

Boltzmann-Vlasov Equation for a Quantum Plasma

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In this paper a new equation is derived which is a quantum mechanical analog of the classical collisionless Boltzmann equation. To these ends a new quantum mechanical distribution function is employed which is particularly useful in this case. Quantum corrections for longitudinal plasma oscillations are evaluated for a low-density plasma, and it is found that the leading contribution ($\sim \hbar^2$) is due to exchange (Pauli principle).

1. INTRODUCTION

A NATURAL starting point for many investigations of quantum statistical mechanics is the use of a so-called quantum mechanical distribution function (q.m.d.f.).¹ Probably the best known example of a q.m.d.f. is Wigner's function² defined by

$$F(\mathbf{r}, \mathbf{k}) = (2\pi)^{-3} \int d^3y \rho(\mathbf{r} - \frac{1}{2}\mathbf{y}, \mathbf{r} + \frac{1}{2}\mathbf{y}) e^{i\mathbf{k} \cdot \mathbf{y}}. \quad (1)$$

Here $\mathbf{k} = (m/\hbar)\mathbf{v}$ is the wave vector and ρ is the (one-particle) density matrix. For simplicity of notation we use here a one-particle description, the generalization to N particles being straightforward. We do not wish to give an analysis of the properties of Wigner's function since this has been done elsewhere.³ Here we wish to point out however, that $F(\mathbf{r}, \mathbf{k})$ as defined by (1) satisfies an equation of motion which is similar to the classical Liouville equation for the classical probability distribution in phase space. In fact, the equation satisfied by (1) goes directly over into the classical Liouville equation in the limit of $\hbar = 0$. Mean values of observables may be obtained from F in many cases by simply treating F as if it were a classical probability function. For instance, integrating (1) over all \mathbf{k} space yields immediately the diagonal element of the density matrix which is the (observable) particle density in configuration space

$$\int F(\mathbf{r}, \mathbf{k}) d^3k = \rho(\mathbf{r}, \mathbf{r}). \quad (2)$$

We wish to emphasize however, that F is not an observable which, of course, it cannot be since this would put it at variance with the exclusion principle. F is merely a calculational aid very much like the wave function. Independently found by the author, yet already briefly mentioned in the literature,⁴ is the

following q.m.d.f.

$$\tilde{F}(\mathbf{r}, \mathbf{k}) = (2\pi)^{-3} \psi(\mathbf{r}) c^*(\mathbf{k}) e^{-i\mathbf{k} \cdot \mathbf{r}}. \quad (3)$$

Here $c^*(\mathbf{k})$ is the complex conjugate of the Fourier transform of the wave function

$$c(\mathbf{k}) = (2\pi)^{-3} \int d^3r \psi(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{r}}. \quad (4)$$

Equation (3) is valid for a pure state. For a mixed state we have

$$\tilde{F}(\mathbf{r}, \mathbf{k}) = (2\pi)^{-3} \sum_n w_n \psi_n(\mathbf{r}) c_n^*(\mathbf{k}) e^{-i\mathbf{k} \cdot \mathbf{r}}, \quad (5)$$

with ψ_n a complete system and w_n the probability of occurrence of the n th state. The q.m.d.f. (5) has already been successfully employed by the author⁵ to disentangle internal and external degrees of freedom in the Liouville equation for a gas consisting of complex molecules. We will see in Part 2 that the requirements of indistinguishability of N particles may be met in a very simple way by \tilde{F} . This fact constitutes the real advantage \tilde{F} has in our particular problem. Before proceeding to the main object of this paper, i.e., the derivation of an equation for the collective motion of an electron plasma and the subsequent determination of a dispersion relation for this motion, we will briefly quote some of the basic properties of \tilde{F} .

1. The Liouville equation satisfied by \tilde{F} which is easily obtained from the definition (3) together with the Schrödinger equation for ψ :

$$H\psi = \left(-\frac{\hbar^2}{2m} \nabla^2 + V \right) \psi = -\frac{\hbar}{i} \frac{\partial \psi}{\partial t} \quad (6)$$

is the following:

$$\left(\frac{\partial}{\partial t} + \frac{\hbar}{m} \mathbf{k} \cdot \nabla_r - i \frac{\hbar}{2m} \nabla_r^2 \right) \tilde{F} = -\frac{i}{\hbar} [\exp(-i \nabla_r \cdot \nabla_k) - 1] V(\mathbf{r}) \tilde{F}. \quad (7)$$

The operator on the right-hand side of Eq. (7) is

⁵ O. von Roos, J. Chem. Phys. **31**, 1415 (1959).

¹ J. M. Irving and R. W. Zwanzig, J. Chem. Phys. **19**, 1173 (1951); J. Ross and J. G. Kirkwood, J. Chem. Phys. **22**, 1094 (1954); S. Ono, Progr. Theoret. Phys. (Kyoto) **12**, 113 (1954); A. W. Saenz, Phys. Rev. **105**, 546 (1957); J. S. Dahler, J. Chem. Phys. **30**, 1447 (1959).

² E. Wigner, Phys. Rev. **40**, 749 (1932).

³ T. Takabayasi, Progr. Theoret. Phys. (Kyoto) **11**, 341 (1954); J. E. Moyal, Proc. Cambridge Phil. Soc. **45**, 99 (1949).

⁴ T. Takabayasi, reference 3.

defined by:

$$[\exp(-i\nabla_r \cdot \nabla_k) - 1]V\tilde{F} = \sum_{n=1}^{\infty} \frac{(-i)^n}{n!} (\nabla_r \cdot \nabla_k)^n V(\mathbf{r})\tilde{F}(\mathbf{r}, \mathbf{k}), \quad (8)$$

and the gradient ∇_r only operates on the potential $V(\mathbf{r})$. An alternative expression is possible with the aid of the identity:

$$\exp(\pm \alpha \nabla_r \cdot \nabla_k) \phi(\mathbf{r}, \mathbf{k}) = (2\pi\alpha)^{-3} \int d^3x d^3k' \phi(\mathbf{r} + \mathbf{x}, \mathbf{k}') \times \exp\left(\pm \frac{i}{\alpha} (\mathbf{k}' - \mathbf{k}) \cdot \mathbf{x}\right), \quad (9)$$

and is

$$[\exp(-i\nabla_r \cdot \nabla_k) - 1]V\tilde{F} = (2\pi)^{-3} \int d^3x d^3k' [V(\mathbf{r} + \mathbf{x}) - V(\mathbf{r})]\tilde{F}(\mathbf{r}, \mathbf{k}') \times \exp(-i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{x}). \quad (10)$$

Remembering that $\mathbf{k} = (m/\hbar)\mathbf{v}$, we see that Eq. (7) for \tilde{F} goes directly over into the classical Liouville equation by taking the limit $\hbar = 0$.

$$\lim_{\hbar \rightarrow 0} \{\text{Eq. (7)}\} \rightarrow \left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla_r \right) \tilde{F} = -\frac{1}{m} \nabla_r V(\mathbf{r}) \cdot \nabla_v \tilde{F}. \quad (11)$$

2. The connection between \tilde{F} and F already mentioned by Takabayasi⁴ is

$$\exp\left(\frac{1}{2}i\nabla_r \cdot \nabla_k\right)\tilde{F} = F, \quad (12)$$

which follows directly from (3) and (9).

3. The integral of any function of \mathbf{r} and \mathbf{k} $G(\mathbf{r}, \mathbf{k})$ with \tilde{F} over all phase space is equivalent to the quantum mechanical mean of the so called well ordered product.⁴ In other words, if

$$G(\mathbf{r}, \mathbf{k}) = \sum_{\alpha, \beta} a_{\alpha\beta} \mathbf{r}^\alpha \cdot \mathbf{k}^\beta, \quad (13)$$

then

$$\int G(\mathbf{r}, \mathbf{k}) \tilde{F}(\mathbf{r}, \mathbf{k}) d^3r d^3k = \left\langle \psi \left| \sum_{\alpha, \beta} a_{\alpha\beta} \mathbf{r}^\alpha \cdot \left(\frac{1}{i} \nabla_r \right)^\beta \right| \psi \right\rangle, \quad (14)$$

so that the momentum operator always acts on the right of the conjugate position operator.

4. It is

$$\int \tilde{F}(\mathbf{r}, \mathbf{k}) d^3k = \rho(\mathbf{r}, \mathbf{r}), \quad (15)$$

and

$$\int \tilde{F}(\mathbf{r}, \mathbf{k}) d^3r = \sum_n \omega_n |c_n(\mathbf{k})|^2, \quad (16)$$

i.e., the integration of \tilde{F} over half of the phase space yields the probability distribution of the conjugate

space. The analog does not always hold in more complicated cases. For instance $\hbar \int \mathbf{k} \tilde{F} d^3k$ is *not* the current density \mathbf{j} . But it is easy to show that

$$\mathbf{j} = \Re \left\{ \hbar \int \mathbf{k} \tilde{F}(\mathbf{r}, \mathbf{k}) d^3k \right\}, \quad (17)$$

where $\Re\{\phi\}$ means the real part of ϕ .

In Part 2 of this paper we will derive an equation for the singlet distribution function⁶ $\tilde{F}(v, k, t)$ of an electron plasma by employing essentially the same statistical arguments as those used in the derivation of the Vlasov equation.⁷ In Part 3 the equation obtained will be linearized. The first case then to be considered is the case of distinguishable particles. Solutions $\sim e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}$ will be seen to exhibit the same dispersion relation as the "plasmons" introduced by Bohm and Pines.⁸ Subsequently the dispersion relation of density fluctuations $\sim e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}$ will be obtained for the case of fermions with due regard to exchange in lowest order of a perturbation expansion with respect to $\hbar\omega_p/kT$ (the ratio of a "plasma quantum" to the thermal energy, ω_p being the classical plasma frequency: $\omega_p^2 = 4\pi e^2 N/m$). It will be shown that the leading contribution to the dispersion relation is due to exchange in this case.

2. DERIVATION OF THE QUANTUM MECHANICAL COLLISIONLESS BOLTZMANN EQUATION

The starting point of the derivation is Eq. (7) which we will write down for an N electron system:

$$\left(\frac{\partial}{\partial t} + \sum_{j=1}^N \mathbf{k}_j \cdot \nabla_{r_j} - \frac{i\hbar}{2m} \sum_{j=1}^N \nabla_{r_j}^2 \right) \tilde{F}_N(\mathbf{r}_1 \cdots \mathbf{r}_N; \mathbf{k}_1 \cdots \mathbf{k}_N, t) = -\frac{i}{\hbar} [\exp(-i \sum_{j=1}^N \nabla_{r_j} \cdot \nabla_{k_j}) - 1] \sum_{i < j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \times \tilde{F}_N(\mathbf{r}_1 \cdots \mathbf{r}_N; \mathbf{k}_1 \cdots \mathbf{k}_N, t). \quad (18)$$

We already introduced the Coulomb potential of the electrons explicitly. The fact that we consider only the *electron* distribution function in Eq. (18) implies that we treat the ions as an immobile background homogeneously distributed which does not disturb the electron distribution with the only purpose to neutralize the space charge in thermal equilibrium. We define singlet, doublet, etc., distribution functions as usual by:

$$\begin{aligned} \tilde{F}_S(\mathbf{r}_1 \cdots \mathbf{r}_S; \mathbf{k}_1 \cdots \mathbf{k}_S, t) \\ = V^S \int (d^3r d^3k)^{N-S} \tilde{F}_N(\mathbf{r}_1 \cdots \mathbf{r}_N; \mathbf{k}_1 \cdots \mathbf{k}_N, t). \end{aligned} \quad (19)$$

⁶ Singlet, doublet, etc., distribution functions for an N -body system are here of course defined in the same way as usual (see Part 2).

⁷ N. N. Bogoliubov, Astia Doc. No. AD-213317, Air Force Cambridge Research Center (unpublished).

⁸ D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953).

The integration takes place over all phase space of N - S particles as indicated by $(d^3r d^3k)^{N-S}$ in formula (19). We obtain an equation for the singlet distribution function by integrating Eq. (18) over all sets of coordinates $\mathbf{r}_j, \mathbf{k}_j$ but one. Performing this operation, observing the fact that \tilde{F}_N is symmetric with respect to interchange of $\mathbf{r}_i, \mathbf{k}_i$ with any $\mathbf{r}_j, \mathbf{k}_j$, discarding surface integrals in the usual fashion, the following equation is obtained:

$$\left(\frac{\partial}{\partial t} + \frac{\hbar}{m} \mathbf{k} \cdot \nabla_{\mathbf{r}} - i \frac{\hbar}{2m} \nabla_{\mathbf{r}}^2\right) \tilde{F}_1(\mathbf{r}, \mathbf{k}, t) = \frac{ie^2 N}{\hbar} [\exp(-i \nabla_{\mathbf{r}} \cdot \nabla_{\mathbf{k}}) - 1] \int d^3r' d^3k' |\mathbf{r} - \mathbf{r}'|^{-1} \times \tilde{F}_2(\mathbf{r}, \mathbf{r}'; \mathbf{k}, \mathbf{k}', t). \quad (20)$$

Here N is the number of particles per cm^3 . Equation (20) is not a closed equation. It entirely corresponds to the first equation of the B-B-G-K-Y hierarchy of equations in classical statistical mechanics.⁹ In order to close Eq. (20) we may express \tilde{F}_2 as a functional of \tilde{F}_1 . Turning for a moment to the classical case we know that the collisionless Boltzmann equation is obtained by merely replacing F_2 by a product of F_1 functions.⁷ This of course, is equivalent of saying that the correlation between the particles is negligibly small. The same conclusion cannot be drawn immediately for \tilde{F}_2 of Eq. (20) since it is not an observable. However, it is rather obvious that a neglect of correlation means in this case that the wave functions which determine \tilde{F}_2 may be expressed by a product of properly symmetrized single-particle functions in the case of indistinguishable particles. With this assumption it is easily shown that the following formula holds:

$$\tilde{F}_2(\mathbf{r}, \mathbf{r}'; \mathbf{k}, \mathbf{k}', t) = (1 + E) \tilde{F}_1(\mathbf{r}, \mathbf{k}, t) \tilde{F}_1(\mathbf{r}', \mathbf{k}', t), \quad (21a)$$

with $E=0$ for distinguishable particles,

$$E = \pm \exp[-i(\mathbf{k} - \mathbf{k}') \cdot (\mathbf{r} - \mathbf{r}')] P_{\mathbf{k}\mathbf{k}'} + \text{sign for bosons, } - \text{sign for fermions.} \quad (21b)$$

$P_{\mathbf{k}\mathbf{k}'}$ is the permutation operator defined by $P_{\mathbf{k}\mathbf{k}'} \phi(\mathbf{k}, \mathbf{k}') = \phi(\mathbf{k}', \mathbf{k})$. Equations (21a) and (21b) are proven in the Appendix. A comparison of Eqs. (21) with the equivalent formulation for the Wigner function (1) as given by Ross and Kirkwood¹⁰ reveals the advantage of the q.m.d.f. (5) over (1) in our case. In fact, according to Ross and Kirkwood the two-particle Wigner function is only expressible by means of a complicated integral operator as a functional of the product of two single-particle distributions. We now obtain from (20) using (21) a closed equation for the motion of a quantum plasma which is the direct analog of the Vlasov

equation.¹¹ It is, dropping the index 1 of the singlet distribution function:

$$\left(\frac{\partial}{\partial t} + \frac{\hbar}{m} \mathbf{k} \cdot \nabla_{\mathbf{r}} - i \frac{\hbar}{2m} \nabla_{\mathbf{r}}^2\right) \tilde{F}(\mathbf{r}, \mathbf{k}, t) = \frac{ie^2 N}{\hbar} [\exp(-i \nabla_{\mathbf{r}} \cdot \nabla_{\mathbf{k}}) - 1] \int d^3r' d^3k' |\mathbf{r} - \mathbf{r}'|^{-1} (1 + E) \times \tilde{F}(\mathbf{r}, \mathbf{k}, t) \tilde{F}(\mathbf{r}', \mathbf{k}', t). \quad (22)$$

In order to simplify Eq. (22), we are now changing the normalization from \mathbf{k} space to velocity space by requiring that

$$\int d^3k \tilde{F}(\mathbf{r}, \mathbf{k}, t) = \int d^3v \tilde{F}'(\mathbf{r}, \mathbf{v}, t). \quad (23)$$

Dropping the prime again we then notice that the exchange term on the right-hand side of Eq. (22) may be written as [using Eq. (21b) and the substitution $(m/\hbar)(\mathbf{v} - \mathbf{v}') = \mathbf{u}$]

$$\int d^3r' d^3v' |\mathbf{r}_1 - \mathbf{r}'|^{-1} E \tilde{F}(\mathbf{r}, \mathbf{v}, t) \tilde{F}(\mathbf{r}', \mathbf{v}', t) = (\pm \hbar/m)^3 \int d^3r' d^3u |\mathbf{r}_1 - \mathbf{r}'|^{-1} \exp[-i\mathbf{u} \cdot (\mathbf{r} - \mathbf{r}')] \times \tilde{F}(\mathbf{r}, \mathbf{v} - (\hbar/m)\mathbf{u}, t) \tilde{F}(\mathbf{r}', \mathbf{v}, t). \quad (24)$$

Here we distinguished the position coordinate \mathbf{r} in the potential by an index since the gradient $\nabla_{\mathbf{r}}$ in Eq. (22) only operates on the potential. Formula (24) may be simplified by using the Fourier transform in velocity space for \tilde{F} defined by

$$\tilde{F}(\mathbf{r}, \mathbf{v}, t) = (2\pi)^{-3} \int d^3l \tilde{f}(\mathbf{r}, \mathbf{l}, t) \exp(i\mathbf{l} \cdot \mathbf{v}). \quad (25)$$

Expressing the first d.f. on the right-hand side of Eq. (24) with the aid of Eq. (25) we see that

$$\int d^3r' d^3v' |\mathbf{r}_1 - \mathbf{r}'|^{-1} E \tilde{F}(\mathbf{r}, \mathbf{v}, t) \tilde{F}(\mathbf{r}', \mathbf{v}', t) = \pm \left(\frac{\hbar}{m}\right)^3 \int d^3l \left| \mathbf{r}_1 - \mathbf{r} - \frac{\hbar}{m} \mathbf{l} \right|^{-1} \tilde{f}(\mathbf{r}, \mathbf{l}, t) \exp(i\mathbf{l} \cdot \mathbf{v}) \times \tilde{F}\left(\mathbf{r} + \frac{\hbar}{m} \mathbf{l}, \mathbf{v}, t\right). \quad (26)$$

Operating now with $\exp(-i \nabla_{\mathbf{r}} \cdot \nabla_{\mathbf{k}}) - 1$ on expression (26) yields by using formula (9)

$$\left[\exp\left(-i \frac{\hbar}{m} \nabla_{\mathbf{r}} \cdot \nabla_{\mathbf{v}}\right) - 1\right] \int d^3r' d^3v' E \tilde{F}(\mathbf{r}, \mathbf{v}, t) \tilde{F}(\mathbf{r}', \mathbf{v}', t)$$

⁹ A set of equations derived independently by N. N. Bogolubov, M. Born, H. S. Green, J. G. Kirkwood, and J. Yvon.

¹⁰ J. Ross and J. G. Kirkwood, J. Chem. Phys. 22, 1094 (1954), Appendix B.

¹¹ A. Vlasov, J. Phys. (U.S.S.R.) 9, 25 (1945).

$$\begin{aligned}
&= \pm (2\pi)^{-3} \int d^3l d^3x d^3v' \left\{ \left| \mathbf{x} - \frac{\hbar}{m} \mathbf{l} \right|^{-1} - \frac{m}{\hbar} l^{-1} \right\} \tilde{f}(\mathbf{r}, \mathbf{l}, t) \\
&\quad \times \tilde{F}'\left(\mathbf{r} + \frac{\hbar}{m} \mathbf{l}, \mathbf{v}', t\right) \\
&\quad \times \exp\left(-\frac{im}{\hbar}(\mathbf{v}' - \mathbf{v}) \cdot \mathbf{x} + i\mathbf{l} \cdot \mathbf{v}'\right). \quad (27)
\end{aligned}$$

In the last expression we dropped the index of \mathbf{r} since it is not necessary any longer. The integration over \mathbf{x} is straightforward and we obtain for the exchange part of Eq. (22) the following final expression:

$$\begin{aligned}
&\frac{ie^2N}{\hbar} [\exp(-i\nabla_r \cdot \nabla_k) - 1] \int d^3r' d^3v' |\mathbf{r} - \mathbf{r}'|^{-1} E \\
&\quad \times \tilde{F}(\mathbf{r}, \mathbf{v}, t) \tilde{F}'(\mathbf{r}', \mathbf{v}', t) \\
&= \mp i \frac{\hbar e^2 N}{m^2} \int d^3l \exp(i\mathbf{l} \cdot \mathbf{v}) \tilde{f}(\mathbf{r}, \mathbf{l}, t) \left\{ l^{-1} \tilde{F}'\left(\mathbf{r} + \frac{\hbar}{m} \mathbf{l}, \mathbf{v}, t\right) \right. \\
&\quad \left. - \frac{1}{2\pi^2} \int d^3v' \frac{P}{|\mathbf{v} - \mathbf{v}'|^2} \tilde{F}'\left(\mathbf{r} + \frac{\hbar}{m} \mathbf{l}, \mathbf{v}', t\right) \right\}, \quad (28)
\end{aligned}$$

where P means the principal value for the integration over \mathbf{v}' . The \pm sign refers to the two cases: bosons (+) or fermions (-). The first term on the right-hand side of Eq. (22), i.e., the term without the exchange operator E can be handled in an analogous fashion. We do not report here the fairly simple calculations but quote the final result. The equation satisfied by $\tilde{F}(\mathbf{r}, \mathbf{v}, t)$ is

$$\begin{aligned}
&\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla_r - i \frac{\hbar}{2m} \nabla_r^2\right) \tilde{F}(\mathbf{r}, \mathbf{v}, t) \\
&= i \frac{e^2 N}{\hbar} \int d^3r' d^3v' \tilde{F}'(\mathbf{r}', \mathbf{v}', t) \frac{1}{2\pi^2} \int d^3u \frac{P}{u^2} \\
&\quad \times \exp[i\mathbf{u} \cdot (\mathbf{r} - \mathbf{r}')] \left[\tilde{F}'\left(\mathbf{r}, \mathbf{v} + \frac{\hbar}{m} \mathbf{u}, t\right) - \tilde{F}(\mathbf{r}, \mathbf{v}, t) \right] \\
&\quad \mp i \frac{e^2 N \hbar}{m^2} \int d^3l \exp(i\mathbf{l} \cdot \mathbf{v}') \tilde{f}(\mathbf{r}, \mathbf{l}, t) \left[l^{-1} \tilde{F}'\left(\mathbf{r} + \frac{\hbar}{m} \mathbf{l}, \mathbf{v}, t\right) \right. \\
&\quad \left. - \frac{1}{2\pi^2} \int d^3v' \frac{P}{|\mathbf{v} - \mathbf{v}'|^2} \tilde{F}'\left(\mathbf{r} + \frac{\hbar}{m} \mathbf{l}, \mathbf{v}', t\right) \right], \quad (29)
\end{aligned}$$

\tilde{f} is defined by Eq. (25). Equation (29) is the starting point for our investigations of the quantum plasma. It is the quantum mechanical analog of the collisionless Boltzmann equation. Two properties of Eq. (29) are established immediately: 1. If \tilde{F} is solely a function of velocity [$\tilde{F} = \tilde{F}(\mathbf{v})$] then Eq. (29) is identically

satisfied. 2. By taking the limit $\hbar=0$ Eq. (29) goes directly over into the classical collisionless Boltzmann equation (Vlasov equation¹¹).

3. LINEARIZATION AND DETERMINATION OF DISPERSION RELATIONS

Equation (29) constitutes a rather difficult integral equation. The problems of most physical interest however, are those in which the overwhelming majority of particles is in thermal equilibrium. We therefore linearize Eq. (29) by putting

$$\tilde{F} = F_0(\mathbf{v}) + F_1(\mathbf{r}, \mathbf{v}, t), \quad (30)$$

and consider $F_1 \ll F_0$ so that terms quadratic in F_1 may be neglected. Specifically we assume:

$$F_1(\mathbf{r}, \mathbf{v}, t) = \alpha(\mathbf{K}, \mathbf{v}, t) \exp(i\mathbf{K} \cdot \mathbf{r}). \quad (31)$$

Entering Eq. (29) with this expression and neglecting terms of order higher than the first in α yields the following equation:

$$\begin{aligned}
&\left(\frac{\partial}{\partial t} + i\mathbf{K} \cdot \mathbf{v} + i \frac{\hbar K^2}{2m}\right) \alpha(\mathbf{K}, \mathbf{v}, t) \\
&= i \frac{4\pi e^2 N}{\hbar} \frac{1}{K^2} \int d^3v' \alpha(\mathbf{K}, \mathbf{v}', t) \left[F_0\left(\mathbf{v} + \frac{\hbar}{m} \mathbf{K}\right) - F_0(\mathbf{v}) \right] \\
&\quad \mp i \frac{4\pi e^2 N \hbar}{m^2} \int d^3v' \frac{P}{|\mathbf{v} - \mathbf{v}'|^2} \left\{ \alpha(\mathbf{K}, \mathbf{v}', t) \right. \\
&\quad \times \left[F_0(\mathbf{v}) - F_0\left(\mathbf{v} + \frac{\hbar}{m} \mathbf{K}\right) \right] - \alpha(\mathbf{K}, \mathbf{v}, t) \\
&\quad \left. \times \left[F_0(\mathbf{v}') - F_0\left(\mathbf{v}' + \frac{\hbar}{m} \mathbf{K}\right) \right] \right\}. \quad (32)
\end{aligned}$$

The last term of Eq. (32) is due to exchange. For distinguishable particles it must be omitted. Furthermore, in this case we assume $F_0(\mathbf{v})$ to be the Maxwell-Boltzmann distribution

$$F_0(\mathbf{v}) = (\epsilon/\pi)^{3/2} \exp(-\epsilon v^2), \quad \epsilon = m/2kT. \quad (33)$$

The equation governing the motion of the Fourier transform (31) of the perturbed distribution in the case in which the particles may be considered distinguishable reads then:

$$\begin{aligned}
&\left(\frac{\partial}{\partial t} + i\mathbf{K} \cdot \mathbf{v} + i \frac{\hbar K^2}{2m}\right) \alpha(\mathbf{K}, \mathbf{v}, t) \\
&= i \omega_p^2 \frac{m}{\hbar} \frac{1}{K^2} \left[F_0\left(\mathbf{v} + \frac{\hbar}{m} \mathbf{K}\right) - F_0(\mathbf{v}) \right] \\
&\quad \times \int d^3v' \alpha(\mathbf{K}, \mathbf{v}', t). \quad (34)
\end{aligned}$$

We introduced the classical plasma frequency

$$\omega_p = (4\pi e^2 N/m)^{1/2}. \quad (35)$$

A solution of Eq. (34) is easily possible by employing a Laplace transformation with respect to time in exact analogy to Landau's procedure.¹² We do not wish to perform these calculations here since this would essentially mean a repetition of Landau's calculations.¹² However, a dispersion relation for plasma oscillations is found from Eq. (34) by assuming a time dependence of α in the form

$$\alpha(\mathbf{K}, \mathbf{v}, t) = \beta(\mathbf{K}, \mathbf{v}) e^{-i\omega t}. \quad (36)$$

Inserting (36) into (34) we find after division by $i(-\omega + \mathbf{K} \cdot \mathbf{v} + \hbar K^2/2m)$ and integration over \mathbf{v} that

$$1 = \omega_p^2 \frac{m}{\hbar K^2} \int d^3v \frac{F_0(\mathbf{v} + (\hbar/m)\mathbf{K}) - F_0(\mathbf{v})}{-\omega + \mathbf{K} \cdot \mathbf{v} + (\hbar K^2/2m)}, \quad (37)$$

which leads after a simple substitution to the dispersion relation

$$1 = \omega_p^2 \int d^3v \frac{F_0(\mathbf{v})}{(\omega - \mathbf{K} \cdot \mathbf{v})^2 - (\hbar K^2/2m)^2}. \quad (38)$$

This relation is the same as that obeyed by the "plasmons" of Bohm and Pines.⁸ We would like to make two remarks of caution at this point. First, we know that α , being the Fourier transform of F_1 [Eq. (31)], is not in general an observable. So it seems that a dispersion relation as Eq. (38) is somewhat artificial. However, Eq. (15) of the introduction shows that a simple integration over the velocity space is all that is needed to generate an observable from α , in this instance the density distribution. But this integration does not affect the spacial and temporal dependence. In other words, the (observable) density distribution displays the very same frequency versus wave-vector relationship as the (unobservable) perturbed q.m.d.f. does. Secondly, the integral in Eq. (38) is strictly speaking not defined because of a singularity for those values of \mathbf{v} for which the denominator vanishes. This poses a problem which has been investigated by various authors for the classical case.¹³ We cannot enter into a detailed analysis here but wish to point out that the proper choice for the integration in (38) is to take the principal value and that strictly speaking all solutions $\sim e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}$ are damped but this damping is particularly small if Eq. (38) is satisfied.

We now turn back to Eq. (32). Our aim is to obtain the quantum corrections in lowest order to the classical dispersion relation valid for an electron plasma of low density. In order to do this we expand α and F_0 in

powers of \hbar by writing:

$$\begin{aligned} \alpha(\mathbf{K}, \mathbf{v}, t) &= \beta(\mathbf{K}, \mathbf{v}) e^{-i\omega t}, \\ \beta &= \beta_0 + \hbar \beta_1 + \hbar^2 \beta_2 + \dots, \\ \omega &= \omega_0 + \hbar \omega_1 + \hbar^2 \omega_2 + \dots. \end{aligned} \quad (39)$$

For $F_0(\mathbf{v})$ we take the Fermi distribution:

$$F_0(\mathbf{v}) = \frac{2}{N} \left(\frac{m}{\hbar} \right)^3 \left[\exp \left(\frac{m\mathbf{v}^2 - 2\delta}{2kT} \right) + 1 \right]^{-1}. \quad (40)$$

Since the classical limit is obtained¹⁴ for $\delta \rightarrow -\infty$ we find the expansion in powers of \hbar correct to order \hbar^3 :

$$\begin{aligned} F_0(\mathbf{v}) &= F(\mathbf{v}) + \left(\frac{2\epsilon\hbar}{m} \right)^3 \frac{N}{2} \\ &\quad \times \exp(-\epsilon\mathbf{v}^2) [2^{-3} - \exp(-\epsilon\mathbf{v}^2)], \end{aligned} \quad (41)$$

$$F(\mathbf{v}) = (\epsilon/\pi)^{3/2} \exp(-\epsilon\mathbf{v}^2),$$

with ϵ from (33). Inserting Eqs. (39) and (41) into (32) and comparing equal powers of \hbar gives the following set of equations:

$$(-\omega_0 + \mathbf{K} \cdot \mathbf{v})\beta_0 = \omega_p^2 \int d^3v' \beta_0(\mathbf{K}, \mathbf{v}') \frac{\mathbf{K} \cdot \nabla_{\mathbf{v}}}{K^2} F(\mathbf{v}), \quad (42)$$

$$\begin{aligned} (-\omega_0 + \mathbf{K} \cdot \mathbf{v})\beta_1 + \left(-\omega_1 + \frac{K^2}{2m} \right) \beta_0 &= \omega_p^2 \int d^3v' \beta_1(\mathbf{K}, \mathbf{v}') \frac{\mathbf{K} \cdot \nabla_{\mathbf{v}}}{K^2} F(\mathbf{v}) \\ &\quad + \omega_p^2 \int d^3v' \beta_0(\mathbf{K}, \mathbf{v}') \frac{(\mathbf{K} \cdot \nabla_{\mathbf{v}})^2}{2K^2 m} F(\mathbf{v}), \end{aligned} \quad (43)$$

$$\begin{aligned} -\omega_2 \beta_0 + \left(-\omega_1 + \frac{K^2}{2m} \right) \beta_1 + (-\omega_0 + \mathbf{K} \cdot \mathbf{v})\beta_2 &= \omega_p^2 \int d^3v' \beta_2(\mathbf{K}, \mathbf{v}') \frac{\mathbf{K} \cdot \nabla_{\mathbf{v}}}{K^2} F(\mathbf{v}) \\ &\quad + \omega_p^2 \int d^3v' \beta_1(\mathbf{K}, \mathbf{v}') \frac{(\mathbf{K} \cdot \nabla_{\mathbf{v}})^2}{2K^2 m} F(\mathbf{v}) \\ &\quad + \omega_p^2 \int d^3v' \beta_0(\mathbf{K}, \mathbf{v}') \frac{(\mathbf{K} \cdot \nabla_{\mathbf{v}})^3}{6m^2 K^2} F(\mathbf{v}) \\ &\quad + \frac{\omega_p^2}{m^2} \int d^3v' |\mathbf{v} - \mathbf{v}'|^{-2} \{ \beta_0(\mathbf{K}, \mathbf{v}) \mathbf{K} \cdot \nabla_{\mathbf{v}} F(\mathbf{v}') \\ &\quad - \beta_0(\mathbf{K}, \mathbf{v}') \mathbf{K} \cdot \nabla_{\mathbf{v}} F(\mathbf{v}) \}. \end{aligned} \quad (44)$$

Equation (42), being of order \hbar^0 , is of course just the

¹⁴ F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, New York, 1940), p. 151.

¹² L. Landau, J. Phys. (U.S.S.R.) **10**, 25 (1946).

¹³ N. G. van Kampen, Physica **21**, 949 (1955); F. Berz, Proc. Phys. Soc. (London) **B69**, 939 (1956).

classical Vlasov equation from which we obtain the well-known classical dispersion relation for ω_0

$$1 = \omega_p^2 \int d^3v \frac{F(\mathbf{v})}{(\omega_0 - \mathbf{K} \cdot \mathbf{v})^2}. \quad (45)$$

From Eq. (43) follows by observing (42) and (45) that

$$\omega_1 = 0. \quad (46)$$

There are no effects to first order in \hbar . It is a matter of simple algebra to show subsequently by utilizing Eqs. (42), (43), (45), and (46) that ω_2 from Eq. (44) is given by:

$$\begin{aligned} \omega_2 = & \left[\int d^3v \frac{F(\mathbf{v})}{(\omega_0 - \mathbf{K} \cdot \mathbf{v})^3} \right]^{-1} \left\{ \frac{1}{8} \frac{K^4}{m^2} \int d^3v \frac{F(\mathbf{v})}{(\omega_0 - \mathbf{K} \cdot \mathbf{v})^4} \right. \\ & - \frac{\omega_p^2}{2m^2 K^2} \int d^3v d^3v' |\mathbf{v} - \mathbf{v}'|^{-2} \\ & \times \frac{\mathbf{K} \cdot (\mathbf{v}' - \mathbf{v}) \mathbf{K} \cdot \nabla_v F(\mathbf{v}') \mathbf{K} \cdot \nabla_{v'} F(\mathbf{v})}{(\omega_0 - \mathbf{K} \cdot \mathbf{v})^2 (\omega_0 - \mathbf{K} \cdot \mathbf{v}')}. \end{aligned} \quad (47)$$

This then is the first non-vanishing quantum correction we were looking for. Expression (47) may be simplified considerably by noting that our interest lies mostly in density distributions which are spread out over regions considerably larger in volume than λ_D^3 where $\lambda_D = (kT/4\pi e^2 N)^{1/2}$ is the Debye-Hückel length.

In this case, an expansion in powers of K is allowed. This expansion yields for the classical dispersion relation Eq. (45) the well-known result

$$\omega_0 = \omega_p \left[1 + \frac{3}{2} (\lambda_D K)^2 \right]. \quad (48)$$

To lowest order in K equation (47) then leads to:

$$\begin{aligned} \omega_2 = & + \frac{\omega_p}{4m^2 K^2} \int d^3v d^3v' \frac{[\mathbf{K} \cdot (\mathbf{v}' - \mathbf{v})]^2}{|\mathbf{v}' - \mathbf{v}|^2} \\ & \times \mathbf{K} \cdot \nabla_v F(\mathbf{v}) \mathbf{K} \cdot \nabla_{v'} F(\mathbf{v}'). \end{aligned} \quad (49)$$

This integral can be done in an elementary manner with the result:

$$\omega_2 = -\frac{7}{60} \frac{\omega_p \epsilon}{m^2} K^2, \quad (50)$$

so that the final result is

$$\begin{aligned} \omega = & \omega_0 + \hbar^2 \omega_2 \\ = & \omega_p \left\{ 1 + \left[\frac{3}{2} - \frac{7}{120} \left(\frac{\hbar \omega_p}{kT} \right)^2 \right] (\lambda_D K)^2 \right\}. \end{aligned} \quad (51)$$

The quantum correction exhibited by Eq. (51) is really a very small correction. Even when $\hbar \omega_p \approx kT$, i.e., at electron densities of about 10^{15} particles per cm^3

and at room temperature this correction is an order of magnitude smaller than the classical correction of Eq. (48).

In conclusion we would like to point out that Eq. (32) (the linearized collisionless Boltzmann equation for the quantum distribution function) is felt to be a good approximation also for a *high* density electron plasma of a metal for instance. The neglect of collisions should not be a deterrent for actual applications of Eq. (32) since the Pauli principle vastly inhibits collisions.

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APPENDIX

Here we wish to prove the relationship (21) which expresses the doublet distribution function by singlet functions in case of negligible interactions. The definition (5) for \tilde{F} may be written specifically

$$\begin{aligned} \tilde{F}_2(\mathbf{r}, \mathbf{r}'; \mathbf{k}, \mathbf{k}', t) = & \sum_{\alpha, \beta} \omega_{\alpha\beta} \psi_{\alpha\beta}(\mathbf{r}, \mathbf{r}', t) c_{\alpha\beta}^*(\mathbf{k}, \mathbf{k}', t) \\ & \times \exp[-i(\mathbf{k} \cdot \mathbf{r} + \mathbf{k}' \cdot \mathbf{r}')]. \end{aligned} \quad (A)$$

Here $\alpha\beta$ is a set of quantum numbers for a two electron configuration. The singlet distribution function is given by:

$$\tilde{F}_1(\mathbf{r}, \mathbf{k}, t) = \sum_{\alpha} \omega_{\alpha} \psi_{\alpha}(\mathbf{r}, t) c_{\alpha}^*(\mathbf{k}, t) \exp(-i\mathbf{k} \cdot \mathbf{r}). \quad (B)$$

Under the assumption of no interaction the two-particle wave function $\psi_{\alpha\beta}$ may be expressed by

$$\psi_{\alpha\beta} = \frac{1}{\sqrt{2}} \{ \psi_{\alpha}(\mathbf{r}) \psi_{\beta}(\mathbf{r}') \pm \psi_{\alpha}(\mathbf{r}') \psi_{\beta}(\mathbf{r}) \}, \quad (C)$$

and a similar expression for $c_{\alpha\beta}(\mathbf{k}, \mathbf{k}')$,

Inserting (C) and the analogous expression for $c_{\alpha\beta}^*$ into (A) gives the desired result provided that

$$\omega_{\alpha\beta} = \omega_{\alpha} \omega_{\beta}, \quad (D)$$

namely

$$\begin{aligned} \tilde{F}_2(\mathbf{r}, \mathbf{r}'; \mathbf{k}, \mathbf{k}', t) = & \tilde{F}_1(\mathbf{r}, \mathbf{k}, t) \tilde{F}_1(\mathbf{r}', \mathbf{k}', t) \\ & \pm \exp[-i(\mathbf{k} - \mathbf{k}') \cdot (\mathbf{r} - \mathbf{r}')] \\ & \times \tilde{F}_1(\mathbf{r}, \mathbf{k}', t) \tilde{F}_1(\mathbf{r}', \mathbf{k}, t), \end{aligned} \quad (E)$$

where the \pm sign refers to bosons (fermions). Expression (D) is of course true if particle interactions are neglected.

Note added in proof.—After completion of this work the authors attention was drawn to a recent paper by Ehrenreich and Cohen [H. Ehrenreich, M. H. Cohen, Phys. Rev. **115**, 786 (1949)], in which an equation was derived [Eq. (8) in the above mentioned paper] which is identical with our Eq. (34). It is felt that our derivation has the advantage of physical lucidity.