Interpretation of the Relaxation Time for the Electrical Conductivity of Elemental Metals Using the Fluctuation Dissipation Theorem

Tadashi Hirayama
National Astronomical Observatory of Japan, Mitaka, Tokyo, Japan 118-8588
(Dated: September 28, 2011)

In an earlier paper we reported that an empirical formula of the electrical conductivity \( \sigma = e^n/\tau_0 \) agrees with experiments within \( \sim 20\% \) for the most of pure elemental metals at room temperature ranges. Here \( \tau_0 = h/k_B T \) is assumed for ‘all’ metals and \( G \) is summed electron numbers in each atomic shell: e.g. \( G = 6 \) for \( Cr(3d^44s^1) \). In this paper, we find that the above \( \tau_0 \) can be deduced if the autocorrelation time of electron fluctuating velocity in a simple fluctuation dissipation theorem is converted to \( 2 < \Delta E > < \Delta \tau > / k_B T \), and if this \( < \Delta E > < \Delta \tau > \) is assumed equal to \( h/2 \) of the Heisenberg’s minimum uncertainty. This corresponds to the closest approach, or head-on collisions. Independent from this, we find that \( \tau_{\text{electron}} = n_{\text{atom}} \) is appropriate for \( \sigma \) in most elemental metals. In discussing temperature dependence of \( \sigma \sim T^{-5} \), besides use of the Debye temperature unit (\( \Theta_D \)), the temperature unit of \( \Theta_B \equiv \hbar \omega_{pi} / k_B \) is found to be equally acceptable. Here \( \omega_{pi} \) is the ion plasma frequency, only depending on \( n_{\text{electrons}} \) unlike somewhat ambiguous \( \Theta_D \).

1. Introduction

In the previous paper [1] (Paper I), we found empirically that absolute experimental values of the electrical conductivity \( \sigma \) for most of the pure elemental metals at room temperature can be well reproduced \( (\sim 20\%) \) by

\[
\sigma = \frac{n_{\text{atom}} e^2}{m G} \tau_0, \tag{1}
\]

where the relaxation time \( \tau_0 \) is assumed to be

\[
\tau_0 = \frac{h}{k_B T} \tag{2}
\]

for ‘all’ metals. Here \( n_{\text{atom}} \) is the number density of atom in each metal and \( m \) is the true electron mass. The factor \( G \) is integer and is summed numbers of outer electrons in the electron configuration of each atom such as \( G = 1 \) for \( Cu(4s^1) \), \( G = 1+2 = 3 \) for \( In^{49}(5s^24p^1) \), or \( G = 1+4 = 5 \) for \( Nb^{41}(3d^44s^1) \). These \( G \) values are empirically selected to match the observed \( \sigma \). Note that we treat metals of normal geometrical size at ordinary pressure.

In contrast to our formulae, the conventional Drude form \( \sigma = ne^2\tau/m^* \) requires the values of \( Z = n/n_{\text{atom}} \) for \( n \) (the electron number density), \( m^* \) (the effective electron mass), and in particular \( \tau \) (the relaxation time). This is always presented in well-read standard textbooks [2][3], but unfortunately they do not present conclusive ways how to calculate ‘absolute values’ of \( \sigma \). As noted in paper I, though Lifshitz and Pitaevskii [2] and Abrikosov [3] suggest the form of \( \tau_0 \sim h/k_B T \), how accurate their ‘~’ signs is not clear, nor they treat nonmonovalent metals. These issues are of fundamental importance, but they are forgotten or ignored as research works in the world of solid state physics today.

Now, examples of the ratio of \( \tau_0 \) from eq.(2) to \( \tau_{\text{obs}} \) determined from eq.(1) using the experimental resistivity and \( G = 1 \) are \( \tau_0/\tau_{\text{obs}} = 0.98(\text{Na}), 0.97(\text{K}), 0.99(\text{Rb}) \), 1.05(Cu), and 0.95(Au) at room temperature ranges (hereafter \( T_{\text{room}} \)). Because of this remarkable closeness to unity, it is tempting to assume that there may be an extremely simple explanation for \( \tau_0 = h/k_B T \), which is the major theme of this paper.

For this purpose, first we search for the connection of \( \tau_0 \) to the fluctuation dissipation theorem, FDT [2][3]. In order to reproduce \( \tau_0 = h/k_B T \), we find that by converting \( H = \frac{1}{2} \int_{-\infty}^{\infty} < m \{ \mathbf{v}(t) \} \mathbf{v}(t) > dt \) used in a simple FDT to \( H = (\Delta E)^2 > 1/(\Delta \tau)^2 \), this \( H \) must take the minimum value of \( h/2 \) expected from the uncertainty principle.

Secondly, we find that the electron number density \( n \) which does not appear in eq.(1) is satisfied by \( n = n_{\text{atom}} \), i.e. \( Z = 1 \), which is of course only applicable to ‘conductivity of elemental metals’.

Since eqs.(1) and (2) reproduce the experiments quite well for the most metals at \( T_{\text{room}} \), we can reproduce the observed ‘absolute values’ of \( \rho = 1/\sigma \) at low temperature ranges where \( \rho \propto T^5 \) is observed, if we employ the Grüneisen-Bloch formula. The Debye temperature \( \Theta_D \) itself used here as a temperature unit is however as is well-known dependent upon the temperature where it is determined or upon methods of derivation, and thus not unique. Then we attempt to use the ion-plasma temperature \( \Theta_B \) as an alternative unit, determined from \( k_B \Theta_B = \hbar \omega_{pi} \). Here \( \omega_{pi} = (n e^2 Z^2 / \epsilon_0 M)^{1/2} \) is the ion plasma angular frequency where \( M \) is the ion mass. We find that use of the \( \Theta_B \)-unit for the electrical resistivity and specific heat \( C_v \) is equally acceptable, or even better in that it requires only the knowledge of \( n \), hence unique.

2. Interpreting Relaxation Time

The classical representation of the fluctuation dissipation theorem (FDT) for the isotropic electrical conductivity
\[ \sigma = n e^2 \tau_K/m, \]  
\[ \tau_K = \frac{m}{k_B T} \int_0^{\infty} < v(0)v(t) > dt. \]  

Thus in order to obtain \( \tau_K = \tau_0 \) \((G = 1 \text{ is implicitly assumed in eq.}(3))\), we need

\[ H = \frac{\tau_K k_B T}{2} = \frac{1}{2} \int_0^{\infty} < mv(0)v(t) > dt = \frac{\hbar}{2} \]  

Here \( v(t) \) is the fluctuating electron velocities parallel to the given electric field. (Thermal fluctuation is of course expected without electric fields, and is on the order of \((4f(1 - f)/N)^{1/2}\), in unit of the average energy where \( f(\epsilon) \) is the Fermi distribution function and \( N \) is the total number of electrons in a volume \( V \). Thus the fluctuation is occurring around the Fermi energy \( E_F \) with the width \( \approx 2k_B T \). See detail in Appendix A.)

Besides an obvious relation of the autocorrelation of \( < v(0)v(t) > = < v(t_1)v(t + t_1) > \) for any \( t_1 \) in the assumed stationary stochastic processes, we adopt \( H = \frac{1}{2} mv(0)v(t) \Delta t, \) where \( \Delta t \) is chosen to reproduce the value of \( H \). This may be not unreasonable if we consider that the autocorrelation function rapidly decreases as \( \exp(-t/\tau) \) for the relaxation processes. We approximate \( H = \frac{1}{2} mv^2 \Delta t \), and interpret (4) as expressing

\[ H = \frac{1}{2} mv^2 \Delta t = \frac{\hbar}{2}. \]  

If \( mv = \hbar k \) and \( v(t) \Delta t = \Delta x \) are used, we still obtain

\[ H = \frac{1}{2} \langle \hbar k(t) \times v(t) \Delta t \rangle = \frac{1}{2} \hbar \langle k \Delta x \rangle = \frac{\hbar}{2}. \]  

While the minimum given in the Heisenberg relation is \( <(\Delta E)^2 >^{1/2} <(\Delta t)^2 >^{1/2} \rangle = (\Delta E)_{\text{rms}}(\Delta t)_{\text{rms}} = \hbar/2 \), it was necessary to adopt it to match \( \tau_0 \).

Reversing the logic, assume that \( H = < \frac{1}{2} mv^2 \Delta t > \) takes the minimum uncertainty value of \( h/2 \) as suggested in eq. (6) or (7), and assume that eqs. (3) and (4) hold, we obtain \( \tau_0 = \tau_K \) and reach \( \tau_0 = \hbar/k_B T \). Though it seems rather difficult to escape from this statement, we later in §4 discuss relation to the case of \( \rho = 1/\sigma = \infty \) \( T^5 \) and physical meaning of eq. (1) at the end of §4 and in §6 (See also Appendix B).

3. \( n/n_{\text{atom}} \) in Multi-Band Metals

Though eq.(1) needs only values of \( n_{\text{atom}} \), naturally we wish to know \( n \) or \( Z = n/n_{\text{atom}} \). This \( Z \) value is tabulated only for 20 metals in Kittel’s table \( \ref{4} \), while the other quantities are tabulated for almost all metals, indicating that \( Z \) is not easy to assign. Let us recall the well-known derivation \( \sigma = j_x/E_x \) for a single band as preparation for multi-band metals; e.g. each one of five ‘d’ and one ‘s’ bands in Cr(3d\(^5\)4s\(^1\)). We rewrite the current density as

\[ j_x = -e \int v_x f dk' = -e \int \frac{\hbar k_x (f - f_0)}{m} dk', \]  

using \( mv_x = \hbar k_x \), \( dk' = 2\pi dk/(2\pi) \text{ and } \int v_x f dk' = 0 \), while \( f_0 \) and \( f \) are unperturbed and perturbed Fermi distribution function, respectively. Given the electric field \( E_x \) in the \( x \) direction entering the ‘steady’ Boltzmann equation

\[ \frac{\partial f}{\partial t} - e E_x \frac{\partial f}{\partial k_x} \approx -e E_x \frac{\partial f_0}{\partial k_x} = -\frac{f - f_0}{\tau_0}, \]  

we obtain from eq. (8)

\[ \frac{\sigma}{e^2 \tau_0/m} = -\int k_x \frac{\partial f_0}{\partial k_x} dk' = \int k_x \frac{dk}{4\pi^3} = n, \]  

by eliminating \( (f - f_0) \) and using \( k \)-independent \( \tau_0 \) of eq. (2). Because of the factor \( \partial f_0/\partial k_x \), not only those bands in which the state density does not extend beyond the Fermi energy do not contribute to \( \sigma \) such as 3d\(^{10}\) of Cu as noted in Paper I (see e.g. ref. [12] Fig.7,12, left), but also only electrons having the energy of \((1 \pm 2k_B T/E_F)E_F \cong E_F \) are contributing to \( \sigma \) (\( E_F \)=Fermi energy=2-7eV for \( Z=1 \)). Partial integration over \( dk_x \) within the primitive cell leads to the second equality. The final equality leads to \( n \), \( n = k_x^3/3\pi^2 \) and \( k_F = (2mE_F)^{1/2}/h \) hold. This means that \( \sigma/(e^2\tau_0/m) \) does not depend upon the state density of electrons at \( E_F \), nor respective bands, but it is simply equal to \( n \). Note that even for the multi-bands discussed below, the departure from \( dk = 4\pi k^2 dk \) (by a multiple factor of 1.2-1.6 for most metals) appears to change only the value of \( E_F \). The rough derivation above may be sufficient for the discussion below.

For multi-band metals, we adopt the total resistivity

\[ \rho = \Sigma \rho_i, \]  

where \( \rho_i \equiv 1/\sigma_i \) as in Aschcroft and Mermin [3] (see eqs.(13.20-22) and discussions followed). The average momentum equation can be obtained from eq. (9) by multiplying by \( mv_x/n \) and integrated over \( dv \), where \( \partial f/\partial t \) leads to the inertia term \( mV_x/dt \) below.

\[ mV_x/dt = -eE_x - mV_x/\tau_0 = 0. \]  

Obviously electrons are on the average decelerated (or ‘resisted’) by collisions with ions or by phonon scattering \((-mV_x/\tau_0) \). If there are different kinds of ions such as impurity, we should add up \( \Sigma n V_x/\tau_x = mV_x/\tau_\text{tot} \) as the summed resistance (as in the Matthiessen rule). We assume that the same situation occurs among the different bands in elemental metals which may behave independently or additively. This means that for the multi-bands metals \( \tau_0 \) should be replaced by \( \tau_\text{tot} \), where \( \tau_\text{tot} \) is given
by $1/\tau_{\text{tot}} = \Sigma(1/\tau_i)$. As a result of $\rho_i = m/(ne^2\tau_i)$, the total resistivity is $\rho = \Sigma\rho_i = m/(ne^2\tau_{\text{tot}})$. Further we assume that every $\tau_i$ is equal to $\tau_0 = \hbar/k_B T$, as can be surmised by the derivation for the single band. Because $G$ is found to be the sum of outer electron numbers in electron configuration, which is nothing but numbers of responsible bands, $1/\tau_{\text{tot}} = \Sigma(1/\tau_i) = G/\tau_0$ results, leading to $\rho = e^2/\tau_0 n/(mG)$.

Since we found $\sigma = e^2\tau_0 n_{\text{atom}}/(mG)$ in eq. (1) empirically from $G \approx G_{\text{obs}}$, it is compatible with the above only when $Z_{\text{eff}} \equiv n/n_{\text{atom}} = 1$ holds. Namely the ‘effective’ valence electron number $Z_{\text{eff}}$ responsible for the electrical conductivity is ‘unity’ for the most of elemental metals!

This is consistent with $G=1$ for Cu(3d$^{10}$2s$^1$), while e.g. for the cohesive energy, use of $Z$(Cu)=$11$ may be relevant [10]. It seems thus unnecessary to introduce the effective electron mass $m^*$ to find $\sigma$ and $\lambda$ (thermal conductivity, discussed in Paper I), if not for other purposes.

Summarizing, we assume $\tau_0$ for each $i$-band and $\rho = \Sigma\rho_i \propto \Sigma(1/\tau_i) = \Sigma_i 1/\tau_0 = G/\tau_0$. Since this $\rho = mG/(ne^2\tau_0)$ must be equal to $\rho = mG/(n_{\text{atom}} e^2\tau_0)$ from the empirical eq. (1), we obtain for $\rho$ of all elemental metals

$$Z_{\text{eff}} = n/n_{\text{atom}} = 1.$$  (13)

Thus e.g. in Al([Ne]3s$^2$3p), $Z_{\text{eff}}$ is 1 for $\rho$, different from $Z_{\text{eff}} = 3$ for the cohesive energy, for example. Besides, $G=1$ for Al is compatible with the experimental $\rho$ (Paper I). Note that our assertion of eqs. (1) and (2) holds whether $Z_{\text{eff}}$ is 1 or not.

4. Two Temperature Units

To proceed on the theoretical interpretation of $\tau_K$, we extend the resistivity to low temperature ranges, by adopting the Grüneisen-Bloch function $F_{\text{GB}} = F_{\text{GB}}(T)$ (see e.g. eq(9.62) in ref. [2]); $F_{\text{GB}} \propto T$ for $T_{\text{red}} \gg 1$, $F_{\text{GB}} \propto T^5$ for $T_{\text{red}} \ll 1$, and $F_{\text{GB}}(1) = 1$. Here $T_{\text{red}} = T/\Theta_D$ and $\Theta_D$ is the Debye temperature ($T_{\text{red}} = T_{\text{mel}}$). Thus we extend our formulae of eqs. (1) and (2) to the following, assuming that the Grüneisen-Bloch formula is valid.

$$\rho = \frac{mG}{e^2 n_{\text{atom}} \tau_{\alpha}} \left(\frac{1}{\tau_{\alpha}}\right) = \frac{F_{\text{GB}}(T)/T}{\tau_0 F_{\text{GB}}(\Theta_{\alpha})/\Theta_{\alpha}}$$  (15)

Here the subscript $\alpha$ stands either for D or P the ion-plasma temperature (‘D’ for Debye and ‘P’ for plasma). For the high temperature range where $F_{\text{GB}} \propto T$ holds, eq. (15) gives $\tau_0 = \tau_0 \propto T^{-1}$ and we obtain $\rho \propto T$.

Figure 1 in upper right shows the temperature dependency of the observed electrical resistivity $\rho$ divided by temperature, $\rho/T$[\Omega m/K], in unit of $\rho(\Theta_D)/\Theta_D$ for 19 metals. We adopted the same metals used in Fig. 2 for easy rough comparison. Here the Debye temperature $\Theta_D$ is adopted from Kittel [3], which is empirically determined from the lattice specific heat at constant volume $C_V$ in low temperature regions of $C_V \propto T^3$. Because the tabulated temperature steps for $\rho$ [11] are too sparse, i.e. $T$(K)=[78, 273, 573, 973], logarithmic interpolation is made to obtain the ‘observed’ $\rho(\Theta_D)$. Since we are interested whether a different unit as compared to the Debye temperature unit can be employed, this kind of roughness is not problematic. A general trend of proportionality from $T^3$ (dashed line in the middle of the figure) to constant, coinciding roughly with the $F_{\text{GB}}(\Theta_{\text{mel}})$, is apparent. At higher temperature of $T/\Theta_D > 2$, however, the departure from constancy of $\rho/T$ becomes appreciable, so that we plotted in red cross signs the observed points in the range $0.5T_{\text{mel}} < T < T_{\text{mel}}$, where $T_{\text{mel}}$ is the melting points of each metal (factor 0.5 in $0.5T_{\text{mel}}$ is arbitrarily chosen). Discussions hereafter neglect these points.

For reference in the lower right, we show the $\rho/T$-ratio using $\Theta_D$ from ref. [12] determined at the temperature near 1/2 of the to-be-determined Debye temperature from the data plots of experimental $C_V$.

Because of the well-known ambiguity of adopting the Debye temperature (empirically from specific heat, acoustic speeds or $\rho$ itself), and its temperature depen-
dency due to the various fitted temperatures as shown above), we in this paper attempt to use another temperature $\theta_P$ expected from the ion plasma angular frequency $\omega_{\text{pi}}$ as defined below:

$$\theta_P \equiv \hbar \omega_{\text{pi}} / k_B, \quad \omega_{\text{pi}} \equiv (n e^2 Z^2_{\text{eff}} / \epsilon_0 M)^{1/2}$$

(16)

Here $n$ is the electron number density, $\epsilon_0$ is the permittivity of vacuum (1/4$\pi$ in c.g.s. Gauss unit) and $M/\text{kg}$ is mass of each atom. The only unknown parameter in determining $\theta_P$ is the ratio of $n / n_{\text{atom}} \equiv Z_{\text{eff}}$, which we take unity for all the elemental metals from eq. [13].

Mostly $\theta_D / \theta_P$ is 0.9~1.2, while in alkali, In and Tl it is very close to 1/2 and near 2 in Mo, Rh, W, Os and Ir ($\theta_D$ differs among various metals more than $\theta_P$).

The dispersion relation is $\omega = \omega_{\text{pi}} k / (k_{\text{TP}}^2 + k^2)^{1/2}$. Here $k_{\text{TP}} = (e^2 D(E_F) / \epsilon_0)^{1/2} = (4k_F / \pi a_0)^{1/2} \leq n^{1/3}$ is the Thomas-Fermi shielding wave number, where $D(E_F)$ is the electron state density at the Fermi energy, $k_F$ is its wave number and $a_0$ is the Bohr radius (e.g. ref. [8] in eqs.(17.55) and (26.4)).

Figure 1 left plots $[\rho(T)/T] / [\rho(\theta_P)/\theta_P]$ against $T / \theta_P$ as in the Debye-plotting. Both plots either by use of Debye or Plasma temperature unit are found quite similar, indicating that to adopt $\theta_P$ is not out of question, irrespective of theoretical reasoning. Full black lines are all $F_{\text{GB}}$ functions, passing through the point of $(1,0,1,0)$, and of course it is identical to the ones used which should be the upper envelope of the observed data points near $X$ (abscissa) $\approx 0.5$. The much simplified eq. (17) is, if any merit in it, to show the $\theta$ dependency clearly. At the same time $X = X_{\text{red}}$ and $Y = \sin^4(T_{\text{red}} \times 3\pi/2)$, and $Y = 1$ for $X > 1/3$ give an identical curve, which is in some cases convenient since the same $X$ value as the Grüneisen curve is used; e.g the maximum ratio between two curves is 1.6 at $X_{\text{red}} = 0.2$.

Figure 2 left plots the observed $C_P/(3R)$ from ref. [11] (upper) and $C_V/(3R)$ calculated from $C_P/(3R)$ (lower), discussed below against $T / \theta_P$, and in the right, similar plots against $T / \theta_D$ both for 19 metals. Here $R$ is the gas constant. The temperature step is again sparse; [100, 200, 298.15, 400, 600] K. If we compare the left $C_V/(3R)\text{ (plsm)}$, meaning plasma, and, right $C_V/(3R)\text{(Dhy)}$, there is no large difference between the two, and the $C_V/(3R)\text{ (plsm)}$ by the use of the ion plasma temperature shows smaller scatter from the Debye function (full lines). Thus use of the plasma temperature as the temperature unit, which needs no adjustments from experiments, is not restricted to the resistivity as in Fig.1 such that eqs.(14) and (15) with $\alpha = P$ may be allowed to be one possible standard.

Below are some remarks. The bottom curves are $C_P/C_V$ from $C_P/(JK^{-1} \cdot \text{mol}^{-1}) = C_V + (3\alpha T)^2 V_m / \lambda$ for

FIG. 2: Specific heat (usual one from lattice) vs. temperature. Experimental values of $C_P/(3R)$ and $C_V/(3R)$ are plotted against $T / \theta_P$ in black cross marks ($\alpha = P$, left and $\alpha = D$, right). Red plus signs are those at temperatures $0.5T_{\text{melt}} < T < T_{\text{melt}}$ as in Fig. 1. Upper 5-full lines are all the same Debye functions. Two bottom figures (left and right) plot $C_P/C_V$ for each metal used for conversion from $C_P$ to $C_V$. 

Below are some remarks. The bottom curves are $C_P/C_V$ from $C_P/(JK^{-1} \cdot \text{mol}^{-1}) = C_V + (3\alpha T)^2 V_m / \lambda$ for
each metal. Here \( \alpha_0 = \alpha_l(T) \) is the linear thermal expansion coefficient \([11]\), \( \chi \) is the isothermal compressibility \([3]\), and \( V_m \) is the volume/mol=atomic weight/metal density. The down-shifted plot denoted as \( C_V/3R \) (Dby,\( 1/2 \)) as in Fig.1 shows naturally smaller scatter than the plot denoted as \( C_V(Dby) \) from the Debye temperature determined at much lower temperature. Red plus plots are for \( 0.5T_{\text{melt}} < T < T_{\text{melt}} \) as before. Full lines are all the same exact Debye functions, which again passes (1,1)-point and the limiting value is \( 1.05014=1/0.95225 \). Dashed line is the limiting \( C_V \propto T^3 \).

If the same correction factor \( C_V/C_D \) is tentatively applied to \( \rho(T) \) in Fig.1, the corrected plot becomes closer to \( \rho/T=\text{constant} \) for \( T/T_a \geq 1 \). It is clear that some kind of small correction to \( \rho/T \) is needed, because the electron density will decrease due to larger separation between atoms when temperature increases.

The first conclusion of this section is that use of \( \Theta_P \) from the ion plasma frequency as a temperature unit gives reasonable temperature dependence for both the resistivity and specific heat, and it is unique as compared to \( \Theta_P \), such that eqs.\((14) \) and \((15) \) for \( \alpha=P \) may be more appropriate. Now the applicable range of \( \tau_K \) is restricted to e.g. \( \rho(T)/T \approx \rho(\Theta_P)/\Theta_P \), meaning the deflection angle be \( \theta > \pi/2 \) as seen particularly in the sin\(^2\)(\( \theta/2 \))-plot of Fig.1. The latter implies the close encounter, or a small impact parameter, and suggests, as the second conclusion of this section, that the minimum uncertainty of \( h/2 \) is maintained for \( \tau_K \) and hence \( \tau_0 \) may well be due to the close collisions. These arguments could have been presented by employing the Debye temperature unit, but now by the use of \( \Theta_P \) these become less ambiguous.

We note a similarity between the present close collision and the electron in the first Bohr orbital in atomic hydrogen, where the quantized angular momentum \( mvr = h \) is conserved in the circular and closest orbital. In the present case of the elastic collision in a hyperbolic orbital, the angular momentum is still conserved, and its minimum absolute value is \( mvr = hkr = h/2 \).

### 5. Electron Specific Heat

The electron specific heat, discernible only below a few Kelvin or so, is given by \( C_{Ve} = \pi^4D(E_F)k_B^2T/3 \), where \( D(E_F) \) is the number of states per energy per atom. For the free electron model \( D(E_F) = 3/(2E_F) \) holds, leading to \( C_{Ve} = \pi^2k_B^2T/2E_F \). The ratio \( C_{Ve,\text{obs}}/C_{Ve,\text{theo}} \) is conventionally expressed by \( m^*/m \) (\( m^* \)=the thermal effective electron mass), and \( m^*/m \) amounts to 10 or more for transition metals if the free electron model is used for the theoretical \( C_{Ve,\text{theo}} \) (see e.g. ref.\([2]\), table 6.2).

However if we adopt \( D(E_F) \) from the extensive calculation of Moruzzi \textit{et al.}\([10]\) and \( C_{Ve,\text{obs}} \) from ref.\([3]\), we find on the average \( m^*/m = 1.48 \pm 0.89 \) for 30 metals down to the period starting from Rb to In. If we exclude six metals showing \( m^*/m > 2.0 \), the average becomes \( m^*/m = 1.11 \pm 0.29 \), which is quite satisfactory.

Values of \( m/m^* \) for excluded six metals are 2.6(Sc), 2.4(V), 2.5(Mn), 4.9(Sr), 3.1(Y), and 2.4(Nb). For example, Sr shows a sharp drop in \( D(E_F) \) near \( E_F \)\([10]\), suggesting that \( D(E_F) = 0.31 \) could have been much larger, and accordingly \( m/m^* \) may become closer to unity. A similar situation is seen in \( Y \) (\( D(E_F) = 1.41 \)), which has a steep peak of \( D(E) \) just below \( E_F \).

Thus we can safely say that the theoretical understanding of \( C_{Ve} \) is rather satisfactory for the elemental metals (except perhaps for semi-metals not included in Moruzzi \textit{et al.}) so that we need not concern it when discussing other physical quantities.

### 6. Discussion and Conclusion

We found that the empirically well established \( \tau_0 = h/k_B T \) for the room temperature range in elemental metals (Paper I) can be deduced in the following way. We take conversion

\[
\int_0^\infty \frac{m}{h}v_0(t)v(t)dt = \frac{mv_0^2}{2} = \frac{\Delta E\Delta t}{m} > 0 \quad (18)
\]

(see Appendix A for the second equality), and assume

\[
\Delta E\Delta t = h/2,
\]

then we obtain

\[
\tau_K \equiv \frac{h}{k_B T} \int_0^\infty < v(0)v(t) > dt = \frac{h}{k_B T} = \tau_0. \quad (20)
\]

Further simplified \( \tau_0 \)-derivation is to assume from the outset that the relaxation time \( \tau_0 \) in the steady Boltzmann equation is equal to the autocorrelation time of the normalized fluctuating thermal velocity \( \tau_K \) as in eq.\((B1)\). Namely

\[
-eE_x \frac{\partial f_0}{\hbar \partial k_x} = -\frac{f - f_0}{\tau_K},
\]

where

\[
\tau_K = \int_0^\infty < v(0)v(t) > dt \quad (22)
\]

This might be regarded as a basis of derivation of the simple classical FDT, if so wished. Then we evaluate \( \tau_K \), assuming eq.\((19) \) and using eq.\((18) \). In this case \( \tau_0 \) entering the steady Boltzmann equation should better be called ‘correlation time’ rather than ‘relaxation time’. At the same time the once discarded ‘collision time’, if not by all people, be retained because without notion of ‘collisions’, \( \tau_0 = h/k_B T \) cannot be understood in closest collisions.

For the wider temperature ranges, we can well reproduce the observed ‘absolute’ values of electrical resistivity \( \rho \) by eqs.\((14) \) and \((15) \), exception being \( T \) higher than a fraction of \( T_{\text{melt}} \). Here the latter assumes the Grünisen-Bloch function, where only the relative \( \rho \) values can be given as eq.\((9.62) \) of ref.\([2]\).
Further, we find that $n_{\text{atom}}$ used in eqs.(1) and (14) is equal to $n$, i.e. $Z_{\text{eff}} = 1$ for $\rho$ and for the thermal conductivity too (Paper I), though only in elemental metals, and not necessarily applicable to other applications (a short summary above eq.(13)).

If we accept $Z_{\text{eff}}=1$, the temperature unit from the ion-plasma frequency, $k_{B}\Theta_{P} = \hbar\omega_{p}$, becomes useful, in that the unique temperature value only dependent upon the electron density $n$ can be defined such that the observed $\rho/T$ and $C_{v}$ can be represented quite similarly or slightly better than use of $\Theta_{P}$ unit (Figs.1-2). Regarding the excitation of ion-plasmons in eq. (16) of $\hbar\omega_{pi}$, one might think of equilibration with the ubiquitous black-body radiation inside the metal, though one needs a careful study.

Eq. (19) $\langle \Delta E\Delta t \rangle = \hbar/2$, is applicable to the large angle scattering, implying close collisions with small impact parameters. We mentioned at the end of §4 the similarity of the quantized angular momentum $mv\theta = \hbar$ in the first Bohr orbital. Another comparison is to use a harmonic oscillator (one-dimensional, 1-D) where $\Delta E\Delta t = \hbar/2$ is realized in the closest oscillation with a Gaussian wave function, and to consider collisions with the scattering angle of $\theta = \pi$, i.e. 1-D head-on collisions (zero impact parameters). Difference between the two is bounded or unbounded motion, but with the same closest approach, giving the same $\langle \Delta E\Delta t \rangle = \hbar/2$.

### Appendix A: Fluctuation Amplitudes

In order to find the amplitude of energy fluctuations, we use the fluctuation of electron numbers $\Delta N$ in a volume $V$ as given in Landau and Lifshitz [16], eq.(113.6)

$$\langle (\Delta N)^2 \rangle = G_{N} f \times (1 - f), \tag{A1}$$

which is derived from partial derivative of the Fermi distribution function $f = 1/\{\exp[(\epsilon - \mu)/k_{B}T] + 1\}$ with respect to the chemical potential $\mu$. This $\mu$ is practically the same as the Fermi energy $E_{F}$. Here $G_{N}$ is a scalar of states number given by

$$G_{N} = d \left[ \frac{4\pi}{3} \frac{p^{3}}{\hbar} \right] V = \frac{k^{3}dk}{\pi^{2}k} \frac{3}{2} \frac{de}{E_{F}}, \tag{A2}$$

where use is made of $p = \hbar k$, $n = 3\pi^{2}k_{B}^{3}, dk/k_{P} = de/2E_{F}$, and $N = nV$ ($G_{N} = DNde$, where $D$ is the conventional state density). Multiplying eq. (A1) by $\epsilon^{2}$ and using $\langle (\Delta E)^{2} \rangle = \langle (\epsilon\Delta N)^{2} \rangle$, we find

$$\sqrt{\langle (\Delta E)^{2} \rangle} < \frac{\langle E \rangle}{2} = \left[ \frac{3f(1-f)}{2N} \frac{de}{E_{F}} \right]^{1/2} \propto \frac{1}{\sqrt{N}} \tag{A3}$$

The relative fluctuation eq.(A3) is dependent upon sizes ($\propto 1/\sqrt{N}$) as in the Boltzmann distribution and dependent upon the width of energy spectrum $de$. Besides, it is appreciable only near $\epsilon \approx E_{F}$ (max $f(1-f)$) such that below $\epsilon \sim E_{F} - 2k_{B}T$, $f$ is saturated at unity so that there is no fluctuations in $\Delta N$ nor $\Delta E$ there. Thus

$$\sqrt{\langle (\Delta E)^{2} \rangle} = \langle mv^{2}/2 \rangle \tag{A4}$$

should hold, where $mv^{2}/2$ is the thermal energy measured from the center value of $\epsilon = E_{F}$. Note that if we adopt $f(1-f)de \approx de \approx k_{B}T$, this becomes identical to the problem-answer at the end of §113 in ref.[10].

### Appendix B: Correlation Time in FDT

As emphasized by Kubo [9] in p.580, unless one introduces some physical models the FDT does not give useful answers, even though it may be correct. This is shown in the ‘simplest example of the independently moving charged particles in the classical system’ (p.585), i.e. eq.(4). Utilizing a normalized velocity function $v(t)/v_{T}$ where $v_{T} = (k_{B}T/m)^{1/2}$ and introducing the normalized autocorrelation function $C$, eq.(4) becomes

$$\tau_{K} = \int_{0}^{\infty} \frac{v(0)}{v_{T}} \frac{v(t)}{v_{T}} dt = \int_{0}^{\infty} C(t) dt = \tau_{\text{cor}}. \tag{B1}$$

This is almost a definition of correlation time as seen in $C(t) = C(0)\exp(-t/\tau_{\text{cor}})$. But if it is so, $\tau_{0} = \tau_{K}$ might be used directly in the Boltzmann equation eq.(9).
[12] G. Burns, in *Solid State Physics* Vol. 4 (Academic Press, 1985).
[13] Phys. Soc. of Japan, *Butsuri-Deta-Jiten, Data Book of Physics* (Asakura-shoten, Tokyo, 2006) [in Japanese].
[14] K. Mendelsohn, Can. J. Phys. 34, 1315 (1956).
[15] K. Levy et al., Phys. Rev. Lett. 43, 1822 (1979).
[16] L. L. Landau and E. M. Lifshitz, *Statistical Physics I* (Nauka, Moscow, 1976) [Japanese translation].