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On The Electrical Resistivity of Liquid Metals: Constant Pressure

by

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Abstract

A theory is given for the structure-dependent scattering as a function of temperature which is responsible for the resistivity of a simple liquid metal such as sodium or one of the other alkalis. If we assume that the total disorder of the liquid contributes to the resistivity we may introduce the radial distribution function of the liquid into the analysis. This description of the disorder is equivalent to a distribution of correlated density fluctuations given in terms of the radial distribution function. The temperature dependence of the resistivity then arises from the temperature dependence of the radial distribution curve which in turn is due to the correlated thermally activated density fluctuations in the liquid. Results are obtained for both the constant pressure and constant volume cases.

Measurements of the temperature dependence of the resistivity at constant pressure of sodium and mercury are reported and described. The behavior of sodium and mercury are quite similar and agree qualitatively with the theory.

Comparison is made between our calculations and Ziman's theory. It is concluded that the temperature dependence of the short-range order in the liquid rather than plasma scattering is responsible for the temperature dependence of the electrical resistivity.

Introduction

Recent theoretical and experimental work indicates a rebirth of interest has occurred in the structure and properties of liquids⁽¹⁾⁽²⁾, particularly of the simpler metals. The purpose of this report is to try to correlate the various structural aspects of a simple metallic liquid with its electrical resistivity at constant pressure.

The major conceptual problems to be overcome in our case are the description of the detailed arrangement of the residual ion-cores and the specification of the eigenstates of the conduction electrons. Contrary to the case for solids, the ion cores of a liquid metal cannot be located on regularly arranged lattice sites. The only apparently significant structural information is that given by the local radial distribution function $n(r)$. Since there is no reliable theory for this parameter we introduce an experimental distribution, $\bar{n}(r)$, which is determined from appropriate x-ray or neutron scattering data.

The case for the eigenfunctions of the conduction electrons is just as complex to treat.⁽²⁾ However, on the basis of certain fairly reliable experimental results some reasonably simple assumptions can be put forward. The relatively high electrical conductivities of liquid metals, even though several times smaller than for solids, imply the electric current carriers are quite mobile. This, plus the fact that Hall constant data and optical constant data characterize a free electron behavior, indicate that it is reasonable to treat the problem as if the electrons are almost free.⁽²⁾ Based upon this assumption it is possible to calculate the scattering of the electrons in a straight forward fashion.

If any physical system exists in a given eigenstate which does not change during a scattering process, we have the case of elastic scattering. In this case the Born approximation for free electrons applies⁽³⁾ and the scattering cross-section is expressible in terms of an appropriate distribution function⁽⁴⁾. In addition, for negligible energy transfers, the momentum transfer is essentially unique for each scattering angle θ . That is, $|\Delta \vec{p}| = \hbar |\vec{k}| = 2 \hbar |\vec{k}| \sin \frac{1}{2} \theta$ is the momentum transferred by scattering through an angle θ . $\hbar \vec{k}$ is the momentum of the incident electron.

Now if we realize that the resistivity arises from the total disorder of the system then such questions as the temperature dependence of the resistivity depend on the temperature dependence of the radial distribution function $\bar{n}(r)$. We consider such problems in a general way by the following analysis.

One can readily show that the resistivity is given by

$$\rho = \frac{mv_{\max}}{N^* e^2 \lambda} = \frac{m}{N^* e^2 \tau} \quad (1)$$

N^* = effective number of carriers/cm³; $v_{\max}$ = velocity of an electron at the Fermi surface; λ = mean-free-path of an electron; and τ = mean-free-time between successive scatterings.

For the case of a simple monovalent metal such as sodium we may reasonably presume N^* independent of temperature. Thus the effective structure dependence of ρ appears in $1/\tau$ where

$$\frac{1}{\tau} = v_{\max} \int_0^\pi S(\theta) (1-\cos\theta) d\omega \quad (2)$$

$d\omega = 2\pi \sin\theta d\theta$ (θ being the scattering angle) and $S(\theta) d\omega$ is the differential scattering cross-section for the conduction electrons of 1 cm^3 of liquid.

$S(\theta)$, the unit scattering power, is evaluated by means of the Born approximation to give⁽⁵⁾

$$S(\theta) = \left| \frac{1}{4\pi} \frac{2m}{\hbar^2} \int v_p(\vec{r}) e^{i\vec{k} \cdot \vec{r}} d\vec{r} \right|^2 \quad (3)$$

$\vec{K} = \vec{k} - \vec{k}'$ is the so-called scattering vector. For an arbitrary array of atoms the scattering potential, $v_p(\vec{r})$, is expressed by

$$v_p(\vec{r}) = \sum_{n=1}^{N/V} \left[v_n(\vec{r} - \vec{r}_n) - v_0 \right]$$

$v_n(\vec{r} - \vec{r}_n)$ = the potential due to the ion in the n th atomic cell of the liquid. $v_n(\vec{r} - \vec{r}_n)$ can be assumed to be essentially zero outside its cell. v_0 is the so-called average "inner" potential of the liquid

and can be estimated from the refractive index of the liquid for electrons. By substitution

$$f(\theta) = \frac{-2m}{4\pi\hbar^2} \sum_{n=1}^{N/V} \int \left[v_n(\vec{r}-\vec{r}_n) - v_o \right] e^{i\vec{K}\cdot\vec{r}} d\vec{r} \quad (4)$$

where $S(\theta) = |f(\theta)|^2$. Replacing the variable $\vec{r}$ by $\vec{R} = \vec{r}-\vec{r}_n$ we obtain a more convenient result ,

$$f(\theta) = \frac{-2m}{4\pi\hbar^2} \sum_n F_n(\vec{K}) e^{i\vec{K}\cdot\vec{r}_n}$$

where $F_n(\vec{K}) = \int \left[v_n(\vec{R}) - v_o \right] e^{i\vec{K}\cdot\vec{R}} d\vec{R}$ is called the form factor of the nth cell.

$S(\theta)$ now takes the form

$$S(\theta) = |f(\theta)|^2 = \left(\frac{2m}{4\pi\hbar^2} \right)^2 \sum_{n,m} F_n(\vec{K}) F_m^*(\vec{K}) e^{i\vec{K}\cdot(\vec{r}_n - \vec{r}_m)} \quad (5)$$

Thus, if we let $\vec{r}_m = \vec{r}_n + \vec{r}_j$ one may write

$$S(\theta) = \left(\frac{2m}{4\pi\hbar^2} \right)^2 \sum_{n,j} F_n(\vec{K}) F_{n+j}^*(\vec{K}) e^{-i\vec{K}\cdot\vec{r}_j} \quad (6)$$

For an isotropic system such as a simple liquid (6) becomes

$$S(\theta) = \left(\frac{2m F(\vec{K})}{4\pi\hbar^2} \right)^2 \frac{N}{V} \left[1 + \sum_j c_j \frac{\sin K r_j}{K r_j} \right] \quad (7)$$

where all the $F_n(\vec{K})$ are assumed to be equal (i.e., a homogeneous liquid). as an appropriate average structure one represents the neighbors about any one atom by a continuous distribution $4\pi r^2 \bar{n}(r)$.

$4\pi r^2 \bar{n}(r) dr$ = the number of neighbors lying between r and $r+dr$.

The summation is then replaced by an integral

$$S(\theta) = \frac{N}{V} \left(\frac{2m F(\vec{K})}{4\pi\hbar^2} \right)^2 \left\{ 1 + \int_0^\infty 4\pi r^2 [\bar{n}(r) - n_0] \frac{\sin Kr}{Kr} dr + \int_0^\infty 4\pi r^2 n_0 \frac{\sin Kr}{Kr} dr \right\} \quad (8)$$

$n_0 = N/V$, the average atomic density.

$z(r) = [\bar{n}(r) - n_0]$ is a correlation function which describes the correlations in the relative positions of different particles. Also, $z(r) \rightarrow 0$ rapidly with increasing r . The first integral on the right side of (8) has significant contributions only from small r . The second integral is zero for $K > 0$, and thus can be neglected.

From diffraction theory it can be shown that

$$I(\vec{K}) = 1 + \int_0^\infty 4\pi r^2 [\bar{n}(r) - n_0] \frac{\sin Kr}{Kr} dr \quad (9)$$

where $I(\vec{K})$ is the so-called interference function and is measured by X-ray or neutron diffraction. Therefore

$$S(\theta) = \frac{N}{V} \left(\frac{m F(\vec{K})}{2\pi\hbar^2} \right)^2 I(\vec{K}) \quad (10)$$

From this result we see that the essential temperature dependence of ρ is due to the temperature variation of $I(\vec{K})$, which according to (9) results from the temperature dependence of $z(r)$, the correlation function.

Now the temperature dependence of $z(r)$ and hence of ρ , arises from the thermally-induced density fluctuations in the liquid associated with the thermal motions of the ion-cores. One can show this by a direct application of fluctuation theory (6). Because of interactions between atoms of the liquid the volume or density fluctuations are spacially correlated and this correlation is given by $z(r)$. Thus we can account for the temperature dependence of ρ by means of the temperature dependence of the structure.

If G = the Gibbs free energy per unit volume of liquid, and $\bar{G}$ = the average value of G (i.e., for a uniform density n_0), the variation of free energy from point-to-point due to density fluctuations is

$$G \cong \bar{G} + \frac{1}{2} A_1 (\bar{n} - n_0)^2 + \frac{1}{2} A_2 (\nabla \bar{n})^2 \quad (11)$$

where A_1 and A_2 are > 0 ($A_2 \gg A_1$).

An arbitrary density fluctuation can always be described in terms of its Fourier components. Also, because of their orthogonality the total free energy change is the sum of the free energy changes associated with each Fourier component. Therefore, if we have

$$\bar{n}(\mathbf{r}) - n_0 = \sum_{\mathbf{g}} n_{\mathbf{g}} e^{i\mathbf{g} \cdot \mathbf{r}} \quad (12)$$

$$\text{then } \Delta G_{\mathbf{g}} = \frac{V}{2} \sum_{\mathbf{g}} (A_1 + A_2 g^2) |n_{\mathbf{g}}|^2 \quad (13)$$

$$\text{since } n_{\mathbf{g}} = \frac{1}{V} \int (\bar{n} - n_0) e^{-i\mathbf{g} \cdot \mathbf{r}} d\mathbf{r}$$

$$(n_{\mathbf{g}}^* = n_{-\mathbf{g}})$$

The thermodynamic probability of the $\mathbf{g}$ th Fourier term is given by

$$w = \exp \left[\frac{-V}{kT} (A_1 + A_2 g^2) |n_{\mathbf{g}}|^2 \right]$$

$$\text{Hence } \langle |n_{\mathbf{g}}|^2 \rangle = \frac{kT}{V(A_1 + A_2 g^2)}$$

$$\text{Thus } \int z(\mathbf{r}) e^{-i\mathbf{g} \cdot \mathbf{r}} d\mathbf{r} = \frac{V}{n_0} \langle |n_{\mathbf{g}}|^2 \rangle - 1$$

$$= \frac{kT}{n_0 (A_1 + A_2 g^2)}$$

By Fourier inversion this gives

$$z(r) = \frac{kT}{4\pi n_o A_2} \frac{e^{-\gamma r}}{r} \approx \frac{kT}{4\pi n_o r A_2} \quad (\gamma \ll 1)$$

By substitution and integration we then get

$$S(\theta) = \frac{N}{V} \left(\frac{m F(\vec{K})}{2\pi \hbar^2} \right)^2 \left\{ 1 + \int_0^\infty \frac{kT e^{-\gamma r}}{4\pi n_o r A_2} \frac{\sin Kr}{Kr} 4\pi r^2 dr \right\} \quad (14)$$

which leads to the approximate result

$$S(\theta) = \frac{N}{V} \left[\frac{m F(\vec{K})}{2\pi \hbar^2} \right]^2 \left\{ \frac{n_o A_2 K^2 + kT}{n_o A_2 K^2} \right\} \quad (15)$$

(since $\gamma \ll 1$).

We then find that

$$\frac{1}{\tau} = \frac{v_{\max}}{4\pi} \left[\frac{m}{\hbar^2 k_{\max}^2} \right]^2 \int_0^{2k_{\max}} |F(\vec{K})|^2 (n_o K^3 + \frac{kTK}{A_2}) dK \quad (16)$$

Equation (16) now expresses the temperature dependence of ρ at constant pressure of a simple monovalent metallic liquid.

At first glance this result would seem to indicate a simple linear temperature dependence for ρ . However, both n_0 and A_2 are also temperature dependent. n_0 depends upon temperature due to the normal thermal expansion of the liquid. Hence, we have

$$n_0 = \bar{n}_0 [1 - \alpha(T - T_m)] \quad (17)$$

where α = the volume coefficient of expansion, $\bar{n}_0$ = the particle density at the melting point and T_m = the melting temperature. Thus n_0 contributes an additional temperature term.

On the other hand, A_2 exhibits a more complicated temperature dependence. We investigate this by considering the physical significance of A_2 . In equation (11) we saw how free energy variations could be expressed in terms of density fluctuations. The first term on the right hand side represents the increase in free energy due to presence of a local gradient in density of the liquid. The second term gives rise to surface tension since it describes the contribution from incipient surfaces between regions differing in density. This requires that $A_2 > 0$, otherwise we would have a negative surface tension. Since $\frac{1}{2}A_2(\bar{\nabla n})^2$ is defined at constant pressure we expect that A_2 should be essentially constant near T_m but will tend to decrease at a slightly increasing rate at sufficiently high temperatures.

The net effect of this high temperature variation of A_2 is to cause the second term

$$K |F(\vec{K})|^2 \frac{kT}{A_2} dK$$

of the integrand in (16) to exhibit a temperature dependence greater than the first power in T at temperatures sufficiently high enough above T_m (A_2 can no longer be treated as constant). In the temperature range just above T_m , ρ should show an essentially linear dependence on T .

A similar analysis may be applied in calculating the resistivity as a function of temperature constant volume. In this case we expand the Helmholtz free energy F to obtain

$$F \approx \bar{F} + \frac{1}{2} C_1 (\bar{n} - n_0)^2 + \frac{1}{2} C_2 (\vec{\nabla} \bar{n})^2 \quad (18)$$

This then gives

$$\frac{1}{\chi} = \frac{v_{\max}}{4\pi} \left[\frac{m}{\hbar^2 k^2} \right]^2 \int_0^{2k_{\max}} |F(\vec{K})|^2 \left(n_0 K^3 + \frac{kTK}{C_2} \right) dK \quad (19)$$

C_2 again corresponds to an incipient surface energy term while n_0 is constant with temperature throughout. Likewise, because of the restriction of constant volume, it is expected that the temperature variation of C_2 will not be as marked as for A_2 . The difference

between equations (16) and (19) represents the appropriate correction to transform constant pressure resistivity data to constant volume resistivities.

Experimental Method

The sodium used in this experiment was of 99.95% purity supplied by the A. D. Mackay Company. The mercury specimens were of triple-distilled mercury. Two different designs for the measuring cells were used for sodium and mercury respectively. Figure 1 shows a schematic diagram for each cell. The current and potential leads were of platinum.

Because of the highly reactive nature of the sodium, the sodium cells were filled in an argon gas-filled dry box. The impurity content of the argon in the dry box was kept to within one part per million. The actual filling of the cell was done by means of a medical syringe after the cell and syringe had been thoroughly cleaned. The sodium was heated to 10° or 15° above its melting point for filling. All components were brought into the dry box before filling. After filling a set of copper-constantan thermocouple leads were sealed into the pyrex glass specimen cell midway between the potential leads. No oxidation or reaction of the sodium was observed during the filling.

After the filling the sodium cell was placed in a pyrex container already in the dry box and was sealed with a pyrex stopper.

For best results in filling the cell was pre-heated. The syringe itself was heated by a nichrome heater wire wound about the syringe.

The mercury cell was filled in air. The cell was first evacuated and then connected to an open mercury reservoir so that the mercury was forced into the cell by the atmospheric pressure.

An electrical resistance tube furnace was used to heat the specimens above room temperature. A temperature gradient of about 1°C was maintained across the specimen. Temperature was measured by means of the copper-constantan thermocouple which had been calibrated by the National Bureau of Standards.

The resistivity measurements on mercury below room temperature were carried out as follows. The mercury cell was inserted into an insulated furnace with a nichrome heating element closed off at one end. The whole assembly was then immersed in a dry-ice and acetone temperature bath. The furnace current was varied to control the specimen temperature. The temperature gradient across the specimen was about 1°C .

The resistivity was determined by measuring the potential drop across the specimen and the electric current flowing through the specimen. The specimen current itself was determined by measuring the potential drop across a one-ohm standard resistor connected in series with the specimen. Measurements were also made in the reverse current direction in order to eliminate thermal emfs. The potentiometer used was a Rubicon model 2786 low thermal emf instrument, with a

Keithly model 149 milli-microvoltmeter as a null indicator. Since the resistivity $\rho = RA/l$, the bore of the pyrex capillary and the length between the potential leads were measured by an optical comparator to within .01% accuracy at room temperature. Temperature corrections were made from known values of the thermal expansion coefficient of pyrex.

Experimental Results

The essential results of our measurements are given by the data plotted in Figure 2, for pure sodium, and in Figure 3, for pure mercury. The resistivity of sodium was measured from the melting point up to 350°C at one atmosphere pressure. The resistivity of mercury was measured from the melting point up to 260°C at one atmosphere pressure. In both cases it can be seen that up to about 80°C above the melting point ρ vs. T is linear in temperature. Above this temperature range both curves show a slight concave upward curvature with increasing temperature. The initial slope of the curve for sodium is .0342 $\mu\text{-ohm cm}/^\circ\text{C}$, while for mercury it is .0845 $\mu\text{-ohm cm}/^\circ\text{C}$. These results are in general agreement with those reported by Freedman and Robertson⁽⁷⁾. The difference in absolute values of our resistivities is probably due to the difference in thermal expansion coefficients and conductivities of the specimen holders used in the two experiments. Our specimen cells were of pyrex glass while Freedman and Robertson used stainless steel.

Discussion

Our calculation of the temperature dependence of the resistivity of a simple liquid metal, i.e. sodium, was based on an extension of the method of deformation potentials. That is, we assume that the resistance is due to the total disorder of the liquid. The temperature dependence of this disorder is due to the thermal oscillations of the ion-cores of the liquid and their average spacial correlation as given by $z(r)$. As a consequence the electrons see a temperature dependent fluctuating potential, which is associated with the dilatations produced by the thermally fluctuating ion-cores. We obtained results for both the constant pressure and constant volume cases, which we express below in terms of the mean free paths.

$$\frac{1}{\Lambda_p} = \frac{1}{16\pi E_{\max}^2} \int_0^{2k_{\max}} |F(\vec{k})|^2 \left[n_o k^3 + \frac{kT}{A_2} k \right] dk$$

$$(n_o = \bar{n}_o [1 - \alpha (T - T_m)]) \quad (20)$$

and

$$\frac{1}{\Lambda_v} = \frac{1}{16\pi E_{\max}^2} \int_0^{2k_{\max}} |F(\vec{k})|^2 \left[n_o k^3 + \frac{kT}{C_2} k \right] dk$$

$$(n_o = \bar{n}_o) \quad (21)$$

In both cases it was shown that a linear temperature dependence of the resistivity is to be expected in the vicinity of the melting point with a gradually increasing slope appearing at higher temperatures. This inherent non-linear behavior was shown to be related to the temperature dependence of the surface tension of the liquid. Measurements made on sodium and mercury show qualitative agreement with these results in the constant pressure case. Measurements are now being carried out for the constant volume case.⁽⁸⁾

It has frequently been the practice to discuss a residual resistance at 0°K as determined by a linear extrapolation of the high temperature data. This is hardly a realistic physical point of view as one would expect $\rho \propto T^5$ as $T \rightarrow 0^{\circ}\text{K}$, or something similar depending on the similarity of the liquid to a collection of Debye oscillators.

Considerable theoretical interest has been shown in the function $|F(\vec{K})|$, the Fourier transform of the scattering potential⁽⁹⁾. Because we assumed a quasi-free electron model for the liquid $|F(\vec{K})|$ should be relatively small. This can be justified by the method of the pseudopotential as pointed out by Ziman.⁽⁹⁾

Even though the actual potential acting on the electrons is usually very strong and varies rapidly in space the kinetic energy of the valence electrons near the nucleus is nearly large enough to compensate the action of the actual ion-core potential. In normal metals, one can then treat this compensation as though the valence electrons were scattered by a weak pseudopotential.⁽⁹⁾

Because of the thermal fluctuations in density one would naturally expect $|F(\vec{K})|$ to exhibit some temperature dependence. However, since $|F(\vec{K})|$ results from integration only over a given atomic cell, its temperature dependence will hardly be discernible and so we can treat it as constant. Estimates of $|F(\vec{K})|$ may be obtained following arguments first put forward by Ziman.⁽⁹⁾ A more direct approach to the problem may be possible by the method of Augmented Plane Waves first introduced by Slater and co-workers⁽¹⁰⁾.

In general, the tendency has been to separate the resistivity into two terms, (a) a temperature independent term called the structure term, and (b) a temperature dependent term more recently associated with "plasma scattering".⁽⁹⁾ As a matter of fact, as we have already indicated, both terms are structure terms since they both arise from correlations in the density fluctuations in the liquid. For example, the temperature dependence found by Ziman and others⁽⁹⁾ based on a "plasma" term can be shown to be essentially equivalent to the temperature term we have derived. The primary distinction between the "plasma" theory and the correlated fluctuation model is that the plasma model considers the system to be a random one whereas we treat the problem in terms of the actual physical symmetry of the liquid.

A further point concerning the thermal term in ρ is the fact that the high temperature behavior of ρ is essentially non-linear for both constant pressure and constant volume. This result is really not new since the temperature dependence of the compressibility should lead to similar behavior in Ziman's result. Basically, such temperature behavior arises from the anharmonic character of the ion-core oscillations in both cases. Ultimately we are led to the conclusion that temperature variations of the correlation function $z(r)$ determine the essential temperature dependence of the resistivity of a simple metal. Measurements of $z(r)$ as a function of temperature at constant volume are currently being carried out⁽¹¹⁾ to test this result.

As we can see from Figures 2 and 3, there is a considerable similarity in the behavior of the resistivity as a function of temperature at constant pressure for both sodium and mercury. This is interesting since the electronic structures of the two elements are quite dissimilar. Furthermore, our calculations are based upon assumptions which best apply to sodium. No explanation can be given for this result at the present time.

In the case of resistivity measured at constant volume, sodium and mercury exhibit very different behavior. Sodium shows a resistivity increase while mercury shows a decreasing resistivity with increasing temperature. Unfortunately, in the case of sodium and other alkali metals, these resistivity measurements are only carried out to less

than 100°C above their melting points. Any deviation from a linear temperature dependence for ρ can hardly appear, particularly since the precision in the constant volume measurements is significantly less than those at constant pressure. For this reason we are currently carrying out more precise constant volume measurements to higher temperatures.

In conclusion, we presume that the temperature-dependent electrical resistivity of a pure simple liquid metal is due to the total disorder of the liquid. This disorder is due to the correlated density fluctuations distributed throughout the liquid. These density fluctuations are described quantitatively by the correlation function, $z(r)$, of the liquid. Thus the temperature dependence of $z(r)$ describes the temperature dependence of the disorder and hence the resistivity.

For the case of constant volume behavior, $|\bar{V} \bar{n}|/\bar{n}_0$ is a measure of the volume strain associated with a density fluctuation. From this one can readily see that the parameter C_2 in equation (19) is given approximately by

$$C_2 = 1/\beta_{l,v} \bar{n}_0 \quad (22)$$

where $\beta_{l,v}$ = the appropriate compressibility of the liquid. Substituting (22) into (21) gives a result similar to that found by Ziman⁽⁹⁾ for the resistivity at constant volume.

In order to compute $F(\vec{K})$, the scattering effect on the conduction electrons, we assume that the electrons are nearly free. That is, each electron is assumed to move in the fields of the ion-cores and an average potential due to all the other electrons. The magnitude of this field is small compared to the kinetic energy of the electrons. The average field contributed by the other electrons acts to essentially screen out the effective field of an ion-core beyond its associated atomic volume.

$F(\vec{K})$ is the Fourier transform of the screened potential associated with a given atomic cell in the liquid. In general, $F(\vec{K})$ will fluctuate slightly from one cell to another with the density fluctuations of the liquid. Since the ion-core fields are almost completely screened near the nucleus the only effect of thermal fluctuations is to disturb the form of $V_{pn}(\vec{r}-\vec{r}_n)$ near the boundary of the n^{th} atomic cell. However, this will primarily affect the small angle scattering because of the form of $F(\vec{K})$. A similar effect is seen in the temperature dependence of $I(\vec{K})$ in that (16) and (19) indicate that the temperature term is proportional to K instead of K^3 , hence small angle scattering is more favored.

In general, $F(\vec{K})$ will have the following form. $F(\vec{K})$ has its maximum value at $K = 0$. In the vicinity of $K = 0$ the maximum is fairly flat. As we go to higher values of K , $F(\vec{K})$ decreases more

and more rapidly at first, then approaches zero more slowly as K tends towards the value $1/2R$, where R is a measure of the size of an atomic cell. The high angle scattering which is due to the potential near the nucleus is essentially independent of temperature. In any case we can see that the effect of temperature on $F(\vec{K})$ is quite small and so we neglect it.

Ziman has attempted to describe the scattering in a liquid in a rather unique way. What he did was to break up $F(\vec{K})$ into two parts; (a) a pseudopotential term, and (b) a plasma term. He then says that the plasma term dominates the small-angle scattering and hence the temperature dependence of ρ , while the pseudopotential dominates the high-angle scattering. This is not quite so since the pseudopotential term probably is the dominant one at all angles. However, as we have already seen the pseudopotential term is basically insensitive to temperature. On the other hand, the plasma term has a small inherent temperature dependence that we can neglect. The primary temperature dependence of ρ arises from the increasing randomization of the state of short-range order in the liquid by the thermal oscillations of the ion-cores. This effect originates from the temperature dependence of $I(\vec{K})$, i.e., of $z(r)$, and includes contributions from both the pseudopotential and plasma terms in $F(\vec{K})$. In this sense we obtain an expression for the resistivity at constant volume which is analogous

to Ziman's result. As to the question of the behavior shown by mercury we defer discussion until we consider the constant volume effects.⁽⁸⁾

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1a

A, B, Pt. leads for carrying current
C, D, Pt. leads for measuring potential drop

1b

1mm I.D. x 6mm O.D.
pyrex glass capillary
with Pt. leads

Resistivity of pure liquid sodium at
constant pressure (1 atm.)

Resistivity of pure liquid mercury at
constant pressure (1 atm.)

Figure Captions

- Figure 1(a) Schematic representation of the liquid sodium measuring cell.
- Figure 1(b) Schematic representation of the liquid mercury measuring cell.
- Figure 2 Resistivity vs. temperature behavior of liquid sodium at 1 atmosphere pressure. The dashed line is a linear extrapolation of the data obtained near the melting point.
- Figure 3 Resistivity vs. temperature behavior of liquid mercury at 1 atmosphere pressure. The dashed line is a linear extrapolation of the data obtained near the melting point.