Plasma Theory of Electron-Phonon Interaction in Metals

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The transport theory of an electron gas recently developed is extended to include the interaction with the ions in a metal. The perturbation of the lattice vibrations induced by an anistropy of the electron distribution is calculated. Subsequently the ionic degrees of freedom are eliminated from the transport equation of the electrons in favor of a long-range electron correlation term. The influence of this term becomes important at long wavelengths (in the far infrared) but constitutes a small perturbation for the eigenfrequencies of collective motion of the electron gas. Nevertheless the dispersion relation for the collective oscillations shows that the contributions due to the phonon interaction are of the same order of magnitude as the influence of thermal agitation.

1. INTRODUCTION

RECENTLY the author derived a quantum mechanical transport equation[1] for a "free" electron gas in which the coulomb forces between the electrons were taken into account in the sense of long-range correlations. Close encounters, i.e., binary collisions were neglected so that the equation derived is entirely equivalent to the classical collision less Boltzmann equation. The ions were treated as a uniform background of a smeared out positive charge density without any dynamical properties of their own. Actually, of course, the ions form positive charge concentrations localized at the lattice sites and they perform small oscillations about their equilibrium positions. Naturally this is going to influence the electron distribution. The ions by virtue of their interaction potential with the "free" or conduction electrons will induce a polarization of the electron cloud which in turn will affect the ionic motion. It is precisely this interplay between ions and conduction electrons we wish to investigate in this paper. To be sure the electron phonon interaction has been investigated in the past.[2] But these treatments are essentially limited to zero temperature. We intend to give a derivation in what follows, which is based on statistical concepts. In fact, we assume that the majority of both the electrons and the phonons are in statistical equilibrium at a given temperature and that the electron-phonon interaction gives rise to a polarization of both the electron distribution and the phonon distribution which is triggered by an external force field. If the external fields are small we may treat the ensuing polarization of the medium also as small and linear equations for the perturbed distribution result. In part 2 we will give the actual derivation of the transport equation of the electrons in the presence of the lattice ions. Two new terms will appear in this equation. The first term which is present even if the ions are rigidly fixed in their equilibrium positions and therefore has the periodicity of the lattice, will be eliminated in part 3. In part 4 finally the dispersion relation for the electron plasma oscillations is derived and some comments about the applicability of the theory to problems of physical interest, particularly the optical properties of metals in the far infrared, are made.

[1] O. von Roos, Phys. Rev. **119**, 1174 (1960); hereafter referred to as I.

[2] J. Bardeen and D. Pines, Phys. Rev. **99**, 1140 (1955); D. Bohm and I. Staver, Phys. Rev. **84**, 836 (1952). S. Nakajima, *Proceedings of the International Conference on Theoretical Physics, Kyoto and Tokyo, September 1953* (Science Council of Japan, Tokyo, 1954). H. Fröhlich, Phys. Rev. **79**, 845 (1950).

2. DERIVATION OF THE ELECTRON TRANSPORT EQUATION

If the quantum mechanical distribution function $\tilde{F}(\mathbf{r},\mathbf{k},t)$ for the electrons introduced in I is split into a large and a small part according to:

$$\tilde{F}=F_0(\mathbf{k})+F_1(\mathbf{r},\mathbf{k},t)$$
$$=F_0(\mathbf{k})+\int d^3K dw\,\alpha(\mathbf{K},\mathbf{k},w)e^{i(\mathbf{K}\cdot\mathbf{r}-wt)} \quad (1)$$

then we know from I that $\alpha(\mathbf{K},\mathbf{k},w)$ satisfies the following equation if only electron-electron interactions are taken into account:

$$\left(-w+\frac{\hbar}{m}\mathbf{K}\cdot\mathbf{k}+\frac{\hbar}{2m}\mathbf{K}^2\right)\alpha(\mathbf{K},\mathbf{k},w)$$
$$=w_P^2\frac{m}{2\hbar}\frac{1}{K^2}[F_0(\mathbf{k}+\mathbf{K})-F_0(\mathbf{k})]\int\alpha(\mathbf{K},\mathbf{k}',w)d^3k'$$
$$-w_P^2\frac{m}{2\hbar}\int d^3k'|\mathbf{k}-\mathbf{k}'|^{-2}\{\alpha(\mathbf{K},\mathbf{k}',w)[F_0(\mathbf{k}+\mathbf{K})$$
$$-F_0(\mathbf{k})]-\alpha(\mathbf{K},\mathbf{k},w)[F_0(\mathbf{k}'+\mathbf{K})-F_0(\mathbf{k}')]\}. \quad (2)$$

$F_0(\mathbf{k})$ in the above formulas is the Fermi Dirac distribution. $\mathbf{k}=(m/\hbar)\mathbf{v}$ is the wave vector of the electron. Otherwise the symbols used are the same as in I to which the reader is referred for more details. From the definition of $\tilde{F}$ as given in I it is easy to discover that $\alpha(\mathbf{K},\mathbf{k},w)$, i.e., the Fourier transform of the perturbed distribution function may be written as

$$\alpha(\mathbf{K},\mathbf{k},w)=\rho(\mathbf{K}+\mathbf{k},\mathbf{k}), \quad (3)$$

where $\rho(\mathbf{k}',\mathbf{k})$ is the density matrix in momentum space. Equation (1) therefore is equivalent to the assumption that the density matrix consists of large diagonal elements given by the thermal equilibrium distribution and small off diagonal elements. This establishes a connection with the work by Ehrenreich and Cohen.[3] To recapitulate, Eq. (2) is valid if any electron-ion interaction is neglected. In order to introduce the latter we assume that there exists a potential energy of interaction between the ions at positions $\mathbf{R}_j$ and an electron at position $\mathbf{r}$ of the following form

$$V_{\text{inter}}=\sum_j V(\mathbf{R}_j-\mathbf{r}). \tag{4}$$

The sum runs over all N ions inside a fixed and large periodicity volume. Later we will take the limit $V\to\infty$ since we are only interested in bulk properties and the formulas simplify somewhat in this limit. The exact form of the interaction potential $V(\mathbf{R}_j-\mathbf{r})$ between an ion and an electron need not be specified at the moment. For large interparticle distances however, it will become an attractive Coulomb potential:

$$V(\mathbf{R}_j-\mathbf{r})\to-\frac{e^2}{|\mathbf{R}_j-\mathbf{r}|}. \tag{5}$$

For simplicity we assume singly charged ions so that for each ion there is one conduction electron. For small distances a screening by the core electrons has to be taken into account.[4] We now assume that the ions perform small oscillations about their equilibrium positions $\mathbf{R}_j^0$ so that we may write:

$$\mathbf{R}_j-\mathbf{r}=\mathbf{R}_j^0-\mathbf{r}+\mathbf{a}_j, \tag{6}$$

and

$$V(\mathbf{R}_j-\mathbf{r})=V(\mathbf{R}_j^0-\mathbf{r})-\mathbf{a}_j\cdot\nabla_r V(\mathbf{R}_j^0-\mathbf{r}). \tag{7}$$

Clearly the $\mathbf{a}_j$ signify the amplitudes of oscillation of the individual ions. Considering the potential (4) as an external potential to which the electrons are coupled we know from I that it will give rise to a term:

$$(i/\hbar)[\exp(-i\nabla_r\cdot\nabla_k)-1]V_{\text{inter}}(\mathbf{r})\tilde{F}(\mathbf{r},\mathbf{k},t), \tag{8}$$

on the right-hand side of Eq. (29) of I. In the linearized version, corresponding to Eq. (2), in which the external potential is regarded as small the Fourier transform of the following term has to be added to the right-hand side of Eq. (2):

$$(i/\hbar)[\exp(-i\nabla_r\cdot\nabla_k)-1]V_{\text{inter}}F_0(\mathbf{k}), \tag{9}$$

where V_{inter} is given by Eqs. (4) and (7). Turning now to the ionic motion we know that, if the interaction with the conduction electrons is disregarded, an adequate description is given by the phonon hamiltonian[5]:

$$H_P=\hbar\sum_{\beta,i} w_\beta(\mathbf{Q}_i)[b_\beta^+(\mathbf{Q}_i)b_\beta(\mathbf{Q}_i)+\tfrac{1}{2}]. \tag{10}$$

In this expression β (running from 1 to 3) is the polarization of the lattice wave and $\mathbf{Q}_i$ is a vector in the reciprocal lattice. There are N different $\mathbf{Q}_i$ in the first Brillouin zone indicated by the sum over i. The $3N$ possible frequencies $w_\beta(\mathbf{Q}_i)$ are solely determined by ion-ion interactions. They are therefore the "bare" phonon frequencies of Bardeen and Pines.[6] The operators b and b^+ satisfy the well known commutation relations:

$$[b_\beta(\mathbf{Q}_i),b_\alpha^+(\mathbf{Q}_j)]=\delta_{\beta\alpha}\delta_{ij}. \tag{11}$$

All other commutations vanish. Expressed by the b and b^+ the ionic displacements are given by[5] (greek subscripts indicate cartesian components):

$$a_{j\beta}=\left(\frac{\hbar}{2MN}\right)^{\frac{1}{2}}\sum_e[w_\beta(\mathbf{Q}_e)]^{-\frac{1}{2}}\{\exp(i\mathbf{Q}_e\cdot\mathbf{R}_j^0)b_\beta(\mathbf{Q}_e)+\exp(-i\mathbf{Q}_e\cdot\mathbf{R}_j^0)b_\beta^+(\mathbf{Q}_e)\}. \tag{12}$$

Here M is the mass of a lattice ion. The coupling with the conduction electrons may be described by the following interaction hamiltonian:

$$H_{\text{inter}}=N_1\sum_j \mathbf{a}_j\cdot\nabla_{R_j^0}\times\int d^3r'd^3k'V(\mathbf{R}_j^0-\mathbf{r}')F_1(\mathbf{r}_1',\mathbf{k}',t). \tag{13}$$

$N_1=N/V$ is the number density of electrons. The sum runs over all N ions of our quantization volume V. The integral over the interaction potential with the (unknown) electronic distribution function arises from the fact that we assume that the phonon degrees of freedom and the electronic degrees of freedom are sufficiently weakly coupled so that the state vector of the complete system is adequately represented by a product of wave functions for the phonons and electrons separately. This is equivalent to the use of Hartree's self consistent field method. It can also be shown to be equivalent to the use of the very same statistical assumptions as made in I, namely that the doublet distribution function splits into a product of singlet distribution functions. To show this we need only introduce a distribution function containing also the phonon variables, establish the Liouville equation in analogy to the procedures employed in I, obtain equations for the singlet distribution functions in terms of the doublet distribution functions and finally make the assumption of negligible correlation as done in I. However, we adopted here the Hamiltonian approach for the phonons since it is mathematically somewhat simpler. Collecting the formulas (10), (12), and (13) we now obtain our first basic equation, i.e., the equation for the state vector of the lattice vibrations coupled to the conduction electrons

$$(H_P+H_{\text{inter}})\Omega=-(\hbar/i)(\partial/\partial t)\Omega. \tag{14}$$

Turning back to the electron distribution and its equation we see that in the spirit of the self consistent

[3] H. Ehrenreich and M. H. Cohen, Phys. Rev. **115**, 786 (1959).
[4] J. Bardeen, Phys. Rev. **52**, 688 (1937).
[5] G. Leibfried in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. 7, part 1.
[6] See Bardeen and Pines, reference 2.

field the interaction term (9) may be written observing Eq. (7):

$$(i/\hbar)[\exp(-i\nabla_r\cdot\nabla_k)-1]\sum_j\{V(\mathbf{R}_j^0-\mathbf{r})F_0(\mathbf{k}) +\langle\Omega|\mathbf{a}_j|\Omega\rangle\cdot\nabla_{R_j^0}V(\mathbf{R}_j^0-\mathbf{r})F_0(\mathbf{k})\}. \quad (15)$$

Corresponding to the expectation value of the interaction potential with respect to the electronic degrees of freedom in Eq. (13) we have the expectation value of the ionic displacements with respect to the ionic degrees of freedom in expression (15). It is the Fourier transform of expression (15) which has to be added to the right-hand side of Eq. (2). Defining:

$$\int d^3u\, V(\mathbf{u})e^{-i\mathbf{K}\cdot\mathbf{u}}=\phi(\mathbf{K}), \quad (16)$$

and observing the definition of the operator $[\exp(-i\nabla_r\cdot\nabla_k)-1]$ [Eq. (10) of I] it is not difficult to discover after some calculation that the Fourier transform (both in space and time) of expression (15) is given by:

$$(i/\hbar)\phi^*(\mathbf{K})[F_0(\mathbf{k}+\mathbf{K})-F_0(\mathbf{k})] \times\sum_j\left\{2\pi\delta(w)\exp(-i\mathbf{K}\cdot\mathbf{R}_j^0) -i\int dt\, e^{iwt}\langle\Omega|\mathbf{a}_j|\Omega\rangle\cdot\mathbf{K}\exp(-i\mathbf{K}\cdot\mathbf{R}_j^0)\right\}. \quad (17)$$

The first term of the sum in expression (17) is due to the static interaction, the lattice ions being fixed at their equilibrium positions. The second term is due to phonon interaction. It is the latter term which contains the distribution function $\alpha(\mathbf{K},\mathbf{k},w)$ by virtue of the coupling H_{inter} Eq. (13) which in turn determines Ω and subsequently the expectation value occurring in (17). We now may write down the second basic equation, i.e., the equation for the electron distribution function in the presence of electron-ion interactions. Dividing (17) by a normalization factor $(2\pi)^4$ from the Fourier transformation and adding the result to Eq. (2) we find:

$$\left(-w+\frac{\hbar}{m}\mathbf{K}\cdot\mathbf{k}+\frac{\hbar}{2m}K^2\right)\alpha(\mathbf{K},\mathbf{k},w) =w_P{}^2\frac{m}{\hbar}\frac{1}{K^2}[F_0(\mathbf{k}+\mathbf{K})-F_0(\mathbf{k})]\int d^3k'\,\alpha(\mathbf{K},\mathbf{k}',w) -w_P{}^2\frac{m}{2\hbar}\int d^3k'|\mathbf{k}-\mathbf{k}'|^{-2}\{\alpha(\mathbf{K},\mathbf{k}',w)[F_0(\mathbf{k}+\mathbf{K}) -F_0(\mathbf{k})]-\alpha(\mathbf{K},\mathbf{k},w)[F_0(\mathbf{k}'+\mathbf{K})-F_0(\mathbf{k}')]\} +[1/(2\pi)^3\hbar]\delta(w)\phi^*(\mathbf{K})[F_0(\mathbf{k}+\mathbf{K})-F_0(\mathbf{k})] \times\sum_j\exp(-i\mathbf{K}\cdot\mathbf{R}_j^0)-[i/(2\pi)^4]\phi^*(\mathbf{K})[F_0(\mathbf{k}+\mathbf{K}) -F_0(\mathbf{k})]\int dt\, e^{iwt}\langle\Omega|\mathbf{a}_j|\Omega\rangle\cdot\mathbf{K}\exp(-i\mathbf{K}\cdot\mathbf{R}_j^0). \quad (18)$$

Equations (14) and (18) constitute the basis for our further investigations. From here we can go either of two ways. Either we eliminate $\alpha(\mathbf{K},\mathbf{k},w)$ from H_{inter} in Eq. (14) by means of Eq. (18). This procedure is essentially the one adopted by Bardeen and Pines which leads to the corrected sound wave frequencies.[6] Or we may eliminate the phonon degrees of freedom by solving Eq. (14) and inserting the result into the expectation value occurring in Eq. (18). It is this latter approach which we actually wish to investigate. In order to do so, we have to solve Eq. (14). Let us define:

$$D_{j\alpha}(t)=\frac{\partial}{\partial R_{j\alpha}{}^0}\int V(\mathbf{R}_j{}^0-\mathbf{r}')F_1(\mathbf{r}',\mathbf{k}',t)d^3r'd^3k'. \quad (19)$$

We then may write for the interaction according to (13) and (12):

$$H_{\text{inter}}=N_1\left(\frac{\hbar}{2MN}\right)^{\frac{1}{2}}\sum_{e,j,\alpha}D_{j\alpha}(t)\frac{\exp(i\mathbf{Q}_e\cdot\mathbf{R}_j^0)}{[w_\alpha(\mathbf{Q}_e)]^{\frac{1}{2}}} \times[b_\alpha(\mathbf{Q}_e)+b_\alpha{}^+(-\mathbf{Q}_e)], \quad (20)$$

and we propose to solve Eq. (14) by considering H_{inter} as a perturbation. Furthermore, we will make the same assumption with respect to the phonons as we did with respect to the electrons, namely that the majority of phonons is in thermal equilibrium. Introducing the occupation number formalism we assume that in 0th order, disregarding H_{inter}, the solution of Eq. (14) is given by:

$$\Omega^{(0)}=\sum_N c^{(0)}(N_j{}^{(\alpha)},t)\Omega(N_j{}^{(\alpha)}), \quad (21)$$

with

$$c^{(0)}(N_j{}^{(\alpha)},t)=Z^{-\frac{1}{2}}\exp\left\{-\frac{\hbar\beta}{2}\sum_{j,\alpha}w_\alpha(\mathbf{Q}_j)N_j{}^{(\alpha)} +i\phi(N_j{}^{(\alpha)})-\frac{it}{\hbar}E(N_j{}^{(\alpha)})\right\}. \quad (22)$$

Here we have

$$\Omega(N_j{}^{(\alpha)})=\Omega(N_1{}^{(\alpha_1)},N_2{}^{(\alpha_2)},\cdots N_j{}^{(\alpha)}\cdots), \quad (23)$$

as eigenstate to the number operator[7]:

$$\sum_{j,\alpha}b_\alpha{}^+(\mathbf{Q}_j)b_\alpha(\mathbf{Q}_j)\Omega(N_1{}^{(\alpha_1)},N_2{}^{(\alpha_2)},\cdots N_j{}^{(\alpha)}\cdots) =(N_1{}^{(\alpha_1)}+N_2{}^{(\alpha_2)}+\cdots N_j{}^{(\alpha)}+\cdots) \times\Omega(N_1{}^{(\alpha_1)},N_2{}^{(\alpha_2)}\cdots N_j{}^{(\alpha)}\cdots). \quad (24)$$

and the summation in (21) extends over all possible sets of $3N$ positive integers $N_j{}^{(\alpha)}$. Furthermore it is:

$$Z=\exp\{-\hbar\beta\sum_{j,\alpha}w_\alpha(\mathbf{Q}_j)N_j{}^{(\alpha)}\},\quad \beta=1/\kappa T, \quad (25)$$

[7] G. Süssmann, Seminarausarbeitung. Institut fur theoretische Physik der Freien Universitat, Berlin, 1950 (unpublished).

the partition function of the phonons at temperature T.

$$E(N_j^{(\alpha)})=\hbar\sum_{j,\alpha} w_\alpha(\mathbf{Q}_j)(N_j^{(\alpha)}+\tfrac{1}{2}), \tag{26}$$

the energy corresponding to the excitation of $N_j^{(\alpha)}$ phonons of polarization α and wave vector $\mathbf{Q}_j$. The random phases $\phi(N_j^{(\alpha)})$ finally are such that:

$$\mathrm{av}\{\exp[i\phi(N_j^{(\alpha)})-\phi(N_j^{(\alpha)\prime})]\}=\delta(N_j^{(\alpha)},N_j^{(\alpha)\prime}) \tag{27}$$

where $\mathrm{av}\{\cdots\}$ means phase average and $\delta(N,N')$ is the Kronecker symbol. In the light of these explanations it is easily seen that the amplitudes $c^{(0)}$ represent the system of phonons in thermal equilibrium. In fact, the density matrix according to (22) is given by

$$\begin{aligned}\rho(N_j^{(\alpha)},N_j^{(\alpha)\prime})&=\mathrm{av}\{c^*(N_j^{(\alpha)\prime})c(N_j^{(\alpha)})\}\\&=Z^{-1}\exp\{-\hbar\beta\sum_{j,\alpha} w_\alpha(\mathbf{Q}_j)N_j^{(\alpha)}\}\delta(N_j^{(\alpha)},N_j^{(\alpha)\prime}),\end{aligned} \tag{28}$$

which is the diagonal representation of thermal equilibrium in the occupation number formalism. Taking the interaction into account, we write

$$\begin{aligned}\Omega=\Omega^{(0)}+\Omega^{(1)}=\sum_N[&c^{(0)}(N_j^{(\alpha)},t)\\&+c^{(1)}(N_j^{(\alpha)},t)]\Omega(N_j^{(\alpha)}),\end{aligned} \tag{29}$$

and obtain the following set of equations for the $c^{(1)}$ using standard first order perturbation theory:

$$\begin{aligned}&\left\{\frac{\hbar}{i}\frac{\partial}{\partial t}+E(N_j^{(\alpha)})\right\}c^{(1)}(N_j^{(\alpha)},t)\\&=-N_1\left(\frac{\hbar}{2MN}\right)^{\frac{1}{2}}\sum_{e,\mathbf{Q}_i,\beta} D_{e\beta}(t)[w_\beta(\mathbf{Q}_i)]^{-\frac{1}{2}}\\&\quad\times\{\exp(-i\mathbf{Q}_i\cdot\mathbf{R}_e^0)(N_i^{(\beta)})^{\frac{1}{2}}c^{(0)}(N_j^{(\alpha)}-\delta_{ij}\delta_{\alpha\beta})\\&\quad+\exp(i\mathbf{Q}_i\cdot\mathbf{R}_e^0)(N_i^{(\beta)}+1)^{\frac{1}{2}}c^{(0)}(N_j^{(\alpha)}+\delta_{ij}\delta_{\alpha\beta})\}.\end{aligned} \tag{30}$$

This equation may readily be solved with the aid of Fourier transformation with respect to time. With the definition

$$D_{e\beta}(t)=\int\bar{D}_{e\beta}(w)e^{-iwt}dw, \tag{31}$$

we obtain from (30) the solution:

$$\begin{aligned}c^{(1)}(N_j^{(\alpha)})=\frac{N_1}{\hbar}\left(\frac{\hbar}{2MN}\right)^{\frac{1}{2}}\sum_{e,\mathbf{Q}_i,\beta}\Bigg\{&\exp(-i\mathbf{Q}_i\cdot\mathbf{R}_e^0)(N_i^{(\beta)})^{\frac{1}{2}}\\&\times\lim_{\epsilon=0}\int dw\frac{\bar{D}_{e\beta}(w)e^{-iwt}}{w-w_\beta(\mathbf{Q}_i)+i\epsilon}c^{(0)}(N_j^{(\alpha)}-\delta_{ij}\delta_{\alpha\beta})\\&+\exp(i\mathbf{Q}_i\cdot\mathbf{R}_e^0)(N_i^{(\beta)}+1)^{\frac{1}{2}}\\&\times\int dw\frac{\bar{D}_{e\beta}(w)e^{-iwt}}{w+w_\beta(\mathbf{Q}_i)+i\epsilon}c^{(0)}(N_j^{(\alpha)}+\delta_{ij}\delta_{\alpha\beta})\Bigg\}.\end{aligned} \tag{32}$$

The solution we took in (32) corresponds to the choice of a retarded Green's function since physically if $D(t)=0$ for $t<t_0$ say then also $c^{(1)}\equiv 0$. Our task is now to determine the matrix element of the ion displacement occurring in the last term on the right-hand side of Eq. (18) with the help of the state vector Ω as given by (29) together with the amplitudes Eqs. (22) and (32). A phase average in the sense of Eq. (27) has also to be performed. The straightforward but somewhat tedious calculations yield eventually the following result:

$$\begin{aligned}&\mathrm{av}\{\langle\Omega|a_{n\delta}|\Omega\rangle\}\\&=\frac{N_1}{2MN}\sum_{N_i^{(\alpha)}}\sum_{e,\mathbf{Q}_i}Z^{-1}\Bigg[N_i^{(\delta)}\frac{\exp[i\mathbf{Q}_i\cdot(\mathbf{R}_n^0-\mathbf{R}_e^0)]}{w_\delta(\mathbf{Q}_i)}\\&\quad\times\Bigg\{\exp[-\hbar\beta\sum_{j,\alpha} w_\alpha(\mathbf{Q}_j)(N_j^{(\alpha)}-\delta_{ij}\delta_{\alpha\beta})]\\&\quad\times\lim_{\epsilon=0}\int dw\frac{\bar{D}_{n\delta}(w)e^{-iwt}}{w-w_\delta(\mathbf{Q}_i)+i\epsilon}\\&\quad+\exp[-\hbar\beta\sum_{j,\alpha} w_\alpha(\mathbf{Q}_j)N_j^{(\alpha)}]\\&\quad\times\lim_{\epsilon=0}\int dw\frac{\bar{D}_{n\delta}^*(w)e^{iwt}}{w+w_\delta(\mathbf{Q}_i)-i\epsilon}\Bigg\}\\&\quad+(N_i^{(\delta)}+1)\frac{\exp[-i\mathbf{Q}_i\cdot(\mathbf{R}_n^0-\mathbf{R}_e^0)]}{w_\delta(\mathbf{Q}_i)}\\&\quad\times\Bigg\{\exp[-\hbar\beta\sum_{j,\alpha} w_\alpha(\mathbf{Q}_j)(N_j^{(\alpha)}+\delta_{ij}\delta_{\alpha\beta})]\\&\quad\times\lim_{\epsilon=0}\int dw\frac{\bar{D}_{n\delta}(w)e^{-iwt}}{w+w_\delta(\mathbf{Q}_i)+i\epsilon}\\&\quad+\exp[-\hbar\beta\sum_{j,\alpha} w_\alpha(\mathbf{Q}_j)N_j^{(\alpha)}]\\&\qquad\times\lim_{\epsilon=0}\int dw\frac{\bar{D}_{n\delta}^*(w)e^{iwt}}{w-w_\delta(\mathbf{Q}_i)-i\epsilon}\Bigg\}\Bigg].\end{aligned} \tag{33}$$

The sums over the occupation numbers may easily be performed noticing that they may be written as a product of geometric series and their derivatives. Using also the fact that

$$\bar{D}_{n\delta}^*(w)=D_{n\delta}(-w), \tag{34}$$

since $D(t)$ is real, we obtain for the Fourier transform of Eq. (33)

$$\int dt e^{iwt}\,\mathrm{av}\{\langle\Omega|a_{j\delta}|\Omega\rangle\}$$

$$=\frac{N_1}{2MN}\sum_{e,\mathbf{Q}_i}\{1-\exp[-\hbar\beta w_\delta(\mathbf{Q}_i)]\}^{-1}$$
$$\times\Big\{\frac{\exp[i\mathbf{Q}_i\cdot(\mathbf{R}_j^0-\mathbf{R}_e^0)]}{w_\delta(\mathbf{Q}_i)}\Big[\frac{\bar{D}_{e\delta}(w)}{w-w_\delta(\mathbf{Q}_i)+i\epsilon}$$
$$+\exp[-\hbar\beta w_\delta(\mathbf{Q}_i)]\frac{\bar{D}_{e\delta}(w)}{-w+w_\delta(\mathbf{Q}_i)-i\epsilon}\Big]$$
$$+\frac{\exp[-i\mathbf{Q}_i(\mathbf{R}_j^0-\mathbf{R}_e^0)]}{w_\delta(\mathbf{Q}_i)}\Big[\frac{\bar{D}_{e\delta}(w)}{-w-w_\delta(\mathbf{Q}_i)-i\epsilon}$$
$$+\exp[-\hbar\beta w_\delta(\mathbf{Q}_i)]\frac{\bar{D}_{e\delta}(w)}{w+w_\delta(\mathbf{Q}_i)+i\epsilon}\Big]\Big\}. \quad (35)$$

From Eqs. (31), (19), and (16) we also have

$$\bar{D}_{e\delta}(w)=i\int d^3k'd^3K'\,K_\delta'\exp(i\mathbf{K}'\cdot\mathbf{R}_e^0)$$
$$\times\alpha(\mathbf{K}',\mathbf{k}',w)\phi(\mathbf{K}'). \quad (36)$$

All we have to do now is to insert expressions (36) and (35) into the appropriate interaction term of the transport Eq. (18) and perform the summations over the lattice sites as indicated. These summations are conveniently done by taking at this point the limit $V=\infty$. In this limit

$$\sum_{\mathbf{Q}_i}\cdots\equiv\frac{V}{(2\pi)^3}\int d^3Q\cdots \quad (37)$$

and

$$\sum_j\exp(i\mathbf{K}\cdot\mathbf{R}_j^0)=(2\pi)^3N_1\sum_n\delta(\mathbf{K}-\mathbf{l}_n). \quad (38)$$

The integration in (37) extends only over the first Brillouin zone. The vectors $\mathbf{l}_n$ belong to the reciprocal lattice.[5] Designating the basis vectors of the lattice by $\mathbf{a}_1\mathbf{a}_2$ and $\mathbf{a}_3$ the $\mathbf{l}_n$ are defined more specifically by:

$$\mathbf{l}_n=\frac{2\pi}{\mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3)}(n_1\mathbf{a}_2\times\mathbf{a}_3+n_2\mathbf{a}_3\times\mathbf{a}_1+n_3\mathbf{a}_1\times\mathbf{a}_2), \quad (39)$$

with arbitrary integers, n_1, n_2, n_3. With the help of (37) and (38) it is found after some calculation that:

$$\int dt\,e^{iwt}\sum_j\mathrm{av}\{\langle\Omega|a_{j\delta}|\Omega\rangle\}\exp(-i\mathbf{K}\cdot\mathbf{R}_j^0)$$
$$=(2\pi)^4i\frac{N_1^2}{M}[(w+i\epsilon)^2-(w_\delta(\mathbf{K}))^2]^{-1}$$
$$\times\sum_n(K_\delta+l_{n\delta})\phi(\mathbf{K}+\mathbf{l}_n)\int d^3k'\alpha(\mathbf{K}+\mathbf{l}_n,\mathbf{k}',w). \quad (40)$$

Using Eqs. (38) and (40) we have finally reached our goal. The two last terms on the right-hand side of the transport Eq. (18) are given by:

$$\frac{N_1}{\hbar}\phi^*(\mathbf{K})[F_0(\mathbf{k}+\mathbf{K})-F_0(\mathbf{k})]\sum_n\delta(\mathbf{K}-\mathbf{l}_n)$$
$$+\frac{N_1^2}{M\hbar}[F_0(\mathbf{k}+\mathbf{K})-F_0(\mathbf{k})]\sum_{n,\delta}\frac{K_\delta(K_\delta+l_{n\delta})}{(w+i\epsilon)^2-[w_\delta(\mathbf{K})]^2}$$
$$\times\phi^*(\mathbf{K})\phi(\mathbf{K}+\mathbf{l}_n)\int d^3k'\,\alpha(\mathbf{K}+\mathbf{l}_n,\mathbf{k}',w). \quad (41)$$

The first term of expression (41) represents the static interaction with fixed lattice ions, the second term represents the response to the ionic motion.

3. ELIMINATION OF THE STATIC INTERACTION

The elimination of the static interaction, the first term of expression (41), is most easily effectuated with the "ansatz":

$$\alpha(\mathbf{K},\mathbf{k},w)=\alpha_S(\mathbf{K},\mathbf{k},w)+\beta(\mathbf{K},\mathbf{k},w)$$
$$=\delta(w)\textstyle\sum_n c_n(\mathbf{l}_n,\mathbf{k})\delta(\mathbf{K}-\mathbf{l}_n)+\beta(\mathbf{K},\mathbf{k},w), \quad (42)$$

suggested by the form of the static interaction. It can be shown (see the appendix) that no contribution toward α_S arises from the phonon interaction term [the second term of expression (41)] provided that the interaction potential (5) is a central potential, an assumption which we will make from now on. In this case $\phi(\mathbf{K})$ is real and depends only on the magnitude of K. We may also neglect the exchange term [the second term on the right-hand side of Eq. (18)] since it gives rise only to small effects.[8] Inserting then α_S into Eq. (18) yields the following set of equations for the coefficients c_n:

$$\Big(\frac{\hbar}{m}\mathbf{l}_n\cdot\mathbf{k}+\frac{\hbar}{2m}\mathbf{l}_n^2\Big)c_n(\mathbf{l}_n,\mathbf{k})$$
$$=[F_0(\mathbf{k}+\mathbf{l}_n)-F_0(\mathbf{k})]\Big\{w_P{}^2\frac{m}{\hbar}\frac{1}{l_n{}^2}\int c_n(\mathbf{l}_n,\mathbf{k}')d^3k'$$
$$+\frac{N_1}{\hbar}\phi(\mathbf{l}_n)\Big\}. \quad (43)$$

Dividing Eq. (43) by $[(\hbar/m)\mathbf{l}_n\cdot\mathbf{k}+(\hbar/2m)\mathbf{l}_n^2]$ and integrating over k gives after a few rearrangements:

$$\int c_n(\mathbf{l}_n,\mathbf{k}')d^3k'=\frac{N_1}{m}\mathbf{l}_n^2\phi(\mathbf{l}_n)\frac{A(\mathbf{l}_n)}{1-w_P{}^2A(\mathbf{l}_n)}, \quad (44)$$

[8] P. A. Wolff, Phys. Rev. 92, 18 (1953).

with

$$A(\mathbf{l}_n)=\left(\frac{m}{\hbar}\right)^2\int d^3k\frac{F_0(\mathbf{k})}{\mathbf{k}\cdot\mathbf{l}_n-\frac{1}{4}\mathbf{l}_n^2}. \tag{45}$$

Inserting Eq. (44) back into (43) finally yields the desired solution.

$$c_n(\mathbf{l}_n,\mathbf{k})=\frac{mN_1}{\hbar^2}\phi(\mathbf{l}_n)[1-w_P^2A(\mathbf{l}_n)]^{-1}\times\frac{F_0(\mathbf{k}+\mathbf{l}_n)-F_0(\mathbf{k})}{\mathbf{k}\cdot\mathbf{l}_n+\frac{1}{2}l_n^2}, \tag{46}$$

$$c_0(0,\mathbf{k})=0.$$

That part of the distribution function which corresponds to α_S and which is given by an inverse Fourier transformation according to Eq. (1) may be written as a series over the reciprocal lattice:

$$\tilde{F}_S=\sum_n c_n(\mathbf{l}_n,\mathbf{k})\exp(i\mathbf{l}_n\cdot\mathbf{r}). \tag{47}$$

It has the periodicity of the lattice and is the statistical average of the motion of a nearly free electron perturbed by a periodic potential.

4. THE DISPERSION RELATION FOR THE ELECTRON PLASMA

In the last section we succeeded in eliminating the static interaction. The transport equation (18) therefore reduces to an equation for β as defined by Eq. (42). Before writing down the equation for β let us introduce two simplications. Firstly, we are only interested in small values of $|\mathbf{K}|$. More specifically, we assume that K is much smaller than the reciprocal of the interparticle spacing. Physically this means that any external perturbation which gives rise to a polarization of the electron distribution or in other words which excites the medium varies appreciably only over many lattice sites. The Fourier transform of an external potential deviates appreciably from zero only for small values of K. This is true for instance for the wave vector of light up to the far ultraviolet. In this case we expect that $\beta(\mathbf{K},\mathbf{k},w)$ rapidly decreases with increasing K and we may neglect the sum over the reciprocal lattice vectors $\mathbf{l}_n$ in the phonon interaction part of expression (41). Secondly, for small K we may write for the phonon-frequencies

$$w_\delta(\mathbf{K})=c_L|\mathbf{K}|, \tag{48}$$

with c_L as the longitudinal velocity of sound.[6] Keeping these simplifications in mind we obtain for the equation obeyed by β:

$$\left(-w+\frac{\hbar}{m}\mathbf{k}\cdot\mathbf{K}+\frac{\hbar}{2m}\mathbf{K}^2\right)\beta(\mathbf{K},\mathbf{k},w)=w_P^2\frac{m}{\hbar}\frac{1}{K^2}[F_0(\mathbf{k}+\mathbf{K})-F_0(\mathbf{k})]\int\beta(\mathbf{K},\mathbf{k}',w)d^3k'+\frac{N_1^2}{M\hbar}\frac{[K\phi(\mathbf{K})]^2}{(w+i\epsilon)^2-c_L^2K^2}[F_0(\mathbf{k}+\mathbf{K})-F_0(\mathbf{k})]\times\int\beta(\mathbf{K},\mathbf{k}',w)d^3k'. \tag{49}$$

The further analysis proceeds along the same lines as in I. Dividing by the bracket on the left-hand side of Eq. (49), integrating over k yields the following condition to be met by w:

$$1=w_P^2\left\{1+\frac{N_1^2}{Mm}\frac{[K^2\phi(\mathbf{K})]^2}{(w^2-c_L^2K^2)w_P^2}\right\}\times\int d^3k\frac{F_0(\mathbf{k})}{[w-(\hbar/m)\mathbf{k}\cdot\mathbf{K}]^2-(\hbar K^2/2m)^2}, \tag{50}$$

which reduces of course to the old dispersion relation [Eq. (38) of I] in the limit $M=\infty$. For small K it is the Coulonb tail of the electron-ion interaction (5) which predominates. We may therefore write to a very good approximation:

$$\phi(\mathbf{K})=-4\pi e^2/K^2. \tag{51}$$

If we also expand the integral in Eq. (50) up to the order K^2 we obtain from Eq. (50):

$$1=w_P^2\left(1+\frac{m}{M}\frac{w_P^2}{w^2-c_L^2K^2}\right)\left[\frac{1}{w^2}+\left(\frac{\hbar}{mw^2}\right)^2\langle\mathbf{k}^2\rangle\mathbf{K}^2\right], \tag{52}$$

where

$$\langle\mathbf{k}^2\rangle=\int d^3k\,\mathbf{k}^2F_0(\mathbf{k}), \tag{53}$$

solving for w we have from (52):

$$\left(\frac{w}{w_P}\right)^2=1+\frac{m}{M}+\frac{2}{m}\frac{E_tK^2}{w_P^2}+\frac{m}{M}\frac{c_L^2K^2}{w_P^2}, \tag{54}$$

with

$$E_t=(1/2m)\hbar^2\langle\mathbf{k}^2\rangle, \tag{55}$$

the mean thermal energy of a "free" conduction electron. For small K the last term in Eq. (54) is entirely negligible. In this case the phonon interaction is seen to shift the actual plasma frequency by a K-independent amount of $m/2M$. Taking conditions as currently encountered in experiments[9] the dispersion

[9] H. Watanabe, J. Phys. Soc. Japan **11**, 112 (1956).

term in Eq. (54) tends to be somewhat larger than the m/M-term. In the experiments by Watanabe[9] the dispersion term ranges from 10^{-5} to 2.10^{-4} depending on the energy transfer of the primary electrons whereas the m/M-term is of the order of 10^{-5} (for Al) which is rather small and may have escaped detection.[10] In conclusion we like to remind the reader that we neglected the electron exchange part of the interaction[11] arguing that it only gives rise to a small contribution to the dispersion relation (54). This contribution has been calculated very recently[12] and found to be small indeed.

The applications of the theory given in this paper are not limited to a determination of a dispersion relation. The optical properties of metals constitute another field of application. For, suppose a (weak) external potential is switched on. This will immediately begin to polarize the medium. For the electron gas the induced charge density ρ_i is given by:

$$\rho_i = eN_1 \int \beta(\mathbf{K},\mathbf{k}',w)d^3k', \tag{56}$$

in Fourier space, where β is the solution of Eq. (49).[13] But this procedure establishes immediately a connection with the concept of a dielectric constant pretty much in the same sense as in investigations by Lindhard and others.[3,14] We also see from Eq. (49) that for very low frequencies ($w \approx 10^{13}$ sec^{-1}) the phonon interaction term becomes important as expected. Of course, the polarization of the ion charge distribution has to be taken into account at these low frequencies. We therefore expect to obtain two contributions for the dielectric constant, one from the electron gas and the other from the ionic motion. A detailed investigation of these topics will be given in a future publication.

[10] This result has also been obtained theoretically by Brout, however, using a different method (R. Brout, 1959 International Plasma Physics Institute, Seattle, Washington).

[11] The second term on the right-hand side of Eq. (2).

[12] H. Kanazawa, S. Misawa, and E. Fujita, Progr. Theoret. Phys. (Kyoto) **23**, 426 (1960).

[13] Equation (49) has of course to be supplemented by an expression for the external potential.

[14] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. **28**, 8 (1954).

APPENDIX

Here we wish to show that the phonon interaction term of expression (41) does not contribute toward the static part of the distribution function given by:

$$\alpha_S = \delta(w)\sum_n c_n(\mathbf{l}_n,\mathbf{k})\delta(\mathbf{K}-\mathbf{l}_n). \tag{A}$$

In fact, inserting this equation into the second term of expression (41) we find it to be proportional to

$$\sum_{\delta,n,m}[F_0(\mathbf{k}+\mathbf{l}_m-\mathbf{l}_n)-F_0(\mathbf{k})](l_{m\delta}-l_{n\delta})l_{m\delta}\phi(\mathbf{l}_m-\mathbf{l}_n)$$
$$\times\phi(\mathbf{l}_m)\int c_m(\mathbf{l}_m-\mathbf{l}_n,\mathbf{k}')d^3k'\delta(\mathbf{K}-\mathbf{l}_m+\mathbf{l}_n), \tag{B}$$

where the double sum runs overall reciprocal lattice vectors defined by Eq. (39). But writing

$$\left.\begin{aligned}\mathbf{l}_m-\mathbf{l}_n&=\mathbf{l}_p\\ \mathbf{l}_m&=\mathbf{l}_p+\mathbf{l}_n\end{aligned}\right\}, \tag{C}$$

expression (B) goes over into:

$$\sum_{\delta,p,n}[F_0(\mathbf{k}+\mathbf{l}_p)-F_0(\mathbf{k})]l_{p\delta}(l_{p\delta}+l_{n\delta})\phi(\mathbf{l}_p)$$
$$\times\phi(\mathbf{l}_p+\mathbf{l}_n)\int c_n(\mathbf{l}_p,\mathbf{k}')d^3k'\delta(\mathbf{K}-\mathbf{l}_p), \tag{D}$$

an expression which contains (with fixed p) the sum

$$\sum_n(l_{p\delta}+l_{n\delta})\phi(\mathbf{l}_p+\mathbf{l}_n)=0,$$

which clearly vanishes provided that ϕ depends only on the magnitude of its vector argument.