dR. \qquad (3.4.4)$$

If we substitute $U(\mathbf{K})$ into the differential scattering cross section $\zeta(\theta)$ using the Born approximation [17,18], one gets

$$\zeta(\theta) = \frac{3}{8} \left| \frac{1}{N} U(\mathbf{K}) \right|^2 \frac{n}{\hbar \upsilon_F E_F}, \qquad (3.4.5)$$

where $n$ is conduction electron concentration. From Eq. (2.4.8) then the mean free path can be rewritten in the form

$$\Lambda_{liq.} = \frac{\left(2E_F\right)^{3/2}}{3\pi} \frac{1}{\langle a \rangle |U|^2} \qquad (3.4.6)$$

where

$$\langle a \rangle |U|^2 = \frac{1}{4k_F^4} \int_0^{2k_F} |U(\mathbf{K})|^2 a(K)K^3 dK \ . \qquad (3.4.7)$$

In the next Chapter we will apply the Ziman theory to liquid metallic hydrogen that has no core electrons.

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