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# BOLTZMANN THEORY AND RESISTIVITY OF METALS

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### Abstract

Often Boltzmann theory works very well. Since the underlying basis of
the theory is firm and well understood, we usually understand when it should
work and when it should not. This article reviews the theory with a special
focus on resistivity of real metals. The formal theory is carefully worked out.
The Bloch-Grüneisen formula is derived and its limitations are examined. A
method is explained for extracting the coupling constant $\lambda_{\text{tr}}$ from resistivity
with the help of band theory.

## I. INTRODUCTION

Figure 1 shows the resistivity [1] of Ti, Zr, and Hf measured at temperatures
up to 300K. The shape of the $\rho(T)$ curves is characteristic of ordinary metals
in which electron-phonon scattering gives the temperature dependence. The
solid lines are fits to the measurements using the Bloch-Grüneisen formula
[2]. This formula is an approximate solution of the Bloch-Boltzmann equation,
with the additional approximation of a Debye phonon spectrum. This works
very well for reasons that will be explained. The fits have three parameters:
the residual resistivity $\rho_0$ which shifts the curves along the vertical axis, the
Debye temperature $\Theta_D$ which scales the curves on the horizontal axis, and
a third parameter, $\lambda_{\text{tr}}/\omega_p^2$, which scales the curves on the vertical axis. The
fitted values are given in table 1. $\rho_0$ is sample dependent and not particularly
important. The value of $\Theta_D$ varies depending on which temperature interval is
fitted. Here I chose compromise values to fit approximately the whole interval

0–300K, obtaining values surprisingly close to Debye temperatures extracted from the low temperature ($T^3$) heat capacity, shown also in table 1 [3]. The interesting parameters are the "Drude plasma frequency" $\omega_p$ and the electron-phonon coupling constant $\lambda_{tr}$, closely related to the constant $\lambda$ which occurs in superconductivity and renormalizes the low $T$ coefficient $\gamma$ of the specific heat. Unfortunately, there is no good way to extract the parameters $\omega_p$ and $\lambda_{tr}$ separately from experiment. However, local density approximation (LDA) band theory seems very often to give reliable values of $\omega_p$ [4,5], so that $\lambda_{tr}$ can be extracted from resistivity data. The values shown in table 1 agree sufficiently well with McMillan's $\lambda$'s [6] extracted from the superconducting $T_c$. The theory works very well indeed for these metals, as for all the s-, p-, and d-band metallic elements.
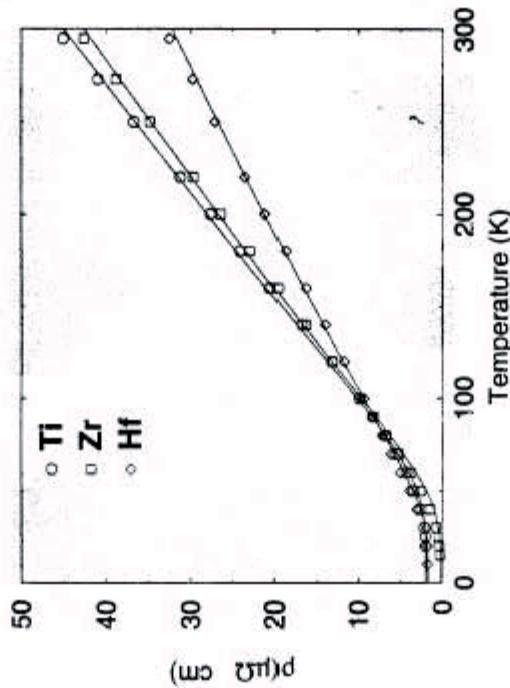


Figure 1. Resistivity of Ti, Zr, and Hf [1] versus temperature. Solid curves are Bloch-Grüneisen fits explained in the text.

| | Ti | Zr | Hf | units |
|---|---|---|---|---|
| calculations | | | | |
| $\Omega_p$ | 3.6 | 3.8 | 4.0 | eV |
| Fermi vel. $\langle v_F^2 \rangle^{\frac{1}{2}}$ | 3.2 | 3.6 | 4.7 | $10^5$ m/s |
| Fitted parameters | | | | |
| Debye temp. $\Theta_D$ | 360 | 300 | 250 | K |
| $\Theta_D$ from sp. heat | 420 | 291 | 252 | K |
| electron-phonon $\lambda_{tr}$ | 0.50 | 0.55 | 0.42 | |
| McMillan's $\lambda$ from $T_c$ | 0.38 | 0.41 | 0.44 | |
| residual resist. $\rho_0$ | 2.0 | 0.3 | 1.8 | $\mu\Omega$ cm |
| $\ell$ at 300K | 27 | 28 | 44 | Å |
| $T$ where $\ell = 10$Å | 775 | 800 | 1350 | K |

Table 1. Calculated parameters for Ti, Zr, and Hf from ref. [5], and parameters fitted to the data of ref. [1] shown in fig. 1.

Boltzmann developed his theory to account for the properties of gases. Drude and Lorentz extended this theory to electrons in metals. Sommerfeld and Bloch [7] produced a quantum version. After Landau enlarged our understanding of this theory, it became conventional to denote materials where the theory works by the misnomer "Fermi liquids". A better name would be "quasiparticle gases", because they are not really liquids, just slightly unusual gases. The Boltzmann transport theory in solids follows automatically from the Landau assumption that the low energy and long wavelength properties are all contained in the quasiparticle distribution function. The Boltzmann equation is a beautiful and successful theory which is often misunderstood and underappreciated. For example, it is natural to believe that because it is a gas theory, it could only work for weakly interacting situations. However, this is not at all true – the theory works beautifully for metallic Pb where $\lambda = 1.5$. It

is also widely believed that the theory only works when the lifetime broadening $1/\tau$ of a quasiparticle is small compared to its excitation energy. Again this is false. In Pb at room temperature, the excitation energy is a few times $k_BT$, but $1/\tau = 2\pi\lambda k_BT$ which is 10 times $k_BT$. It is also often believed that a theory based on a Kubo formula is inherently better than one based on a Boltzmann equation. This is not always false. The Kubo formula is in principle exact and can be used to derive interesting (but tiny!) corrections not in the Boltzmann theory, such as "weak localization" effects. However, it is notoriously difficult to find a good approximate way to evaluate the Kubo formula. As shown by Eliashberg [8], Holstein [9], and Prange and Kadanoff [10], the correct answer to leading order in $1/k_F\ell$ is just the Bloch-Boltzmann theory. Quite often when a Kubo formula is used as a starting point, the end result is equivalent (at best) to an approximate solution of the Boltzmann equation.

Why does this theory work, and where does it fail? No one really knows how to answer the first part, since we are unable to prove that perturbation theory converges. The second part is easy. It is necessary for a quasiparticle to propagate far enough to observe the periodicity of the medium it is in. This enables the quasiparticle to be assigned a wavevector. For metals, typically a mean free path $\ell > 10\text{Å}$ is sufficient. The lifetime broadening must not be so large that the "width" $(1/\tau)$ of the state overlaps with other states at the same wavevector $(1/\tau$ should be smaller than $\Delta E$, the separation of bands [11].) This enables the quasiparticle to be assigned an energy, and thus also a group velocity $\partial\epsilon/\partial\vec{k}$. Failure of the gas model is not at all rare. Liquid and amorphous metals and very dirty alloys are typical cases where the quasiparticle gas model fails and "liquid-like" (i. e. non-"Fermi-liquid"-like) behavior can be expected.

The quasiparticle gas model breaks down also just under ordinary electron-phonon interactions. This was first suggested by Fisk and Webb [12] and proven by Cohen and collaborators [13]. Fig. 2 shows a simple example. The high $T$ data for Hf [14-16] lie somewhat above the extrapolated fit from low $T$, which is not especially surprising. Various complications can be added to the Boltzmann theory at high $T$, most importantly thermal expansion, which tends to reduce phonon frequencies and increase vibrational amplitudes and thus increase the resistivity. However, above $\approx 1350$K the slope of the resistivity becomes much smaller than the low $T$ value. This coincides with the result of the Boltzmann theory that 1350K is the temperature at which the mean free path becomes 10Å. Corrections due to the short mean free path cannot in principle be incorporated into a gas theory based just on the distribution function. Off-diagonal elements $< k|\hat{\rho}|k' >$ of the density matrix now inevitably play a role. Above 1350K, the Boltzmann theory can surely no longer be adequate for Hf.

At the opposite extreme from quasiparticle gases is the regime of localized excitations which move and carry currents by hopping [17]. Conductivities improve as $T$ increases, not because of simple activation into free quasiparticle

bands, but because hopping requires assistance by inelastic events. In this regime, a theory can often be constructed which is built on the occupation probability of the localized states. Here again, off-diagonal matrix elements of the quantum density matrix, this time in "site-space", are not needed.
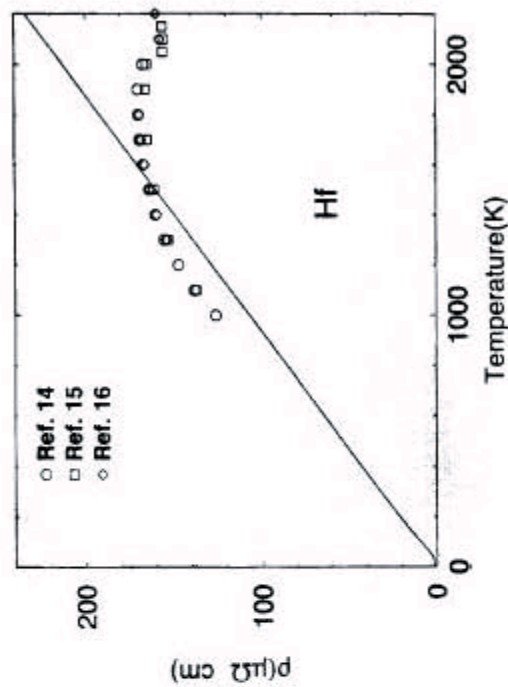


**Figure 2.** Resistivity of Hf [14-16] at high temperature. The solid curve is the same Bloch-Grüneisen fit to the low $T$ data shown in Figure 1.

Contrary to common belief, experiment shows that there is a very large "no man's land" in between these two extremes, the regime of "saturated" resistivity, where simple theoretical pictures have not been found yet, and transport theory becomes in principle very complicated. The phenomena on the other hand are fairly simple, namely transport coefficients are often approximately independent of temperature and disorder, being "saturated" at a "Mott limit" with values that they would have if one took (without justification) the gas theory formulas, but with a mean free path equal to a few angstroms.

Reviews of the quasiparticle gas model for transport are found in the textbooks by Ziman [2], Smith and Jensen [18], Lifshitz and Pitaevskii [19], and Gantmakher and Levinson [20].

## II. SIMPLE THEORY OF RESISTIVITY

In gas theory, the current density $\vec{j}$ is found by summing the current $-e\vec{v}_k$ of each particle,

$$\vec{j} = (-e/\Omega) \sum_k \vec{v}_k F(k) \qquad (1)$$

where the distribution function $F(k)$ is the number of particles in the state $k$, and $\Omega$ is the volume of the sample. The symbol $k$ is short for all relevant quantum numbers $(\vec{k}, n, \sigma)$. The kosher method is to write an evolution equation (the Boltzmann equation) for $F(k)$ and solve it. However, a good qualitative understanding can be found in a much simpler way. The effect of the applied $\vec{E}$-field is to accelerate electrons according to the semi-classical formula

$$\hbar \dot{\vec{k}} = -e\vec{E} \qquad (2)$$

first derived by Bloch [7]. He calculated the time evolution of an electron in a wavepacket, finding that the central wavevector evolved according to Eq. (2). His derivation was for a single band model of a solid. When multiple bands are included, one finds in addition to the semiclassical acceleration, additional oscillatory terms where the $\vec{E}$-field mixes in states from other bands. The oscillation frequencies are the interband transition energies. As long as these frequencies are fast compared to the rate of collisions, the oscillations average to zero in a dc problem. Thus the validity of this semiclassical notion depends on the smallness of a parameter $1/\Delta E\tau$. This parameter is essentially the same as the parameter $1/k_F \ell$ cited in the standard derivations of Boltzmann theory [11].

Because of collisions, the electrons do not accelerate forever, but are on average displaced in $\vec{k}$-space by an amount $\delta \vec{k} = \dot{\vec{k}}\tau$. This means that the actual occupancy of the state $\vec{k} + \delta\vec{k}$ in the field, $F(\vec{k} + \delta\vec{k})$, is the same as the occupancy of the unshifted state $\vec{k}$ without the field, $f(\vec{k})$. Combining these ideas gives a formula for the current,

$$j_\alpha = (-e/\Omega) \sum_k v_{k\alpha} f(\vec{k} - \dot{\vec{k}}\tau) = \sigma_{\alpha\beta} E_\beta \qquad (3)$$

$$\sigma_{\alpha\beta} = (n/m^*)_{\alpha\beta} e^2 \tau \qquad (4)$$

$$(n/m^*)_{\alpha\beta} = \Omega^{-1} \sum_k v_{k\alpha} v_{k\beta} (-\partial f/\partial \epsilon_k) \qquad (5)$$

Equation (5) defines the ratio $n/m^*$ to be a tensor, related to the electron effective mass tensor $(1/m^*)_{\alpha\beta} = \hbar^{-2}(\partial^2 \epsilon/\partial k_\alpha \partial k_\beta)$ in the following way. Integrating Eq. (5) by parts, it can be written as

$$(n/m^*)_{\alpha\beta} = \Omega^{-1} \sum_k (1/m^*)_{\alpha\beta} f(k). \qquad (6)$$

In other words, the $(n/m^*)$ tensor is the inverse effective mass tensor summed over all occupied states. In cubic symmetry, $(n/m^*)$ is a scalar. The product $4\pi e^2(n/m^*) = \omega_p^2$ is called the "Drude plasma frequency" and is in general a tensor. The sum over states in Eq. (6) vanishes for completely filled bands. Thus the numerator $n$ has to do with the density of electrons in partially filled states. This is a slippery concept in a metal. For example, in copper, it seems quite sensible to take $n$ to be one electron per atom, but what does one take for palladium, where not just the $5s$ states but also some of the $4d$ states are exposed at the Fermi surfaces? There is no uniquely satisfying choice, so it is best to insist that $n$ and $m^*$ cannot be separately defined, and only their ratio has a physical meaning.

Eq. (5) provides an appropriate formula for a numerical calculation of $(n/m^*)$ using a band structure calculation. The derivative $(-\partial f/\partial \epsilon_k)$ can be replaced by a delta function $\delta(\epsilon_k - \epsilon_F)$. It is not hard to modify a code which calculates the density of states so that it will also calculate the Drude plasma frequency, and in fact the latter is somewhat easier in that the convergence of the $k$-space summation is quicker. However, it should be remembered that density functional theory (DFT, to which LDA is an approximation) does not encourage us to use the eigenvalues $\epsilon_k$ as quasiparticle excitation energies. The velocities $\vec{v}_k$ which appear in the Boltzmann equation are quasiparticle velocities, and not a property of the ground state. Therefore they should be computed using a quasiparticle band scheme, "GW" being currently the most popular approximation. Given the difficulties of such calculations, it is surely legitimate to use LDA eigenvalues as a tentative model for the excitations. My experience [4,5] has been that for all $s$, $p$, and $d$-band metallic elements, LDA eigenvalues give an amazingly reliable value of $(n/m^*)$. There have been fewer tests for compounds. A complete test requires that the value of $\lambda_{tr}$ extracted from $\rho(T)$ should compare reasonably well with the value of $\lambda$ extracted from $T_c$. Pd$_2$Si [21] and NbO [22] have passed the test very well, while there is some evidence that VO$_2$ [23] and the high $T_c$ superconductors [24] do not. A separate issue concerns whether the value of $\lambda_{tr}$ is required to agree closely with the value of $\lambda$. My experience [25] is that these numbers do agree closely in the few cases where they have been consistently calculated. Further there are good reasons, mentioned in sec. X, why the difference should be small.

The physical interpretation of $(n/m^*)$ can be made explicit from the results above. If there were no collisions, then the presence of an $\vec{E}$-field would cause a current to increase at a rate

$$d j_\alpha/dt = (n/m^*)_{\alpha\beta} e^2 E_\beta \qquad (7)$$

This interpretation of $(n/m^*)$ as the rate of current increase per unit $\vec{E}$-field continues to be valid in the full Boltzmann theory. Unfortunately, the phe-

nomenological collision rate $\tau$ becomes complicated in the full theory, and does not remain a simple scalar quantity. However, it turns out that deviations from scalar behavior of $\tau$ are likely to be small, and the phenomenological formulas derived here are useful and quite accurate representations of the full theory. Thus the role of the full theory is mostly just to give a microscopic theory of the temperature dependent number $\tau$.

There is another way to write Eqs. (4,5) which gives an additional insight. Approximating $(-\partial f/\partial \epsilon_k)$ by a delta function at the Fermi surface, and assuming cubic symmetry, we get

$$\sigma = \frac{e^2}{3\Omega}\sum_k v_k \ell_k \delta(\epsilon_k) = \frac{e^2}{12\pi^3\hbar}\int^{FS} dS_k \ell_k \qquad (8)$$

where $\ell_k = v_k\tau$ is the mean free path. Thus the conductivity is just the area of the Fermi surface times the average mean free path. Thus band theory allows the mean free path to be extracted from the measured resistivity provided the area of the Fermi surface is known. LDA theory may sometimes give a wrong Fermi velocity, but Fermi surface area seems quite robust against possible failures of LDA. Therefore the mean free path estimation is equally robust. For a free electron metal, Eq. (8) is equivalent to $\rho = 335(r_s/k_F\ell)$ in units $\mu\Omega$cm. For more complicated metals, a crude estimate of the area of the Fermi surface might be $6(2\pi/a)^2$ (the area of the Brillouin zone of a simple cubic material.) This gives $\rho = (\pi\hbar a/2e^2)(a/\ell)$, or $193(a/\ell)$ in $\mu\Omega$cm if $a$ is taken to be 3Å. These expressions correctly give the order of magnitude of metallic resistivity. At room temperature, the least resistive metal is Ag, with $\rho = 1.6\mu\Omega$cm, while the most resistive metallic elements have $\rho < 150\mu\Omega$cm. Because $a/\ell$ or $1/k_F\ell$ are the small parameters of the theory, one does not expect Boltzmann theory to be applicable if the resistivity is much higher than $100\mu\Omega$cm, unless the metal is very dilute (i.e. large $\tau$, small $k_F$).

## III. THE BOLTZMANN EQUATION

The Landau hypothesis states that the fundamental object of the theory is the distribution function $F(k,\vec{r},t)$ giving the ensemble average occupancy of state $k$ in a fuzzy region of space-time near $(\vec{r},t)$. The time evolution of $F(k,\vec{r},t)$ in gas theory can be expressed as an evolution equation involving only $F$ and no higher order correlations. The particles propagate coherently and are accelerated by external fields. The equation of motion then necessarily has the form

$$F(\vec{k},\vec{r},t+dt) = F(\vec{k}-\dot{\vec{k}}dt, \vec{r}-\dot{\vec{r}}dt, t) + \text{changes caused by collisions} \qquad (9)$$

or in differential form

$$\frac{\partial F}{\partial t} = -\dot{\vec{k}}\cdot\vec{\nabla}_k F - \dot{\vec{r}}\cdot\vec{\nabla}_r F + C_k[F] \qquad (10)$$

where $C_k[F]$ is the "collision integral", a (usually non-linear) functional of the distribution function $F$. Explicit forms for $C_k[F]$ are written down by use of Fermi's "golden rule" to calculate all the processes which alter the occupancy of state $k$. Although my aim is to derive results which do not depend on the details, nevertheless, to be concrete, here is the form of the collision integral for electrons scattering from phonons:

$$C_k^{out} = -\frac{2\pi}{\hbar}\sum_{\pm}\sum_Q |M(k,k+Q)|^2 \delta(\epsilon_{k+Q} \pm \omega_Q - \epsilon_k)$$
$$\times \left[ F(k)(1-F(k+Q))\left(N(\mp Q)+\frac{1}{2}\pm\frac{1}{2}\right)\right] \qquad (11)$$

Here $N(Q,\vec{r},t)$ is the distribution function for phonons of state $Q = (\vec{Q},j)$, which also evolves in time by a similar rate equation. The two terms, designated by + or −, refer to emission of a phonon of wavevector $-\vec{Q}$ and absorption of a phonon of wavevector $\vec{Q}$ respectively. The superscript "out" designates these processes as ones where the population of electron state $k$ is diminished by scattering out of this state. Each such process is accompanied by the reverse process which repopulates the state $k$. The corresponding part of the collision integral, $C_k^{in}$, is identical to Eq. (3) except that the overall sign is positive rather than negative, and the occupation factors contained in brackets [ ] are altered:

$$[\ ] = \left[(1-F(k))F(k+Q)\left(N(\mp Q)+\frac{1}{2}\mp\frac{1}{2}\right)\right] \qquad (12)$$

While the electron distribution function $F$ is evolving by emission or absorption of phonons, simultaneously the phonon distribution function $N$ is necessarily also evolving. The collision integral for phonons, $C_Q[N]$ can be written down in a similar way, using the same matrix elements $M(k,k+Q)$ for scattering of an electron from $k$ to $k+Q$. However, it is almost always assumed that this is unimportant. The justification is usually that the phonons are kept close to equilibrium by anharmonic scattering, so that $N$ can be replaced by the equilibrium Bose-Einstein distribution $n$.

It is the role of band theory to provide values for the quasiparticle energies $\epsilon_k$ and $\omega_Q$ and for the matrix elements $M$. In principle we need to calculate the quasiparticle bands $\epsilon_k$; but, as mentioned in sec. II, using LDA eigenvalues as a model seems to work well. Density functional theory is designed to give correct values of the phonon energies $\omega_Q$, and LDA is very successful in this, but it is far simpler, when possible, to take the phonon dispersion from neutron scattering experiments. Finally, the least understood part is the matrix

element M. In principle we understand which Feynman diagrams are included in this calculation, but in practise the fully screened and vertex-corrected matrix element can only be calculated in a somewhat uncontrolled way, and there is little experience with this for real metals with non-free-electron-like bands. LDA offers the hope that this matrix element might be well represented by the matrix element between LDA eigenstates of the difference of the self-consistent potential before and after the atoms have been displaced. This calculation is possible in principle, and has recently been carried out successfully, for the metals Al and Nb [26]. This was actually not a calculation of $\rho(T)$, but rather of the superconducting $T_c$, which involves the same quasiparticle energies and matrix elements. In fact, the Eliashberg-Migdal theory used to calculate $T_c$ and the Boltzmann theory for $\rho(T)$ have a great deal in common. They both can be derived "rigorously" by making the Migdal approximation. To find $T_c$ one uses a linearized version of the non-linear integral equations, similar to the linearized Boltzmann equation which will be explained in sec. VI, except that the Eliashberg equations are homogeneous and the Boltzmann equation is inhomogeneous. Both equations are typically solved to variational accuracy by an isotropic ansatz. Corrections are second order in the anisotropy, and enhance by small amounts the values of $T_c$ and $\sigma(T)$. Adding impurities simplifies the theory by eliminating this enhancement. In superconductivity this is the "dirty" limit or isotropic approximation. In resistivity, the loss of anisotropy enhancement of $\sigma$ is known as "deviations from Mattheissen's rule."

In spite of the alarming complexity of the scattering operator, it has a number of elegant properties which can be exploited to simplify the solution and to guide the construction of approximations. As one example, when the distribution functions are replaced by the equilibrium Fermi-Dirac and Bose-Einstein distributions (denoted $f_k$ and $n_Q$), the collision terms necessarily vanish, telling us that these distribution functions are stationary under collisions. More than that, the individual processes which contribute to $C^{out}$ in equilibrium precisely cancel the corresponding reverse process in $C^{in}$. This is known as "detailed balance." More impressive, it is not hard to prove, following Boltzmann's famous "H-theorem", that the equilibrium functions $f_k$ and $n_Q$ are the only ones which are stationary under collisions. The proof will be sketched in section V.

## IV. QUASIPARTICLE LIFETIME

The simplest microscopic property of a quasiparticle which depends on interactions is the relaxation rate $1/\tau_{QP}(k)$. This is the rate at which a single excess particle, injected into state k (creating a disturbance in the previously equilibrated system), relaxes back to equilibrium. Thus at time zero the distribution function F deviates from the equilibrium f by a small excess $\delta F_k(t=0)$,

which is zero for all k' except the chosen state k. Interactions cause this excess to decay exponentially at the rate $1/\tau_{QP}(k)$. The Boltzmann equation gives

$$\frac{\partial}{\partial t}\delta F_k(t) = C_k[F(t)] = \left(\frac{\delta C_k}{\delta F_k}\right)_{eq} \delta F_k \quad (13)$$

Here the functional derivative has been used to linearize the collision integral around equilibrium because the deviation is small. The stationary property $C_k[f] = 0$ of the collision operator evaluated at equilibrium has also been used. Thus we obtain the general result, valid for any quasiparticle and any form of interaction

$$1/\tau_{QP}(k) = -\left(\frac{\delta C_k}{\delta F_k}\right)_{eq} \quad (14)$$

In section X, this result will be rewritten in an equally general but more usable form.

## V. GENERAL PROPERTIES OF THE COLLISION INTEGRAL

The collision integral must satisy three fundamental requirements:

$$\left(\frac{d}{dt}\sum_k F_k\right)_{coll} = 0 \quad (15)$$

$$\left(\frac{d}{dt}\sum_k \epsilon_k F_k\right)_{coll} = 0 \quad (16)$$

$$\left(\frac{dS}{dt}\right)_{coll} = \left(\frac{d}{dt}\sum_k s_k\right)_{coll} \geq 0 \quad (17)$$

The first two of these express the fact that particle number and energy must be locally conserved under collisions, and the last expresses the fact that the average net local entropy cannot decrease under collisions. The formula for the local entropy $S(F)$ is expressed by a standard counting argument [27] as a sum over the entropy $s_k$ contained in each state k, and $s_k$ is

$$s_k/k_B = -(1-F_k)\ln(1-F_k) - F_k \ln F_k \quad (18)$$

Carrying out the time derivatives, and using the collision integral for $(F)_{coll}$, the general relations (15-17) become

$$\sum_k C_k[F] = 0 \quad (19)$$

$$\sum_k \epsilon_k C_k[F] = 0 \quad (20)$$

$$\frac{1}{k_B T} W[F] \equiv \sum_k \ln\left(\frac{1}{F_k} - 1\right) C_k[F] \geq 0 \quad (21)$$

We also assert that Eqs. (19,20) are the only conservation laws obeyed by the theory. Eq. (21) is Boltzmann's marvelous "H-theorem" which he proved from the form of the collision integral for particles of a classical gas. I prefer the view that Eq. (21), together with (19) and (20) do not need to be derived, but constitute fundamental constraints which limit the form of the collision integral. Apparently the most general way to make the entropy stay fixed (which defines equilibrium) is to choose $\ln(1/F_k - 1)$ to be a linear combination of the two additively conserved quantities, that is $\beta(\epsilon_k - \mu)$. Then $F_k \to f_k$ is the Fermi-Dirac distribution. This is the proof mentioned above that $f_k$ is the unique distribution which is stationary under collisions. The results of this section, as well as the previous one and the next one, all become correct statements for Bose gases, under appropriate simple modifications. However, for phonon or photon gases, where particle number is not conserved, the conservation laws analogous to (15) and (19) fail, and the entropy is stationary when $\ln(1/N_Q + 1)$ is proportional to the conserved energy; that is $\beta\omega_Q$.

## VI. LINEARIZED BOLTZMANN EQUATION

### A. Maximum Entropy Production

In equilibrium, entropy is maximum and is constant in time. When a dc $\vec{E}$-field is applied, a steady state current flows, and entropy is produced. $T\dot{S}$ is the rate of Joule heating $\Omega \vec{j} \cdot \vec{E}$. A theory for the conductivity can be derived from the principle that the steady state distribution function $\delta F_k$ is the one which maximizes the entropy production $\Omega\sigma E^2$ at fixed field $\vec{E}$, or equivalently, the one which maximizes the conductivity. Equivalently, it is the one which

minimizes the resistivity $\rho = 1/\sigma$, or minimizes the rate of entropy production $\Omega\rho j^2$ at fixed current $\vec{j}$.

We take as a fundamental postulate the existence of a functional $W[F]$ (given in Boltzmann theory by Eq. (21) above) which gives the rate of heat production arising from collisions when there is a non-equilibrium distribution $F$. Of course, when $F = f$ at equilibrium, there is no heat produced, $W[f] = 0$. This is the absolute minimum of the functional, so $\delta W/\delta F = 0$ at equilibrium. Therefore, to lowest order in $\delta F_k$,

$$W = \frac{1}{2}\sum_{kk'} \delta F_k S_{kk'} \delta F_{k'} = \frac{1}{2}(\delta F, S\delta F) \quad (22)$$

where $S_{kk'}$ is a real symmetric and non-negative matrix, the second functional derivative $\delta^2 W/\delta F_k \delta F_{k'}$. An inner product notation $(A, B)$ for functions in $k$-space provides a useful shorthand.

The hypothesis of maximum entropy production tells us that $\delta F_k$ is to be determined by

$$\frac{\delta}{\delta F_k}(W - \vec{\lambda}\cdot\vec{j}) = 0 \quad (23)$$

where $\vec{\lambda}$ is a Lagrange multiplier. Using Eqs. (1) and (22) we get

$$\sum_{k'} S_{kk'}\delta F_{k'} = -e\vec{\lambda}\cdot\vec{v}_k/\Omega \quad (24)$$

$$\delta F = -S^{-1}(e\vec{\lambda}\cdot\vec{v}/\Omega) \quad (25)$$

$$W_{min} = \frac{1}{2}(\delta F, -e\vec{\lambda}\cdot\vec{v}/\Omega) = \frac{1}{2}\vec{\lambda}\cdot\vec{j} \quad (26)$$

Thus we can identify the Lagrange multiplier $\vec{\lambda}$ as $2\vec{E}\Omega$. Eq. (24) is an inhomogeneous linear integral equation which determines the distribution function $\delta F$. This must be the Boltzmann equation!

Turning back to Boltzmann theory, we need to turn Eq. (10) into such a linear integral equation. The space and time dependence $\partial F/\partial t$ and $\vec{\nabla}_r F$ both vanish because the problem involves an $\vec{E}$-field which is constant in space and time. The acceleration $\dot{\vec{k}}$ is given by Eq. (2) which is zeroth order in $\vec{E}$, so $\vec{\nabla}_k F$ can be replaced by $\vec{\nabla}_k f = \hbar\vec{v}_k(\partial f/\partial\epsilon_k)$ which is zeroth order in $\vec{E}$. The right hand side of Eq. (10) needs also to be expanded to first order in $\vec{E}$. Then the Boltzmann equation reads

$$e\vec{E}\cdot\vec{v}_k(\partial f/\partial\epsilon_k) = -\sum_{k'}\frac{\delta C_k}{\delta F_{k'}}\delta F_{k'} \quad (27)$$

For comparison, Eq. (24) can be written as

$$e\vec{E}\cdot\vec{v}_k(\partial f/\partial\epsilon_k) = -\frac{1}{2}\sum_{k'}(\partial f/\partial\epsilon_k)S_{kk'}\delta F_{k'} \quad (28)$$

This tells us that the linearized collision operator $\delta C_k/\delta F_{k'}$ is equal to $(\partial f/\partial\epsilon_k)S_{kk'}/2$, or more explicitly

$$\frac{\delta C_k}{\delta F_{k'}} = \frac{1}{2}\frac{\partial f}{\partial\epsilon_k}\frac{\delta^2 W}{\delta F_k \delta F_{k'}} \quad (29)$$

The linearized collision operator is asymmetric, being the product of a function of $k$ and a symmetric collision operator. It is convenient to define a symmetric collision operator $Q_{kk'}$,

$$Q_{kk'} \equiv \frac{\delta C_k}{\delta F_{k'}}\frac{\partial f}{\partial\epsilon_{k'}} \quad (30)$$

This operator plays a fundamental role in transport theory. It is real symmetric and non-negative, since it is defined in terms of the real symmetric and non-negative operator $S_{kk'}$ in a symmetric way. Its properties are explained in the next subsection.

## B. Linearized Collision Operator

The conservation laws (19,20) and the H-theorem, Eq. (21) place restrictions on the form of the linearized collision operator. Expanding relations (19-21) to first order in $\delta F_k \equiv F_k - f_k$, we get

$$\sum_{k,k'}\frac{\delta C_k}{\delta F_k}\delta F_{k'} = 0 \quad (31)$$

$$\sum_{k,k'}\epsilon_k\frac{\delta C_k}{\delta F_k}\delta F_{k'} = 0 \quad (32)$$

$$W = T\frac{dS}{dt} = \sum_{k,k'}\delta F_k\left[\frac{-k_BT}{f_k(1-f_k)}\right]\frac{\delta C_k}{\delta F_{k'}}\delta F_{k'} \geq 0 \quad (33)$$

The functional derivative is evaluated at the equilibrium distribution. These three relations are all valid for arbitrary deviations $\delta F_k$. The factor in brackets [ ] in Eq. (33) is just $1/(\partial f/\partial\epsilon_k)$. Thus Eq. (33) is an explicit proof of Eq.

(29). This second proof does not use the hypothesis of maximum entropy production, but makes more explicit use of the H-theorem.

We now turn to the interpretation of the operator $Q_{kk'}$ defined in Eq. (30). Its off-diagonal elements $(k \neq k')$ happen to be $(-1/k_BT)$ times the rate $P_{kk'}$ at which transitions occur between states $k$ and $k'$ in equilibrium. To prove this, consider the electrons all to be in equilibrium except one state $k'$ which is definitely empty. Thus at time zero, $\delta F_k$ is zero for all $k$ except $k'$, for which $\delta F_{k'}$ is $-f_{k'}$. Then calculate the time evolution of the population of a state $k$ other than $k'$. It is allowed to linearize the collision operator, giving

$$-(\partial F_k/\partial t)_{coll} = (\delta C_k/\delta F_{k'})f_{k'} \quad (34)$$

This is the rate at which transitions out of state $k$ would occur into state $k'$ if $k'$ were empty. The actual rate in equilibrium for such transitions is just the expression (34) multiplied by the probability $(1-f_{k'})$ that this state is empty. Thus

$$\frac{\delta C_k}{\delta F_{k'}}f_{k'}(1-f_{k'}) = -k_BTQ_{kk'} = P_{kk'} \quad (35)$$

is the equilibrium rate of transitions from $k$ to $k'$.

Previously it was shown that $-k_BTQ_{kk'}$ was a real-symmetric matrix because it can be regarded as the second functional derivative by the distribution function of the rate of entropy production. Now we can see a more physical reason why $-k_BTQ_{kk'}$ is real and symmetric. Its transpose is the rate $P_{k'k}$ at which reverse transitions $k'$ to $k$ occur. The statement $P_{kk'} = P_{k'k}$ is the principle of detailed balance, which says that in equilibrium each elementary process is balanced on average by its reverse process. If this principle were false, a careful microscopic observer would interpret the imbalance between forward and backward processes as an arrow of time, which should not be available in an equilibrium system.

What about the diagonal elements $Q_{kk}$? The conservation law (31) is valid for an arbitrary deviation $\delta F_k$ from equilibrium. Therefore it follows that

$$\sum_k\frac{\delta C_k}{\delta F_{k'}} = 0 \quad (36)$$

¿From this we also see that

$$\sum_k Q_{kk'} = \sum_k Q_{k'k} = 0 \quad (37)$$

Thus the diagonal element $Q_{kk}$ is related to the off-diagonal elements by a sum rule. Similar to the interpretation of $(\delta C_k/\delta F_k)f_{k'}(1-f_{k'})$ as the equilibrium rate of transitions $k \to k'$, one can argue that $-(\delta C_k/\delta F_k)f_k(1-f_k)$ is the total equilibrium rate into $k$. This must equal the sum of all rates for going

out of k, which is just a way of stating the sum rule in words. The scattering operator in the linearized Boltzmann equation can now be written completely in terms of the equilibrium transition probability $P_{kk'}$ as

$$Q_{kk'} = \frac{1}{k_B T}\left[\sum_{k'} P_{kk'}\delta_{kk'} - P_{kk'}\right]$$ (38)

The first term is the diagonal element $Q_{kk}$. An intimate relation between dissipative scattering processes (Q) and equilibrium fluctuations (P) is not just an artifact of the Boltzmann theory, but is a deep idea in non-equilibrium physics, known as the "fluctuation-dissipation theorem".

Because the scattering operator $\delta C_k/\delta F_{k'}$ becomes symmetric after multiplication by $\partial f/\partial\epsilon_{k'}$, it is convenient to write the distribution function as

$$F_k = f(\epsilon_k - \phi_k) \rightarrow f_k + (-\partial f/\partial\epsilon_k)\phi_k$$ (39)

The "deformation" function $\phi_k$ is the energy shift of the altered distribution. This is closely related to the simple ansatz of Eq. (3), which can be considered as a special case of Eq. (39) with $\phi_k = -e\vec{E}\cdot\vec{v}_k\tau$, describing a rigid shift of the distribution in $k$-space. The form (39) allows a general distortion of the Fermi distribution rather than a rigid shift, and does not restrict in any way the allowed form of the non-equilibrium distribution. Then the collision term of the Boltzmann equation is

$$(\partial F_k/\partial t)_{coll} = \sum_{k'}(\delta C_k/\delta F_{k'})\delta F_{k'} = -\sum_{k'} Q_{kk'}\phi_{k'}$$
$$= (-1/k_B T)\sum_{k'} P_{kk'}(\phi_k - \phi_{k'})$$ (40)

I conclude this section by writing down formulas for the equilibrium rates $P_{kk'}$. These formulas are simpler than the non-equilibrium rates $(\partial F_k/\partial t)_{coll}$ from which they can be derived, usually with considerable effort. For impurity or electron-phonon scattering they are

$$P_{kk'}^{imp} = \frac{2\pi}{\hbar}n_i|V_{kk'}|^2 f_k(1-f_{k'})\delta(\epsilon_k - \epsilon_{k'})$$ (41)

$$P_{kk'}^{ep} = \frac{2\pi}{\hbar}|M_{k,k+Q}|^2 f_k(1-f_{k+Q})$$
$$\times [(n_{-Q}+1)\delta(\epsilon_k - \epsilon_{k+Q} - \omega_{-Q}) + n_Q\delta(\epsilon_k - \epsilon_{k+Q} + \omega_Q)]$$ (42)

where $n_i$ is the number of impurities. For electron-electron (Coulomb) scattering, it is less obvious that the rate to go from k to k' is the relevant one. The microscopic process involves two states $(k_1, k_2)$ scattering into two others $(k_3, k_4)$, with equilibrium probability

$$P_{1234}^{ee} = \frac{2\pi}{\hbar}|M_{1234}|^2 f_1 f_2(1-f_3)(1-f_4)\delta(\epsilon_1 + \epsilon_2 - \epsilon_3 - \epsilon_4)$$ (43)

The linearized scattering operator in the Boltzmann equation can be expressed in a way similar to impurity and electron-phonon scattering, with the transition probability $P_{12}^{ee}$ from state 1 to state 2 given by

$$P_{12}^{ee} = \sum_{34}(P_{1342}^{ee} + P_{1324}^{ee} - P_{1234}^{ee})$$ (44)

which is the correct total rate at which these 4-state events empty state 1 and fill state 2. An equivalent and more conventional way to write the linearized collision operator for the electron-electron problem is

$$(\partial F_k/\partial t)_{coll} = -\frac{1}{k_B T}\sum_{234} P_{1234}^{ee}(\phi_1 + \phi_2 - \phi_3 - \phi_4)$$ (45)

## VII. VARIATIONAL SOLUTIONS

We are now ready to solve the linearized Boltzmann equation. For a real material with a complicated Fermi surface and phonon spectrum, a complete solution is technically demanding. Fortunately, a variational principle permits controlled approximations of variational accuracy. The most complete computational effort is probably the work of Beaulac et al. on copper [28]. One message from that work is that the lowest order trial variational solution is excellent over most of the temperature range.

It is convenient to write the linearized Boltzmann equation (27) and (40) in vector notation

$$X \equiv e\vec{E}\cdot\vec{v}\frac{\partial f}{\partial\epsilon} = Q\phi$$ (46)

Then using Eqs. (1) and (39) the current satisfies

$$\vec{j}\cdot\vec{E} = (\phi, X)/\Omega = (\phi, Q\phi)/\Omega$$ (47)

The scattering operator Q as written in Eq. (38), has a particularly simple form for its diagonal matrix elements,

$$(\psi, Q\psi) = \frac{1}{2k_B T}\sum_{kk'} P_{kk'}(\psi_k - \psi_{k'})^2$$ (48)

Since $P_{kk'}$ is a probability and therefore not negative, this again shows that Q is a non-negative operator. The previous argument simply stated that this is

required by the second law of thermodynamics (that is, it is the H-theorem.) Now we see that this is also guaranteed by the form of the linearized scattering operator.

Thermodynamics makes a stronger statement, namely $\vec{j} \cdot \vec{E}$, being the rate of Joule heating, is strictly positive and never zero. The scattering operator $Q$ has two zero eigenvalues, with corresponding eigenvectors $\psi_i(k) = 1$ and $\psi_2(k) = \epsilon_k$, as follow from the conservation laws (31,37) and (32). These two eigenvectors are deformations of the distribution function which correspond to not altering the number density and the temperature, which is why they do not relax under collisions. It also explains that they do not carry any current, which is mathematically contained in the statement $(\psi_i, X) = 0$ for $i = 1, 2$. This also tells us that the vector $X$ is orthogonal to the null space of $Q$. Therefore in solving (46), we can work always in the space orthogonal to the null space of $Q$, and treat $Q$ as a positive operator. Then we can define a new inner product $< \psi|\psi' > = (\psi, Q\psi')$ in this space, and write a Schwartz inequality

$$\sigma E^2 = \vec{j} \cdot \vec{E} = \frac{(\phi, Q\phi)}{\Omega} \geq \frac{|(\psi, Q\phi)|^2}{\Omega(\psi, Q\psi)} = \frac{|(\psi, X)|^2}{\Omega(\psi, Q\psi)} \equiv \sigma_{trial}[\psi]E^2 \qquad (49)$$

where $\psi$ is an arbitrary vector orthogonal to the null space of $Q$. This is the Kohler variational principle. It tells us that the conductivity is bounded below, and that the "true" conductivity (i.e. the one obtained from an exact solution of the linearized Boltzmann equation) is the minimum value of this functional $\sigma_{trial}[\psi]$. Furthermore, it is not hard to show that the true non-equilibrium distribution $\phi$ is the unique function which minimizes this functional. In a less abstract notation, we can write an inequality for the resistivity. In a coordinate system which diagonalizes the conductivity, the diagonal elements of the resistivity tensor are just reciprocals of the diagonal elements of the conductivity, and

$$\rho_{xx} \leq \rho_{trial,xx}[\psi] = \frac{\frac{\Omega}{2k_B T} \sum_{kk'} P_{kk'}(\psi_k - \psi_{k'})^2}{e^2[\sum_k v_{kx}\psi_k(\partial f/\partial \epsilon_k)]^2} \qquad (50)$$

Equation (50) is a convenient starting point for generating a controlled approximate solution of the Boltzmann equation for the resistivity. Similar variational expressions can be written down for the other dissipative static properties, such as the thermal conductivity and the internal friction. In practise, it is common to use as a variational ansatz for $\phi_k$, defined in Eq. (39), the simple shifted distribution given in Eq. (3), which is equivalent to $\psi_k = -e\vec{E} \cdot \vec{v}_k \tau$. The constant factors $e$, $E_x$, and $\tau$ cancel from Eq. (50), so it is equivalent to put $\psi_k = v_{kx}$ into Eq. (50), yielding

$$\rho_{xx}^0 = \frac{1}{(ne^2/m^*)_{xx}}(1/\tau_{tr}^0)_{xx} \qquad (51)$$

$$(1/\tau_{tr}^0)_{xx} = \frac{1}{k_B T} \frac{\sum_{kk'} P_{kk'}(v_{kx} - v_{k'x})^2}{\sum_k 2v_{kx}^2(-\partial f/\partial \epsilon_k)} \qquad (52)$$

where Eq. (5) has been used to define the $n/m^*$ tensor. The superscript zero designates these expressions as lowest-order variational approximations.

We can estimate the relative importance of the three scattering mechanisms using the formulas (41-43). The impurity and Coulomb matrix elements $V_{kk'}$ and $M_{1234}$ are typically a few eV in size, as is the Fermi energy and $1/N(0)$. The delta functions give densities of states $N(0)$ after integration. The electron-phonon matrix element $M_{k,k+Q}$ has order of magnitude $\sqrt{\epsilon_F \omega_D}$. The factor $1/k_B T$ in eqn.(52) combines with Fermi factors $f(1-f)$ to give another delta function. Then for impurity scattering, $1/\tau \approx n_i\epsilon_F$, while for electron-phonon scattering the result is $1/\tau \approx n_{ph}\omega_D$, where the number of phonons, $n_{ph}$, at higher temperatures is approximately $k_B T/\omega_D$. The Coulomb scattering rate would come out to $1/\tau \approx \epsilon_F$, except that the extra Fermi factors, expressing restrictions on the scattering due to the Pauli principle, bring in the small factor $(k_B T/\epsilon_F)^2$ which counts the number of electron-hole pairs which an electron could create in a scattering process. For dirty metals where $n_i$ is comparable to 1, impurity scattering will dominate. The relative importance of Coulomb to electron-phonon scattering is $(k_B T)^2/n_{ph}\epsilon_F\omega_D$ which is very small except at the low temperatures where $n_{ph}$ goes to zero as $T^3$ (or as $T^5$ when the scattering angles are correctly factored in). In reasonably pure metals, the number of impurities can be reduced to below 1%, and electron-phonon scattering will dominate at room temperature, whereas impurities will always win at low enough temperatures. There is only rarely any temperature interval where the Coulomb scattering dominates, because this requires exceptionally good sample purity. A common measure of a sample's purity is the "residual resistance ratio" (rrr), namely $\rho(300K)/\rho(4.2K)$. Very roughly this ratio is about $300K/n_i\epsilon_F$. A reasonably pure sample should have an rrr of 10 or more. An rrr of $\approx 10^5$ is required in order for Coulomb scattering to equal impurity scattering at 10K. At higher temperatures, phonon scattering rapidly begins to take over.

## VIII. AC FIELD

The resistivity tensor $\rho^0$ in Eq. (51) is written as the product of two tensors, $(n/m^*)$ and $\Gamma^0 = 1/\tau_{tr}^0$. The exact answer can be similarly factorized. One way to think of these tensors is as coefficients in an exact equation

$$0 = \frac{d\vec{j}}{dt} = -\Gamma\vec{j} + e^2 \frac{n}{m^*}\vec{E} \qquad (53)$$

The zero on the left hand side of this equation is put there explicitly to signify that this equation defines the tensor $\Gamma$ only for a very specific microscopic current, namely the one which occurs in steady state with a dc $\vec{E}$-field present. If this field were suddenly turned off, the tensor $\Gamma$ would give the rate at which the current would relax. It is important to realize that not all possible currents relax at this rate. There are many possible microscopic distributions which give the same macroscopic current, and each relaxes at its own rate. In particular, If there is an ac field $\vec{E}e^{-i\omega t}$, Eq. (53) with the left hand side set to $-i\omega\vec{j}$, rather than to zero, is correct only when a different rate $\Gamma(\omega)$ is used. This new relaxation rate must be found by solving an ac linearized Boltzmann equation. The resulting ac conductivity has the form

$$\sigma(\omega) = (\Gamma(\omega) - i\omega\mathbf{1})^{-1}e^2\left(\frac{n}{m^*}\right)$$ (54)

It is probably not a bad approximation to use the dc $\Gamma$ for the ac problem, that is, to use the Drude approximation. This raises the hope of being able to use experiment to separately measure the values of $(n/m^*)$ and $1/\tau_{tr}$. Unfortunately there are two additional problems with this notion. First, there is a many-body enhancement effect which is contained in the Landau version of this theory but vanishes in the dc limit and has therefore been omitted in this article. The enhancement can be modeled by replacing $-i\omega\mathbf{1}$ by $-i\omega(1 + A(\omega))$. The size of this factor is hard to estimate. The electron-phonon contribution to $A(\omega)$ has been worked out [9,29]. It goes away at temperatures of order the Debye temperature. Less is known about other possible contributions to this factor. Second, and perhaps more problematic, experiments in the ac frequency region in interesting metals usually encounter interband transitions which make it very difficult or impossible to separate out the contribution from acceleration within the conduction bands. Therefore, use of an "experimental" value of the Drude plasma frequency requires caution.

## IX. EIGENVECTORS AND EIGENVALUES OF THE COLLISION OPERATOR

Additional insight into the ac field problem and other time-dependent field situations can be found by considering the eigenvalues of the collision operator $Q_{kk'}$. I view this as mainly a formal device; for actual numerical work, the eigenvalue problem is probably not an efficient point of departure. When an $E$-field is applied, it is convenient to study the generalized Hermitian eigenvalue problem

$$Q|i\rangle = \gamma_i \hat{D}|i\rangle$$ (55)

where $\hat{D}$ is chosen to be $(-\partial f/\partial\epsilon)$, a positive real symmetric operator. In the $k$-representation, $\hat{D}$ is diagonal, and Eq. (55) becomes

$$\sum_{k'} Q_{kk'}\chi_i(k') = \gamma_i\chi_i(k)\left(-\frac{\partial f}{\partial\epsilon}\right).$$ (56)

The eigenvalues are $\gamma_i$ and the eigenvectors are $\langle k|i\rangle = \chi_i(k)$. These eigenvectors and eigenvalues obey the relations

$$\langle i|Q|j\rangle = \gamma_i\delta_{ij}$$ (57)

$$\langle i|\hat{D}|j\rangle = \delta_{ij}$$ (58)

$$\sum_i |i\rangle\langle i| = \hat{D}^{-1}$$ (59)

which include orthonormality and completeness. This problem is entirely equivalent to the ordinary Hermitian eigenvalue problem for the operator $\hat{D}^{-1/2}\hat{Q}\hat{D}^{-1/2}$. The eigenvalues $\gamma_i$ are therefore all positive except for the two zero eigenvalues with corresponding eigenvectors 1 and $\epsilon_k$. From Eq. (52) it follows that the transport lifetime, in lowest order variational approximation, is a diagonal matrix element

$$\frac{1}{\tau_{tr}^0} = \frac{\langle v|\hat{Q}|v\rangle}{\langle v|\hat{D}|v\rangle}$$ (60)

where $|v\rangle$ is the velocity vector $\langle k|v\rangle = v_k$. Using the completeness relation Eq. (59) this can be expressed in the eigenvector representation as

$$\frac{1}{\tau_{tr}^0} = \frac{\sum_i \gamma_i|\langle v|\hat{D}|i\rangle|^2}{\sum_i |\langle v|\hat{D}|i\rangle|^2}$$ (61)

Thus the eigenvalues $\gamma_i$ are eigen-relaxation rates, and the transport relaxation rate is a velocity-weighted average of these rates.

Things become more clear when we add a time-dependent $E$-field. The Boltzmann equation Eqs. (10,40) in operator representation is

$$\frac{\partial}{\partial t}\hat{D}|\phi\rangle = -eE(t)\hat{D}|v\rangle - \hat{Q}|\phi\rangle$$ (62)

where $\langle k|\phi\rangle$ is the deviation function $\phi_k$. Expanding this function in the eigenfunctions, Eq. (62) becomes

$$|\phi\rangle = \sum_i \phi_i(t)|i\rangle$$ (63)

$$\frac{\partial \phi_i}{\partial t} = -eE(t)\langle i|\hat{D}|v\rangle - \gamma_i \phi_i \tag{64}$$

which has as a solution

$$\phi_i(t) = -e\langle i|\hat{D}|v\rangle \int_{-\infty}^{t} e^{-\gamma_i(t-t')} E(t'). \tag{65}$$

¿From this, and from Eqs. (1,39), the current is

$$j(t) = -\frac{e}{\Omega}\langle v|\hat{D}|\phi\rangle = \int_{-\infty}^{t} \sigma(t-t')E(t') \tag{66}$$

and the conductivity (in the time domain) is

$$\sigma(t-t') = \frac{e^2}{\Omega}\sum_i |\langle v|\hat{D}|i\rangle|^2 e^{-\gamma_i(t-t')}. \tag{67}$$

This is the formal solution for the linearized Boltzmann equation with a spatially homogeneous applied $E$-field with arbitrary time dependence. For an ac field $Ee^{-i\omega t}$ the current is $\sigma(\omega)Ee^{-i\omega t}$, and the ac conductivity is

$$\sigma(\omega) = \frac{ie^2}{\Omega}\sum_i \frac{|\langle v|\hat{D}|i\rangle|^2}{\omega + i\gamma_i}. \tag{68}$$

It is interesting to define a distribution function $G(\gamma)$ of the velocity weighted relaxation rates $\gamma_i$;

$$G(\gamma) = \frac{\frac{1}{\Omega}\sum_i |\langle v|\hat{D}|i\rangle|^2 \delta(\gamma - \gamma_i)}{\frac{1}{\Omega}\sum_i |\langle v|\hat{D}|i\rangle|^2}. \tag{69}$$

The denominator of Eq. (69) is just $(n/m)_{\text{eff}}$. Using this, the ac conductivity can be written as

$$\sigma(\omega) = ie^2 \left(\frac{n}{m}\right)_{\text{eff}} \int_0^\infty d\gamma \frac{G(\gamma)}{\omega + i\gamma}. \tag{70}$$

The dc limit is

$$\sigma_{\text{dc}} = e^2 \left(\frac{n}{m}\right)_{\text{eff}} \int_0^\infty d\gamma \frac{G(\gamma)}{\gamma} = e^2 \left(\frac{n}{m}\right)_{\text{eff}} \tau_{\text{tr}}. \tag{71}$$

The distribution function $G$ therefore can be seen to have the following moments

$$\int_0^\infty d\gamma\, G(\gamma) = 1 \tag{72}$$

$$\int_0^\infty d\gamma\, \gamma G(\gamma) = \frac{1}{\tau_{\text{tr}}^0} \tag{73}$$

$$\int_0^\infty d\gamma \frac{G(\gamma)}{\gamma} = \tau_{\text{tr}} \tag{74}$$

Eq. (72) follows from the definition (69) of $G(\gamma)$. Eq. (73) follows from the representation Eq. (61) of $1/\tau_{\text{tr}}^0$, and Eq. (74) follows from the definition (71) of $\tau_{\text{tr}}$.

These equations provide another way to think about the accuracy of the lowest order solution of the Boltzmann equation for the dc resistivity. If the distribution function $G(\gamma)$ consisted of just a single delta function of unit weight, $\delta(\gamma - 1/\tau_{\text{tr}})$, the lowest order solution would be exact. There are two extreme cases where this could be true. One case would be if all eigenvalues (except the two zero eigenvalues) of $\hat{Q}$ were equal to $1/\tau_{\text{tr}}$. This is called the "relaxation-time approximation." There is no good reason to believe that it is ever particularly accurate, but with discretion it can be a useful model. The other extreme case is the one which actually occurs for elastic impurity scattering in a spherically symmetric (jellium) medium. In that case, the velocity vector $|v\rangle$ is an eigenvector with eigenvalue $1/\tau_{\text{tr}}$, and all other eigenvectors are orthogonal to it. Therefore there is only one term contributing to either numerator or denominator of Eq. (69). This is not a relaxation time approximation, and the lowest order solution is exact.

In the case of real metals, it is my opinion that over much of the range of impurity concentration and temperature, the situation is similar to the latter case. Only a few eigenvectors $|i\rangle$ of $\hat{Q}$ have significant overlaps with $|v\rangle$. The distribution $G$ has a few sharp peaks, probably not very far apart in $\gamma$ space, and a broader background which does not have too much weight. Therefore the solution for $1/\tau_{\text{tr}}$ is not very different from $1/\tau_{\text{tr}}^0$.

A recent paper [30] claimed to calculate a negative "momentum relaxation rate" in a quantum wire at low temperatures in linearized Boltzmann theory. According to the authors, a consequence of such a negative rate would be a transient "overshoot" of the current response when a dc $E$-field was turned on. Using the general solution Eqs. (66,67), the transient response to a steady field $E(t) = E_0\theta(t)$ which is turned on at $t = 0$ is

$$\frac{j(t)}{E_0} = \frac{e^2}{\Omega}\sum_i |\langle i|\hat{D}|v\rangle|^2 \frac{1 - e^{-\gamma_i t}}{\gamma_i}\theta(t). \tag{75}$$

Because all the $\gamma_i$'s are positive, the current climbs monotonically to its final steady-state value $\sigma_{\text{dc}}E_0$. Thus transient overshoots are forbidden by linear Boltzmann transport theory, and reference [30] must have an error. The impossibility of such a transient effect is a consequence of the H-theorem which requires that the eigenvalues $\gamma_i$ all be positive. Beyond linear approximation,

the H-theorem still requires entropy to increase steadily, but it is apparently possible for transient oscillations of various quantities to occur.

## X. TRANSPORT LIFETIME VERSUS QUASIPARTICLE LIFETIME

The quasiparticle lifetime $\tau_{QP}(k)$ was defined in sec. IV in terms of the rate at which a population imbalance in just state $k$ relaxes back to equilibrium. The general result (14) can be written in a more useful form, using Eqs. (35) and (37),

$$1/\tau_{QP}(k) = \frac{1}{f_k(1-f_k)}\sum_{k'} P_{kk'} \tag{76}$$

This formula is also completely general. In order to compare this result with the transport relaxation rate, Eq. (52), it is useful to average $1/\tau_{QP}(k)$, either over $k$-states at a fixed energy $\epsilon$ (defining $1/\tau_{QP}(\epsilon)$), or over a thermal distribution of excited states, giving $1/\tau_{QP}$.

$$1/\tau_{QP}(\epsilon) = \frac{1}{N(0)}\sum_k \frac{1}{\tau_{QP}(k)}\delta(\epsilon-\epsilon_k) \tag{77}$$

$$1/\tau_{QP} = \frac{1}{N(0)}\sum_k \frac{1}{\tau_{QP}(k)}\left(-\frac{\partial f}{\partial \epsilon_k}\right) = \int_{-\infty}^{\infty} d\epsilon\, \frac{1}{\tau_{QP}(\epsilon)}\left(-\frac{\partial f}{\partial \epsilon}\right) \tag{78}$$

Putting (76) into (78) gives a general result

$$1/\tau_{QP} = \frac{k_B T \sum_{kk'} P_{kk'}}{\sum_k (-\partial f/\partial \epsilon_k)} \tag{79}$$

This has been written in such a way as to emphasize the very close similarity between the quasiparticle relaxation rate and transport relaxation rate given in Eq. (52). Of course, this does not require that $1/\tau_{QP}$ and $1/\tau_{tr}$ should be similar in magnitude. The main way to have them different is for $P_{kk'}$ to be large only when $|v_{kz} - v_{k'z}|$ is small, i.e. for small angle scattering. This is true of electron-phonon events at low $T$ because then only the low energy phonons, which are small $Q$ acoustic phonons, are thermally excited. The corresponding relaxation rates go as $T^3$ for $1/\tau_{QP}$ and $T^5$ for $1/\tau_{tr}^0$. Another case where $1/\tau_{tr} \ll 1/\tau_{QP}$ is when the Coulomb interaction is unscreened, so that the small angle $1/Q^2$ divergence dominates the scattering, as is common in classical plasmas. However, in the usual solid state problems, apart from electron-phonon

scattering at low temperatures, there is usually no strong correlation between the size of the weight function $(v_{kz} - v_{k'z})^2$ and the size of the equilibrium probability $P_{kk'}$, so the rates are about the same.

A general weighted relaxation time can be defined by

$$1/\tau_w = N(0)\frac{\frac{1}{k_B T}\sum_{kk'} P_{kk'}\, w(k,k')}{\sum_{kk'} w(k,k')(-\partial f/\partial \epsilon_k)(-\partial f/\partial \epsilon_{k'})} \tag{80}$$

For the quasiparticle relaxation rate, the weight factor is $w(k,k') = 1$. The approximate form $1/\tau_{tr}^0$ uses for cubic symmetry $w = (\bar{v}_k - \bar{v}_{k'})^2$. For spherical symmetry this becomes $2v_F^2(1 - \cos\theta)$ where $\theta$ is the scattering angle. The average in the denominator cancels the factor $2v_F^2$, yielding the familiar result that the current relaxation rate is weighted by $(1-\cos\theta)$. However, this answer is exact only for the special case of elastic scattering and angular isotropy.

Explicit formulas for the scattering rates can be found by substituting expressions (41-43) into these equations. Using Eq. (42) for the electron-phonon case, before averaging the result is

$$1/\tau_{QP}(k) = \frac{2\pi}{\hbar}\sum_k |M_{kk'}|^2 \quad [(1-f_{k'}+n_{k-k'})\delta(\epsilon_k - \epsilon_{k'} - \omega_{k-k'})$$
$$+ (f_{k'}+n_{k'-k})\delta(\epsilon_k - \epsilon_{k'} + \omega_{k'-k})] \tag{81}$$

This answer agrees completely with the standard result $1/\tau_k = -2\,\mathrm{Im}\,G(k,\omega)$ obtained by the Matsubara method and Migdal's approximation. When averaged over a surface of constant energy $\epsilon$ this becomes

$$1/\tau_{QP}(\epsilon) = \frac{2\pi}{\hbar}\int_{-\infty}^{\infty} d\epsilon' \int_0^{\infty} d\Omega \left[\frac{\sum_{kk'}|M_{kk'}|^2\delta(\Omega - \omega_{k-k'})\delta(\epsilon - \epsilon_k)\delta(\epsilon - \epsilon_{k'})}{N(0)}\right]$$
$$\times \{[1-f(\epsilon') + n(\Omega)]\delta(\epsilon-\epsilon'-\Omega) + [f(\epsilon')+n(\Omega)]\delta(\epsilon-\epsilon'+\Omega)\} \tag{82}$$

Here two extra delta functions have been inserted, as well as two extra integrals which cancel the delta functions. It is conventional to define the quantity in brackets [ ] in Eq. (82) as an electron-phonon spectral function

$$\alpha^2 F(\Omega,\epsilon,\epsilon') \equiv \frac{1}{N(0)}\sum_{kk'}|M_{kk'}|^2\delta(\Omega - \omega_{k-k'})\delta(\epsilon-\epsilon_k)\delta(\epsilon'-\epsilon_{k'}) \tag{83}$$

The peculiar notation $\alpha^2 F$ signifies the resemblance to the phonon density of states $F$. The Migdal approximation consists of using consistently the fact that the temperature and the phonon energies are small compared to the scale on which electron energies vary (the Fermi energy for simple metals.) At this level of accuracy, the $(\epsilon,\epsilon')$ dependence of $\alpha^2 F$ is ignorable because it happens on the scale of electronic energies, while the function is only to be evaluated at energies of order $k_B T$ or $\omega_D$. The value of $\alpha^2 F(\Omega,\epsilon,\epsilon')$ at $\epsilon = \epsilon' = 0$ is called $\alpha^2 F(\Omega)$.

This function was introduced in the Eliashberg theory of superconductivity, and contains all the necessary information about the electron-phonon interaction to calculate $T_c$, after making the approximation of an isotropic gap ("dirty" approximation.) The size of the electron-phonon coupling is measured by the integral over $\alpha^2 F$, called $\lambda$,

$$\lambda = 2 \int_0^\infty \frac{d\Omega}{\Omega} \alpha^2 F(\Omega) \qquad (84)$$

If the value of $\lambda$ is known (for example, from the value of $T_c$) then a good guess for $\alpha^2 F$ is to use the phonon density of states renormalized to obey Eq. (84).

The formula for $1/\tau_{QP}(\epsilon)$ is now

$$\frac{1}{\tau_{QP}(\epsilon)} = \frac{2\pi}{\hbar} \int_0^\infty d\Omega\, \alpha^2 F(\Omega)[f(\epsilon+\Omega) - f(\epsilon-\Omega) + 2n(\Omega) + 1] \qquad (85)$$

When this is evaluated at the Fermi energy $\epsilon = \epsilon_F = 0$, the answer is

$$\frac{1}{\tau_{QP}(0)} = \frac{4\pi}{\hbar} \int_0^\infty d\Omega\, \alpha^2 F(\Omega)[f(\Omega) + n(\Omega)] \qquad (86)$$

and at high temperature the answer becomes approximately

$$\frac{1}{\tau_{QP}(0)} \to \frac{2\pi}{\hbar} \lambda k_B T \qquad (87)$$

A more physical average is the one in Eq. (78,79). After a tedious calculation, the result is

$$\frac{1}{\tau_{QP}} = \frac{4\pi k_B T}{\hbar} \int_0^\infty \frac{d\Omega}{\Omega} \alpha^2 F(\Omega) \left[ \frac{\hbar\Omega/2k_B T}{\sinh(\hbar\Omega/2k_B T)} \right]^2 \qquad (88)$$

At high temperatures, this has the same value, $2\pi\lambda k_B T/\hbar$, as the quasiparticle lifetime at the Fermi surface.

Analogous to $\alpha^2 F$ defined in Eq. (83), it is useful to define a spectral function weighted by "angular" factors in addition to the electron-phonon matrix elements:

$$\alpha_w^2 F(\Omega) \equiv N(0) \frac{\sum_{kk'} |M_{kk'}|^2 w(k,k') \delta(\Omega - \omega_{k-k'}) \delta(\epsilon_k)\delta(\epsilon_{k'})}{\sum_{kk'} w(k,k')\delta(\epsilon_k)\delta(\epsilon_{k'})} \qquad (89)$$

$$\lambda_w = 2\int_0^\infty \frac{d\Omega}{\Omega}\alpha_w^2 F(\Omega) = N(0)\frac{\sum_{kk'}(|M_{kk'}|^2/\omega_{k-k'})w(k,k')\delta(\epsilon_k)\delta(\epsilon_{k'})}{\sum_{kk'} w(k,k')\delta(\epsilon_k)\delta(\epsilon_{k'})} \qquad (90)$$

where the usual $\alpha^2 F$ and $\lambda$ are the versions with $w(k,k') = 1$. Repeating the algebra by which Eq. (79) was converted into Eq. (88), but doing it for the transport relaxation time, Eq. (52), we get

$$\frac{1}{\tau_{tr}^0} = \frac{4\pi k_B T}{\hbar} \int_0^\infty \frac{d\Omega}{\Omega} \alpha_{tr}^2 F(\Omega) \left[ \frac{\hbar\Omega/2k_B T}{\sinh(\hbar\Omega/2k_B T)} \right]^2 \qquad (91)$$

where $\alpha_{tr}^2 F(\Omega)$ uses $w(k,k') = (v_{kz} - v_{k'z})^2$. ¿From Eq. (91) we see that the high temperature limit of $1/\tau_{tr}^0$ is $2\pi\lambda_{tr}k_B T/\hbar$. Eq. (91) is a useful explicit approximate variational solution to the Bloch-Boltzmann equation for the resistivity due to electron-phonon interactions. The messy details of the actual complicated Fermi surface shape, phonon spectrum, and matrix elements are not ignored, but safely hidden in the spectral function $\alpha_{tr}^2 F$. In practise, this function can be calculated with no greater difficulty than $\alpha^2 F$ which is the corresponding property needed for superconductivity, and the level of accuracy of the lowest order theory given here for resistivity is comparable to that of the "dirty" approximation used in the Eliashberg equations. Moreover, the form of Eq. (91) encourages approximate evaluations of $\rho(T)$ by making judicious guesses about the form of $\alpha_{tr}^2 F$.

Finally a last statement about the expected similarity between $\lambda_{tr}$ and $\lambda$. Eq. (90) shows that if the velocity difference $(v_{kz} - v_{k'z})^2$ is not especially correlated with the variation of the matrix elements $|M_{kk'}|^2/\omega_{k-k'}$, then the different ways of weighting the sum should not yield very different answers. Experience so far has not shown much correlation, although counterarguments have been suggested because in the case of high $T_c$ materials, $\lambda_{tr}$, if it makes any sense at all, is a lot smaller than the value of $\lambda$ that would be needed to account for the $T_c$. One can test this to some extent, because if my argument about the similarity of $\lambda_{tr}$ and $\lambda$ is right, then the different tensor components of $\lambda_{tr,\alpha\alpha}$ should be independent also of the Cartesian component $\alpha$ of the velocity. In other words, the anisotropy of the resistivity in a non-cubic material should be predictable from the anisotropy of the $n/m^*$ tensor only. The hexagonal elements have been tested, with reasonable agreement with this hypothesis [5], although the resistivity anisotropy tends to be small and may not always be accurately measured. In the case of Tl, Zr, and Hf shown in Fig. 1, the data shown are on polycrystalline samples, and an averaged theoretical $n/m^*$ tensor was used. For the high $T_c$ compounds, the c-axis resistivity is dramatically different from the (a,b)-plane resistivity, but this anisotropy is sample dependent and the mean free path in the c direction is so short that Boltzmann theory is unlikely to apply. But the a-b plane anisotropy is considerable in both YBa$_2$Cu$_3$O$_7$ and YBa$_2$Cu$_4$O$_8$, and in both cases the LDA value of $\omega_{pxx}^2/\omega_{pyy}^2$, calculated [31,32] before the resistivity anisotropy $\rho_{yy}/\rho_{xx}$ was measured [33,34], agrees well with experiment. This suggests that the quasiparticle transport lifetime (if such a concept makes sense in these materials) is very isotropic, just as the Boltzmann theory suggests it probably should be.

# XI. BLOCH-GRÜNEISEN EQUATION

This famous equation is obtained from the lowest order variational result by making a model for $\alpha_{tr}^2 F$ based on a spherical free electron band structure and a spherical Debye phonon spectrum of a single longitudinal branch. My personal feeling is that such a model has little value in terms of giving insight into real materials properties. The value instead is that the result is a "universal" formula for $\rho(T)$ which can easily be calculated and compared with data. The full Boltzmann theory shows that there is not really any universal formula, but it also shows that the simple result should correctly capture the qualitative features of real resistivities, and that deviations from Bloch-Grüneisen form are often expected to be fairly small compared to say the impurity contribution to the resistivity.

It is useful to write Eq. (83) for $\alpha^2 F$ as a sum over the phonon spectrum.

$$\alpha^2 F(\Omega) = \sum_Q W_Q \delta(\Omega - \omega_Q) \tag{92}$$

$$W_Q = \frac{1}{N(0)} \sum_k |M_{k,k+q}|^2 \delta(\epsilon_k) \delta(\epsilon_{k+q}) \tag{93}$$

It turns out [35] that the weight factor $W_Q$ is equal to $\gamma_Q / \pi N(0) \omega_Q$ where $\gamma_Q$ is the lifetime broadening of the phonon $Q$ caused by electron-phonon interactions. This identity is rigorous within the Migdal approximation. Another general result is that for the low energy acoustic phonons, the lifetime broadening, like the energy $\omega_Q$, is a linear function of the wavevector $|Q|$. Thus at low values of $\Omega$, the weight factor $W_Q$ in Eq. (92) is independent of $Q$, and $\alpha^2 F(\Omega)$ will be proportional to the density of states $F(\Omega)$, that is, proportional to $\Omega^2$. The Debye model is then equivalent to the statement

$$\alpha^2 F_D(\Omega) = \lambda (\Omega/\omega_D)^2 \tag{94}$$

Using this in Eq. (86) or (88), one easily verifies $1/\tau_{QP} \propto T^3$ at low $T$. It is not hard to derive an explicit formula for $\lambda$ in terms of the sound velocity and the electron-phonon deformation potential coupling constant, or, in the jellium model, in terms of more "fundamental" parameters like $k_F$, $M$, and $q_D$. However, I see no real use for these formulas.

A corresponding approximation for $\alpha_{tr}^2 F$ is easy to work out. The weight factor $(\bar{v}_k - \bar{v}_{k'})^2 / 2v_F^2$ becomes $Q^2/2k_F^2$, which just introduces an extra two powers of $\Omega$. Therefore, the Debye model is

$$\alpha_{tr}^2 F_D(\Omega) = 2\lambda_{tr} (\Omega/\omega_D)^4 \tag{95}$$

Using this in Eq. (91), one finds $\rho \propto T^5$ at low $T$. One should definitely not take seriously the "free electron" result $\lambda_{tr} = (q_D/2k_F)^2 \lambda$, even for such a free-electron-like metal as sodium. This model leaves out Umklapps and transverse phonons, which are by no means negligible even for Na.

Inserting Eq. (95) into Eq. (91), the Bloch-Grüneisen formula for the resistivity can be written as

$$\frac{\rho_{BG} - \rho_0}{\lambda_{tr} \omega_D/\omega_p^2} = f_{BG}(T/\Theta_D) = (4\pi)^2 \left(\frac{2T}{\Theta_D}\right)^5 \int_0^{\Theta_D/2T} dz \frac{x^5}{\sinh^2(x)} \tag{96}$$

where the residual resistivity $\rho_0$ has been included. This formula provides a convenient 3-parameter fit to the resistivity, as shown in section I. It is worth mentioning a few aspects of this formula. First, the high temperature limit $f_{BG} \to 8\pi^2 T/\Theta_D$ is approached reasonably rapidly. At $T = \Theta_D$ the slope $d\rho/dT$ is only 5% higher than the limiting high $T$ linear result. Nevertheless, I have found it very helpful when extracting a value of $\lambda_{tr}$ from data, to make a Bloch-Grüneisen fit rather than relying on a high temperature limiting slope. One reason is that at high temperatures, as mentioned previously, thermal expansion or saturation is often beginning to distort the curve, while a fit provides some control over these effects. Second, the Bloch-Grüneisen theory helps to explain why resistivities of metals often appear to be linear in temperature over a surprisingly large range of $T$, down to $\Theta_D/4$ or lower in some cases. The actual formula is certainly not accurately linear in this range. There is an inflection point at $T = 0.36\Theta_D$ at which the curvature vanishes, and the function fools the eye and appears linear around the inflection point. Third, my experience shows that one cannot identify well the inflection point from experimental $\rho(T)$ data. There are several reasons, one of which is the thermal expansion and saturation effects, and another is that the actual theory differs in two ways from the Bloch-Grüneisen formula. First, the actual phonon spectrum is not Debye-like, although this has less qualitative influence than one might imagine. The only material I have studied where this source of deviation from Bloch-Grüneisen is easy to see is $ReO_3$ [21], which has an extreme mass discrepancy between the Re and O atoms, and thus a very big deviation from Debye shape. Second, there are corrections to the lowest order variational solution.

These corrections, although not very big, and disappearing at high temperature, nevertheless are not universal and therefore not so easy to estimate. Pinski [36] has made the most complete study, using a generalized Debye model with $q_D/k_F$ being a parameter of the model. He found that the correction depended a lot on the choice of this parameter, being as large as a 35% reduction of the phonon part of $\rho(T)$ at fairly low $T$ for a particular choice of $q_D/k_F$. However, unless data are plotted in such a way as to exhibit the detailed $T$-dependence at low $T$, the Bloch-Grüneisen formula is usually sufficient for understanding the form of $\rho(T)$, and is likely to improve the accuracy of a

fitted value of the coupling constant $\lambda_{tr}$.

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