Theory of Hot Electrons in Gases, Liquids, and Solids

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Boltzmann's equation for electrons moving in a steady electric field is solved by the method due to Lorentz, Pidduck, and Davydov. Space-time correlations in the medium (gas, liquid, or solid) are included exactly through the use of sum rules of the Van Hove spectral function, $\tilde{S}(\vec{\mathbf{K}},\omega)$. In liquids and solids the rates of momentum and energy transfer are different, the former being structure-dependent, the latter not. The error from neglect of this difference in previous treatments for solids is fortuitously canceled at low and intermediate fields by the error in the single-phonon scattering approximation also employed.

I. INTRODUCTION

HE mass m of an electron is very much smaller than the mass M of an atom. Therefore an electron colliding elastically with an atom will undergo large deflections but very small changes in energy. When an electric field is applied to matter containing electrons which are free to move, these electrons will accordingly attain a steady-state distribution of momenta which will be almost isotropic, even though it may be far from Maxwellian or Fermi-Dirac in form.

These facts facilitate solution of the problem of determining the steady-state momentum distribution function $f(\mathbf{p})$ for electrons moving through aggregations of atoms. Two expansions become rapidly convergent: the expansion of $f(\mathbf{p})$ into Legendre polynomials about the direction of the field, and the Taylor expansion of all energy-dependent quantities in powers of the energy transfer. For electrons moving in gases, the solution is known. In liquids and solids, however, correlations among the atoms cannot be ignored, and their inclusion is the concern of this paper. It will be shown that the known properties of the Van Hove spectral function are sufficient for the problem in hand (Secs. II and III). In the remainder of this section we shall give a brief historical review of the subject.

Lorentz,¹ in 1905, in a paper on "The motion of electrons in metallic bodies," considered the electrons to have a Maxwellian distribution of velocities, made slightly anisotropic by the electric field:

$$f(\mathbf{p}) = e^{-p^2/2mkT} + p_z X(p^2).$$

By solving a simplified Boltzmann equation, he obtained an expression for the drift velocity $v_D = \langle p_z \rangle / m$:

$$v_D = \frac{2}{3} \left(\frac{2}{\pi m k T} \right)^{1/2} e E \Lambda$$

Here E is the electric field, and Λ the mean free path between collisions. This is the correct drift velocity for thermal electrons in gases or nondegenerate semiconductors, in the limit of low fields.

In 1908, experiments by Townsend² on the motion

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of negative ions in gases indicated that at moderate fields electrons are not in thermal equilibrium with the gas molecules, but that they have a kinetic energy which is several times larger. This situation was considered theoretically by Pidduck^{3,4} in 1913 and 1916. Pidduck's starting point in the latter paper is Boltzmann's equation, transformed by a method of Hilbert. He deduces a series of coupled equations by expanding $f(\mathbf{p})$ in Legendre polynomials:

$$f(\mathbf{p}) = \sum_{n} f_{n}(\boldsymbol{\epsilon}) P_{n}[\cos(\mathbf{p},\mathbf{E})].$$

For electrons, where m/M is small, the first two terms are sufficient. Pidduck's equation for f_0 is

$$(x+b)\frac{d^2f_0}{dx^2} + \left(2 + x + \frac{b}{x}\right)\frac{df_0}{dx} + 2f_0 = 0,$$

where

$$x = \epsilon/kT = p^2/2mkT$$
, $b = \frac{1}{3}(eE\Lambda)^2/(2m/M)(kT)^2$.

It is assumed that the collisions are between elastic spheres, i.e., constant Λ . The solution of Pidduck's equation is $f_0 = (x+b)^{b}e^{-x}$. Pidduck also investigated ion motion for m/M=1 and $m/M\gg1$, as well as diffusion in a magnetic field.

In 1934, Landau and Kompanejez⁵ considered the deviation from Ohm's law in semiconductors at high electric fields. They derived a collision term for phonon scattering, assuming emission and absorption of single acoustical phonons. Their equation for f_0 is

$$(x+b^*)\frac{d^2f_0}{dx^2} + \left(1+x+\frac{b^*}{x}\right)\frac{df_0}{dx} + f_0 = 0,$$

where $b^* = \frac{1}{3} (eE\Lambda)/2mc^2kT$, c = sound velocity. Davydov,⁶ in 1935, treated the problem of electrons in gases, and rediscovered the results of Pidduck. In 1936 he extended his results to semiconductors,⁷ and pointed

¹ H. A. Lorentz, Proc. Amst. Acad. 7, 438 (1905); The Theory of Electrons (Dover Publications, Inc., New York, 1952) p. 267. ² J. S. Townsend, Proc. Roy. Soc. (London) A81, 464 (1908).

 ³ F. B. Pidduck, Proc. Roy. Soc. (London) A88, 296 (1913).
 ⁴ F. B. Pidduck, Proc. London Math. Soc. 15, 89 (1916).
 ⁵ L. Landau and A. Kompanejez, Phys. Z. Sowjetunion 6, 163 (1934).

⁶ B. Davydov, Phys. Z. Sowjetunion 8, 59 (1935). ⁷ B. Davydov, Phys. Z. Sowjetunion 9, 433 (1936).

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out an error in the Landau-Kompanejez collision term. This error, the omission of a phase-space factor, was corrected by Landau⁸ in a 1936 paper on the photoelectromotive force in semiconductors. The corrected equation is the same as that of Pidduck and Davydov, with b^* replacing b. It was therefore clear that scattering by phonons is kinetically equivalent to scattering by particles of effective mass M^* , where

$$M^*c^2 = kT$$
.

This fact was pointed out by Davydov⁹ in 1937. Davydov's equation for f_0 may be integrated, even when the mean free path is energy dependent. The result, rederived by Chapman and Cowling¹⁰ in 1939, is

$$f_0 = \exp\left[-\int \frac{xdx}{x+b(x)}\right].$$

In 1951, Shockley¹¹ discussed physically the problem of hot electrons in germanium. He showed (as was pointed out by Landau and Kompanejez) that the transition from linear to nonlinear (non-Ohmic) behavior should occur at $v_D \sim c$. Experimentally, however, it occurs at several times this value. He also gave a derivation of the Davydov result of the equivalence of phonon and particle scattering. Finally, in 1954, Yamashita and Watanabe12 rederived the Landau-Kompanejez-Davydov results for acoustical phonon scattering, and extended these to include scattering by optical phonons.

In the above treatments of hot electrons in semiconductors, it is assumed that energy and momentum transfer occur by emission and absorption of single phonons, and further, that the rates of energy and momentum transfer are governed by the same mean free path. After a discussion of scattering in dense systems in Sec. II, we derive and solve in Sec. III the kinetic equation for hot electrons in dense systems. Finally, we show in Sec. IV that the single-phonon approximation and the assumption of a single mean free path for energy and momentum transfer are both incorrect but that the errors cancel from the final result except for high fields. The criterion $v_D \sim c$ for the limit of the linear region remains correct. The explicit dependence of the present theory on atomic structure is new and of particular importance for liquids.

II. SCATTERING IN DENSE SYSTEMS

Electrons, neutrons, or gamma rays moving through matter are scattered by atoms which are in interaction

with each other, and therefore correlated. A first approximation in the microscopic description of the scattering is the "single-scatterer approximation," in which the scattered amplitude at any point is the coherent sum of amplitudes scattered from individual atoms but the sum of amplitudes *multiply* scattered from different atoms is taken to be negligible. The wave incident on each atom is approximated by a plane wave. A necessary condition for the validity of the singlescatterer approximation is that the average distance between scattering events, i.e., the mean free path Λ , be large compared with the de Broglie wavelength λ of the electron. The same condition is clearly sufficient for the validity of the Boltzmann equation. Whether λ/Λ being small is a sufficient condition in the former case or a necessary condition in the latter is not known.

From the most general point of view, a particle wave moving through a liquid or a solid transfers energy to collective excitations of the system. In the singlescatterer approximation, all the necessary information about the excitations is contained in the Van Hove¹³ space-time pair correlation function $G(\mathbf{R},t)$, or more directly in its Fourier transform $S(\mathbf{K},\omega)$. The probability of an electron, neutron, or gamma ray scattering with the loss of momentum¹⁴ **K** and energy ω (i.e., by creating a density fluctuation of momentum K and energy ω) is proportional to the product of the singleatom differential cross section, and of the spectral function $S(\mathbf{K}, \omega)$. The spectral function must in general be determined by measuring the flux of neutrons, initially with momentum **p** and energy ϵ , emerging with momentum $\mathbf{p} - \mathbf{K}$ and energy $\epsilon - \omega$. However, $S(\mathbf{K}, \omega)$ has some general properties^{15,16} which are true for any quantum-mechanical system. One of these is the detailed balancing condition $(\beta = 1/kT)$

$$S(-\mathbf{K}, -\omega) = e^{-\beta\omega} S(\mathbf{K}, \omega).$$
(1)

This is a consequence of the principle of microscopic reversibility, and of the thermal equilibrium of the system. The other general properties of S are the first two sum rules

$$\langle 1 \rangle \equiv \int d\omega \, S(\mathbf{K}, \omega) = S(\mathbf{K}) \,,$$
 (2)

$$\langle \omega \rangle = \int d\omega \, \omega S(\mathbf{K}, \omega) = K^2/2M$$
. (3)

The first equation is simply the normalization condition-the probability of scattering with momentum transfer K, integrated over all energy transfers, is in the single-scatterer approximation proportional to the

⁸ L. Landau and E. Lifshitz, Phys. Z. Sowjetunion 9, 475 (1936).

 ⁹ B. Davydov, Phys. Z. Sowjetunion 12, 269 (1937).
 ¹⁰ S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Cases* (University Press, Cambridge, England, 1939), Sec. 18.7.

¹¹ W. Shockley, Bell System Tech. J. 30, 990 (1951).

¹² J. Yamashita and M. Watanabe, Progr. Theoret. Phys. (Kyoto) **12**, 433 (1954).

¹³ L. Van Hove, Phys. Rev. 95, 249 (1954).

¹⁴ We set $\hbar = 1$ in this paper. ¹⁵ P. G. De Gennes, Physica **25**, 825 (1959). ¹⁶ A. Rahman, K. S. Singwi, and A. Sjölander, Phys. Rev. **126**, 986 (1962).

structure factor $S(\mathbf{K})$, the Fourier transform of $G(\mathbf{R},0)$. The second sum rule states that the average energy transfer is exactly equal to the free-atom recoil energy for the same momentum transfer, independently of structure or thermal motion. The next sum rule is only approximately structure-independent:

$$\langle \omega^2 \rangle \equiv \int d\omega \, \omega^2 S(\mathbf{K}, \omega) \simeq 2kT \langle \omega \rangle.$$
 (4)

Omitted from (4) are structure-dependent terms which are smaller by the factor

$$\langle \omega \rangle / kT \sim (m/M) \epsilon / kT.$$
 (5)

This quantity, which is essentially the ratio of the energy transferred in a collision to the thermal energy of an atom, is very small except in the case of hot or degenerate electrons at low temperatures. The higher moments of $S(\mathbf{K},\omega)$ are, on the scale of kT, smaller by the factor (5) times Θ_D/T , where Θ_D is the Debye temperature. Thus at sufficiently high temperatures, energy transfer in collisions is well described by the sum rules (2), (3), and (4). We shall use this fact in the next section to reduce the collision term of the Boltzmann equation.

III. THE KINETIC EQUATION FOR ELECTRONS

By symmetry, the steady-state momentum distribution function $f(\mathbf{p})$ of electrons moving in a uniform electric field is a function of p^2 and of the angle ζ between field **E** and momentum **p**. Following Pidduck,³ we expand in Legendre polynomials:

$$f(\mathbf{p}) = f_0(\epsilon) P_0 + f_1(\epsilon) P_1(\cos\zeta) + f_2(\epsilon) P_2(\cos\zeta) + \cdots$$
 (6)

It will be shown in the following paragraph that f_2 is negligible; we have therefore omitted all terms in $P_3(\cos \zeta)$ and higher spherical harmonics.

In the steady state, the number of electrons accelerated by the electric field out of the element d^3p per unit time is

$$e\mathbf{E} \cdot \frac{\partial f}{\partial \mathbf{p}} d^{3}p = eE\frac{p}{m} d^{3}p \{P_{0\frac{1}{3}}(f_{1}'+f_{1}/\epsilon) + P_{1}(\cos\zeta)(f_{0}'+\frac{2}{5}f_{2}'+\frac{3}{5}f_{2}/\epsilon) + P_{2}(\cos\zeta)\frac{1}{3}(2f_{1}'-f_{1}/\epsilon)\} + \cdots, \quad (7)$$

where prime denotes $d/d\epsilon$. This loss is balanced by the net gain in the number of electrons entering and leaving the element d^3p because of collisions. The number scattered from d^3p into $d^3p' = p'^2 dp' d\Omega'$ in unit time is

$$nd\Omega' \int d\omega \, S(\mathbf{K},\omega) \frac{p'}{m} |F(\mathbf{p} \to \mathbf{p}')|^2 f(\mathbf{p}) d^3 p \,. \tag{8}$$

This expression is built up as follows: $f(\mathbf{p})d^{3}p$ is the number of electrons available for scattering out of $d^{3}p$;

n is the number of scattering centers (atoms) per unit volume; $F(\mathbf{p} \rightarrow \mathbf{p}')$ is the scattering amplitude for transition from \mathbf{p} to \mathbf{p}' in collision with a single collision center. The flux of electrons into $d\Omega'$ is the number of possible events $nf(\mathbf{p})d^{3}p$, times the scattering probability $S(\mathbf{K},\omega)|F(\mathbf{p} \rightarrow \mathbf{p}')|^{2}$, times the final velocity and solid angle $(p'/m)d\Omega'$. This is integrated over all energy transfers ω . The momentum transfer \mathbf{K} and energy transfer ω are given by

$$\mathbf{p}' = \mathbf{p} - \mathbf{K}, \quad \epsilon' = \epsilon - \omega.$$
 (9)

Similarly, the number of electrons scattered into d^3p from d^3p' is

$$nd\Omega \int d\omega \, S(-\mathbf{K}, -\omega) \frac{p}{m} |F(\mathbf{p}' \to \mathbf{p})|^2 f(\mathbf{p}') d^3 p'. (10)$$

From unitarity or time reversal and isotropy, the absolute squares of the two scattering amplitudes are equal. The average of the initial and final energies is in each case $\epsilon - \omega/2$. We shall therefore set

$$|F|^2 = \sigma(\epsilon - \omega/2, \theta),$$
 (11)

where $\sigma(\epsilon, \theta)$ is the differential cross section at energy ϵ , with θ the angle between **p** and **p'**. From Eq. (9) it follows that

$$d^{3}p' = (p'/p)(d\Omega'/d\Omega)d^{3}p. \qquad (12)$$

Using (11) and (12), the net number of electrons scattered into d^3p per unit time is, integrating over $d\Omega'$,

$$d^{3}pn \int d\Omega' \int d\omega \, \frac{p'}{m} \sigma(\epsilon - \omega/2, \, \theta) \{ S(-\mathbf{K}, -\omega) f(\mathbf{p}') - S(\mathbf{K}, \omega) f(\mathbf{p}) \} \,. \tag{13}$$

A similar collision term has been written down by Baym.¹⁷ If there is no phonon drag, the detailed balancing condition (1) is valid. Combining (7) and (13), the Boltzmann equation for electrons in a steady electric field is thus

$$e\mathbf{E} \cdot \frac{\partial f}{\partial \mathbf{p}} = n \int d\Omega' \int d\omega \, \frac{p'}{m} \sigma(\epsilon - \omega/2, \, \theta) S(\mathbf{K}, \omega) \\ \times \{e^{-\beta\omega} f(\mathbf{p}') - f(\mathbf{p})\}. \quad (14)$$

Pidduck's method of solution is to expand both sides in Legendre polynomials of $\cos(\mathbf{p}, \mathbf{E})$ and equate coefficients. The left-hand side (LHS) has already been written in this form in Eq. (7). To evaluate the righthand side (RHS) both $f(\mathbf{p})$ and $f(\mathbf{p}')$ are expanded as in (6); terms in $P_n(\cos\zeta')$ are reduced to terms in $P_n(\cos\zeta)$ by the spherical harmonic addition theorem:

 $P_n(\cos\zeta') = P_n(\cos\zeta)P_n(\cos\theta) + \text{terms which give zero}$ on integration over the azimuthal angle.

¹⁷ G. Baym, Phys. Rev. 135, A1691 (1964).

We now expand all energy-dependent quantities of the RHS, to first order in ω outside the bracket, to second order inside. Since K is a function of the energy transfer ω , we must write

$$S(\mathbf{K},\omega) = S(\mathbf{K}_{0},\omega) - \frac{\omega}{4\epsilon} \mathbf{K}_{0} \cdot \frac{\partial}{\partial \mathbf{K}_{0}} S(\mathbf{K}_{0},\omega).$$
(15)

To evaluate the second term, we shall interchange the order of $\partial/\partial K_0$ and $\int d\omega$. Here $K_0 = 2p \sin \frac{1}{2}\theta$ is the momentum transfer in a perfectly elastic collision, i.e., with $\omega = 0$. When we expand in powers of ω as described, and use the sum rules (2), (3), and (4), the RHS of (14) becomes

$$n2\pi \int_{0}^{\pi} d\theta \sin\theta \{A_{0}P_{0} + A_{1}P_{1}(\cos\zeta) + A_{2}P_{2}(\cos\zeta)\}, \quad (16)$$

where

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$$A_{0} = (2m/M)(1 - \cos\theta) \left[\epsilon \sigma (f_{0}' + kTf_{0}'') + (\epsilon \sigma' + 2\sigma)(f_{0} + kTf_{0}') \right]$$

+ term of order $\left(\frac{m}{M} \frac{\epsilon}{kT}\right) \left(\frac{m}{M} \frac{\Theta_{D}}{kT}\right) f_{0}\sigma$

$$A_{1} = -\left[1 - P_{1}(\cos\theta)\right] f_{1}\sigma S(\mathbf{K}_{0}) + \text{term of order}\left(\frac{m}{M}\frac{\epsilon}{kT}\right) f_{1}\sigma,$$

$$4_{2} = -\left[1 - P_{2}(\cos\theta)\right] f_{2}\sigma S(\mathbf{K}_{0})$$

+ term of order $\left(\frac{m}{M} \frac{\epsilon}{kT}\right) f_{2}\sigma$

Now define the "mean free paths" Λ_0 , Λ_1 , and Λ_2 by¹⁸

$$\Lambda_{0}^{-1} = n2\pi \int_{0}^{\pi} d\theta \sin\theta (1 - \cos\theta) \sigma(\epsilon, \theta) ,$$

$$\Lambda_{1}^{-1} = n2\pi \int_{0}^{\pi} d\theta \sin\theta [1 - P_{1}(\cos\theta)] \sigma(\epsilon, \theta) S(\mathbf{K}_{0}) , \quad (17)$$

$$\Lambda_{2}^{-1} = n2\pi \int_{0}^{\pi} d\theta \sin\theta [1 - P_{2}(\cos\theta)] \sigma(\epsilon, \theta) S(\mathbf{K}_{0}) .$$

We equate coefficients of $P_n(\cos\zeta)$ and neglect terms smaller by $(m/M)\epsilon/kT$, to obtain three equations for f_0 , f_1 , and f_2 . The first equation may be integrated once:

$$\frac{1}{3}eE\Lambda_0 f_1 = (2m/M)\epsilon(f_0 + kTf_0').$$
 (18)

The other two equations are

$$eE\Lambda_1(f_0' + \frac{2}{5}f_2' + \frac{3}{5}f_2/\epsilon) = -f_1, \qquad (19)$$

$$\frac{1}{3}eE\Lambda_2(2f_1' - f_1/\epsilon) = -f_2.$$
 (20)

When E is zero, $f_0 = e^{-\epsilon/kT}$ and f_1 and f_2 are zero. At low fields, f_1 is linear in E and f_2 quadratic in E. At high fields, f_2/f_1 is of the order of $eE\Lambda_2/\langle\epsilon\rangle$. By Shockley's arguments¹⁹ about energy balance at high fields, this is of the order of $(m/M)^{1/2}$. Therefore f_2 may be neglected at both low and high fields. We define

$$b(x) = \frac{1}{3} (eE\Lambda_0) (eE\Lambda_1) / (2m/M) (kT)^2.$$
 (21)

Eliminating f_1 between (18) and (19) gives a homogeneous linear differential equation for f_0 :

$$[x+b(x)]\frac{df_0}{dx} + xf_0 = 0.$$
 (22)

When b is constant, $f_0 = (x+b)^b e^{-x}$.

The results above apply to a dilute gas of electrons. For a Fermi gas of electrons, such as in degenerate semiconductors or in metals, the term $e^{-\beta\omega}f(\mathbf{p}')-f(\mathbf{p})$ in (14) is to be replaced by

$$e^{-\beta\omega}f(\mathbf{p}')[1-f(\mathbf{p})]-f(\mathbf{p})[1-f(\mathbf{p}')].$$

Omitting terms with f_2 and f_1^2 , we get

$$\frac{1}{3}eE\Lambda_0 f_1 = (2m/M)\epsilon [f_0(1-f_0) + kTf_0']$$
(23)

and

$$eE\Lambda_1 f_0' = -f_1. \tag{24}$$

The equation for f_0 is now nonlinear:

$$[x+b(x)]\frac{df_0}{dx}+xf_0(1-f_0)=0.$$
 (25)

The solution for constant b is

$$f_0 = \{Ce^x/(x+b)^b + 1\}^{-1}.$$
 (26)

The mean energy and the drift velocity are given in terms of the solutions of (22) or (25) by

$$\langle \epsilon \rangle = kT \frac{\int_{0}^{\infty} dx \, x^{3/2} f_{0}(x)}{\int_{0}^{\infty} dx \, x^{1/2} f_{0}(x)},$$
 (27)

$$v_D = \frac{1}{3} \left(\frac{2kT}{m}\right)^{1/2} \frac{\int_0^\infty dx \, x f_1(x)}{\int_0^\infty dx \, x^{1/2} f_0(x)} \,. \tag{28}$$

¹⁸ The mean free path Λ_1 is the same as that introduced by H. Gerstenkorn [Ann. Phys. (Leipzig) 10, 49 (1952)] and J. M. Ziman [Phil. Mag. 6, 1013 (1961)] in the theory of the resistivity of liquid metals.

¹⁹ Reference 11, p. 1005. The energy-balance argument runs as follows: Electrons gain energy at the rate $v_{D}eE$ from the field, and lose energy at the rate $(v/\Lambda)(m/M)\langle\epsilon\rangle$ by collisions. In the steady state these rates are equal. (There is little difference between the various Λ 's at high fields.) Because $v_{D} \simeq eE\Lambda/mv$ from general kinetic arguments, it follows that $eE\Lambda/\langle\epsilon\rangle \sim (m/M)^{1/2}$.

and

For electrons moving in gases which are sufficiently dilute to obey the perfect gas law (P=nkT), $S(\mathbf{K})=1$ and our result reduces to that of Pidduck, Davydov, and Chapman and Cowling.²⁰ In liquids and solids structure becomes important and two distinct "mean free paths" enter into the problem. Physically, this means that the rates of energy and momentum transfer are different. In (18), the RHS is the average energy lost per collision, while the LHS is the average energy gained from the field between collisions. Thus Λ_0 , which is independent of structure, determines the rate of energy transfer. Similarly, writing (19) or (24) in the form

$$f_1dp + eE\tau_1df_0 = 0$$
, $\tau_1 = \Lambda_1/v$,

we see that this equation represents the balance between the gain in momentum due to drift down the field and the loss due to collisions. Therefore Λ_1 , which is structure-dependent, determines the rate of momentum transfer.²¹

The ratio Λ_1/Λ_0 is close to unity for very hot or highly degenerate electrons since the structure factor tends to one for large momentum transfers. For thermal electrons, however, the efficiency in energy transfer is greater by the factor $1/S(0) \simeq Mc^2/kT$. On the other hand, the magnitude of the average energy transfer to all multiphonon excitations [given by the sum rule (3)] is smaller than that to single phonons only by the factor $M^*/M = kT/Mc^2$. Therefore at low and medium fields we do not differ numerically from the theories of Landau and Kompanejez, Davydov, Shockley, and Yamashita, and Watanabe. The criteria for the limit of the low-field region, where by definition the electron distribution is close to equilibrium (i.e., Maxwellian or Fermi-Dirac) are, respectively,

$$\frac{1}{3}(eE\Lambda_0)(eE\Lambda_1) \sim (2m/M)(kT)^2 \tag{29}$$

 $\frac{1}{3}(eE)$

$$\epsilon_{\rm I}(eE\Lambda_0)(eE\Lambda_1) \sim (2m/M)\epsilon_F kT.$$
 (30)

The criterion (29) reduces to the Landau-Shockley criterion $v_D \sim c$. Using the experimental mean free paths, these fields come out to be about 200 V/cm for electrons in liquid argon and about 20 000 V/cm for the conduction electrons in liquid sodium.

To summarize, we have constructed a hot-electron theory equally valid for gases, liquids, and solids. The primary approximations made are the assumptions of no multiple scattering and a sufficiently high temperature for the average energy transfer to be small compared to thermal energy. The present theory is identical to the Pidduck-Davydov-Chapman-Cowling theory for gases. For solids, in particular semiconductors, it reduces to the Landau-Davydov-Shockley-Yamashita-Watanabe theory only because of a fortuitous cancellation occurring at low and medium fields. For liquids it is new and includes through $S(\mathbf{K}, \omega)$ the structural effects essential therein.

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²⁰ Footnote added in proof. More generally, the sum of x^{-1} times Eq. (22) and the derivative of Eq. (22) with respect to X gives Pidduck's equation for f_0 (of introduction), but with the definition (21) for b(x) and provided the x dependence of b is neglected in the differentiation.

²¹ The fact that equating the P_0 and $P_1(\cos\zeta)$ coefficients gives, respectively, the conditions of energy and momentum balance was pointed out by P. M. Morse, W. P. Allis, and E. S. Lamar, Phys. Rev. 48, 412 (1935).