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# Fluctuations of the Single-Particle Distribution Function in Classical Fluids

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Relaxation-fluctuation theory is developed for the single-particle distribution function of a classical fluid. Fictitious potentials coupling to arbitrary functions of the internal variables are used to extract equilibrium correlation functions from kinetic equations. In particular the autocorrelation function in the microscopic quantity related to the single-particle distribution is studied. Two procedures are developed for the calculation of this function. To lowest order they both result in the same approximate equation of motion. The first procedure assumes a linear functional dependence on the density of the collision term in the exact equation of motion. The second uses a set of variational eigenfunctions of the Liouville operator which were introduced by Zwanzig. The resulting equation of motion is an "effective field" equation which had been proposed phenomenologically by one of the authors in an earlier paper.

## I. INTRODUCTION

The relation between linearized relaxation and equilibrium correlation functions has long been understood.[1] In several earlier papers this relation has been exploited to calculate the density autocorrelation function from kinetic equations.[2-4] In this paper the approach is generalized through the use of fictitious external potentials coupled to arbitrary functions of the internal variables. Most of the calculations are done for correlations of the quantity

$$D(\vec{r},\vec{p})=\sum_{j=1}^{N}\delta(\vec{r}-\vec{r}_j)\delta(\vec{p}-\vec{p}_j),$$

but the method is clearly seen to be more generally applicable.

In Sec. II we consider the linearized relaxation of the single-particle distribution [i.e., the average of $D(\vec{r},\vec{p})$ in the time-dependent ensemble] due to the presence of a fictitious potential coupling to that quantity. This is shown to be the autocorrelation function of the fluctuation of $D(\vec{r},\vec{p})$ from its equilibrium value. This result is expected since it is a special case of linear response theory.[1] By deriving it explicitly, however, we see more clearly how it may be used to calculate the correlation function

$$f(\vec{r},\vec{p},t\,|\,\vec{r}\,',\vec{p}\,')\equiv\langle D(\vec{r},\vec{p},t)D(\vec{r}\,',\vec{p}\,',0)\rangle$$

from a given approximate kinetic equation with a well-defined initial condition.

The quantity $f(\vec{r},\vec{p},t\,|\,\vec{r}\,',\vec{p}\,')$ defined above is a natural momentum-dependent generalization of the van Hove density autocorrelation function $G(\vec{r}-\vec{r}\,',t)$. In terms of $f$, all correlation functions of single-particle quantities are given by simple integral formulas such as

$$\langle\vec{j}(\vec{r},t)\vec{j}(\vec{r}\,',0)\rangle=m^{-2}\int d^3p\,d^3p'\,\vec{p}\,\vec{p}\,'f(\vec{r},\vec{p},t\,|\,\vec{r}\,',\vec{p}\,')$$

for the current-current correlation function.

Beginning in Sec. III we consider approximate calculations of $f(\vec{r},\vec{p},t\,|\,\vec{r}\,',\vec{p}\,')$ appropriate to the high-frequency regime observed in inelastic neutron-scattering experiments. We begin by writing an exact equation of motion for $f$. To illustrate the formalism we introduce a density ansatz for the collision term in the equation of motion in search of a description wherein high-frequency longitudinal oscillations play a dominant role. Since such a mode would dominate the short-time behavior of the system, the coupling constant is fixed by comparison with the short-time expansion of the collision term. The resulting equation is the modified Vlasov equation proposed by Nelkin and Ranganathan,[3] and derived earlier by the present authors[4] in a closely related way.

In Sec. IV we start again from the exact equation of motion, but make use of approximate eigenfunctions of the Liouville operator. The functions we use were introduced by Zwanzig[5] as trial functions of the form

$$\Psi = \sum_{j=1}^{N} \psi(\vec{r}_j, \vec{p}_j)$$

in a variational principle. These functions are constructed here in a slightly modified form so that $D(\vec{r},\vec{p})$ may be expanded in terms of them. With the dynamical approximation that these are in fact eigenfunctions of the Liouville operator with eigenvalue determined by Zwanzig's variational expression, we recover the same modified Vlasov equation derived in Sec. III. For the initial value problem of interest, the explicit appearance of the eigenfunctions and eigenvalues is eliminated, and the final approximate equation of motion is easily solved in closed form.

We conclude the paper with a brief discussion of the physical reasons for the identity of the results in Secs. III and IV, and some indication of how the methods presented here might be used to obtain more accurate approximate descriptions of atomic motions in dense classical fluids.

## II. CORRELATION FUNCTIONS AND LINEARIZED RELAXATION

We consider an $N$-particle classical system in a volume $\Omega$ with the translationally invariant internal Hamiltonian

$$H = \sum_{j=1}^{N} \frac{p_j^2}{2M} + U(\vec{r}_1, \dots, \vec{r}_N) \ . \tag{2.1}$$

For $t < 0$ the system is in a spacially inhomogeneous equilibrium state in the presence of a momentum- and space-dependent external potential $\phi(\vec{r},\vec{p})$. At $t = 0$ this fictitious external potential is switched off, and the system is allowed to relax to a spatially uniform equilibrium state. The $N$-particle distribution function for an ensemble of such systems is the solution of the Liouville equation

$$\partial f_N / \partial t = -iL f_N \ , \tag{2.2}$$

$$\text{where} \ iL \equiv \sum_{j=1}^{N} \left( \frac{\partial H}{\partial \vec{p}_j} \cdot \frac{\partial}{\partial \vec{r}_j} - \frac{\partial H}{\partial \vec{r}_j} \cdot \frac{\partial}{\partial \vec{p}_j} \right) \ , \tag{2.3}$$

and $f_N(X, t \mid \phi)$ depends on the $6N$-dimensional phase-point $X$, the time $t$, and is functionally dependent on $\phi$ through the initial condition

$$f_N(X, t=0 \mid \phi) = \frac{\exp[-\beta(H+W)]}{\int dX \exp[-\beta(H+W)]} \ , \tag{2.4}$$

$$\text{where} \ W = \iint d^3r \, d^3p \, \phi(\vec{r},\vec{p}) D(\vec{r},\vec{p}) \ , \tag{2.5}$$

$$\text{and} \ D(\vec{r},\vec{p}) = \sum_{j=1}^{N} \delta(\vec{r} - \vec{r}_j) \delta(\vec{p} - \vec{p}_j) \ . \tag{2.6}$$

Since we are only interested in the linearized relaxation of the system, it is convenient to define a functional derivative associated with a function $A$ which gives the value of $A$ to first order in $\phi$. Thus if

$$\hat{A}(\cdots \mid \vec{r},\vec{p}) \equiv -\frac{1}{\beta} \left. \frac{\delta A(\cdots \mid \phi)}{\delta \phi(\vec{r},\vec{p})} \right|_{\phi=0} \ , \tag{2.7}$$

then

$$A(\cdots \mid \phi) = A(\cdots \mid \phi = 0) - \beta \iint d^3r \, d^3p \, \hat{A}(\cdots \mid \vec{r},\vec{p}) \phi(\vec{r},\vec{p}) \tag{2.8}$$

plus corrections of higher order in $\phi$.

Since this functional derivative operation commutes with time differentiation and with the Liouville operator, $\hat{f}_N$ also obeys the Liouville equation (2.2). The value of $\hat{f}_N$ at $t = 0$ may be found by expanding (2.4) in $\beta W$ and picking out the kernel of the term of first order in $\phi$. Thus

$$\hat{f}_N(X, t=0 \mid \vec{r},\vec{p}) = \frac{1}{Z} e^{-\beta H} \left[ D(\vec{r},\vec{p}) - \frac{N}{\Omega} f_M(\vec{p}) \right] . \tag{2.9}$$

In (2.9), $Z$ is the canonical partition function for the system with Hamiltonian $H$, and $f_M(\vec{p})$ is a unit normalized Maxwell distribution of momentum. The Liouville equation for $\hat{f}_N$ may be formally solved in terms of this initial condition and the time evolution operator $\exp(-iLt)$ to give

$$\hat{f}_N(X, t \mid \vec{r},\vec{p}) = e^{-iLt} \hat{f}_N(X, t=0 \mid \vec{r},\vec{p}) \ . \tag{2.10}$$

The related-single particle function may be written as

$$\hat{f}_1(\vec{r},\vec{p},t\,|\,\vec{r}',\vec{p}') = \int dX D(\vec{r},\vec{p}) f_N(X,t\,|\,\vec{r}',\vec{p}') . \tag{2.11}$$

Its initial value may be explicitly determined using (2.9). The single-particle distribution function $f_1$ so defined is normalized so that its integral over $\vec{r}$ and $\vec{p}$ is equal to $N$. Putting (2.9) and (2.10) into (2.11) yields

$$\hat{f}_1(\vec{r},\vec{p},t\,|\,\vec{r}',\vec{p}') = \left\langle D(\vec{r},\vec{p})\, e^{-iLt}\left[D(\vec{r}',\vec{p}') - \frac{N}{\Omega} f_M(\vec{p})\right]\right\rangle , \tag{2.12}$$

where $\langle \cdots \rangle$ represents a canonical ensemble average for an equilibrium system with Hamiltonian $H$ and temperature $(k\beta)^{-1}$. By adding and subtracting factors $(N/\Omega)f_M(p)$, (2.12) may be written in terms of the fluctuation $\delta D$ of $D$ from its equilibrium average $(N/\Omega)f_M(\vec{p})$. Thus

$$\hat{f}_1(\vec{r},\vec{p},t\,|\,\vec{r}',\vec{p}') = \langle \delta D(\vec{r},\vec{p},t)\,\delta D(\vec{r}',\vec{p}',0)\rangle , \tag{2.13}$$

$$\text{where} \quad \delta D(\vec{r},\vec{p},t) = e^{iLt}\,\delta D(\vec{r},\vec{p}) , \tag{2.14}$$

and the property

$$\langle ALB\rangle = -\langle (LA)B\rangle \tag{2.15}$$

has been used.

Equation (2.13) states that the relaxation of the one-particle distribution function, linearized with respect to an external potential coupled to the one-particle distribution function, is given by the autocorrelation function of the fluctuations in this quantity in the equilibrium ensemble. This is, of course, a special case of the Kubo result[1] relating equilibrium correlation functions and linear relaxation of an externally imposed disturbance.

The function $\hat{f}_1$ is a momentum-dependent generalization of the van Hove correlation function $G(r,t)$, and can be given an analogous probabilistic interpretation. For this purpose it is more convenient to work with a function $f$ defined by

$$f(x,t\,|\,x') = \langle D(\vec{r},\vec{p},t) D(\vec{r}',\vec{p}',0)\rangle . \tag{2.16}$$

Noting that $N^{-1}D(\vec{r},\vec{p},t)$ is the probability density for finding a particle at $x=(\vec{r},\vec{p})$ at time $t$ for a member system of the thermodynamic ensemble, it is seen that $f(x,t\,|\,x')$ is $N^2$ times the joint probability density for finding a particle at $x$ at time $t$ and one at $x'$ at time zero. Since the probability of finding a particle at $x$ is

$$N^{-1}\langle D(\vec{r},\vec{p})\rangle = f_M(\vec{p})/\Omega .$$

$f(x,t\,|\,x')$ is $(N^2 f_M(\vec{p})/\Omega)$ times the conditional probability that there is a particle at $x$ at time $t$ if there was a particle at $x'$ at time zero. In analogy to $G(r,t)$, $f(x,t\,|\,x')$ can be separated into "self" and "distinct" parts, and similar probability interpretations may be given.

By generalizing to include momentum dependence, we are able to calculate any correlation function of single-particle variables from a knowledge of $f$. Thus consider two quantities

$$A = \sum_{j=1}^{N} a(\vec{r}_j,\vec{p}_j) \quad \text{and} \quad B = \sum_{j=1}^{N} b(\vec{r}_j,\vec{p}_j) .$$

Then $\langle A(t)B(0)\rangle$

$$= \iint d^6x\, d^6x'\, a(x) b(x') f(x,t\,|\,x') . \tag{2.17}$$

In particular the van Hove correlation function is given by

$$\begin{aligned} G(\vec{r}-\vec{r}',t) &= \frac{\Omega}{N}\langle \rho(\vec{r},t)\rho(\vec{r}',0)\rangle \\ &= \frac{\Omega}{N}\iint d^3p\, d^3p'\, f(\vec{r},\vec{p},t\,|\,\vec{r}',\vec{p}') . \end{aligned} \tag{2.18}$$

Several general properties of $f(\vec{r},\vec{p},t\,|\,\vec{r}',\vec{p}')$ can be deduced from the invariance properties of the system. Translational invariance implies that $f$ depends on $\vec{r}$ and $\vec{r}'$ only through the vector displacement $\vec{r}-\vec{r}'$. Also by use of (2.16) one can show that

$$f(\vec{r},\vec{p},-t\,|\,\vec{r}',\vec{p}') = f(\vec{r}',\vec{p}',t\,|\,\vec{r},\vec{p}) . \tag{2.19}$$

If the momenta of all the particles are reversed at the initial instant, the canonical average should not change. Hence

$$f(\vec{r},-\vec{p},-t\,|\,\vec{r}',-\vec{p}') = f(\vec{r},\vec{p},t\,|\,\vec{r}',\vec{p}') . \tag{2.20}$$

Combining (2.19) and (2.20) yields

$$f(\vec{r}',-\vec{p}',t\,|\,\vec{r},-\vec{p}) = f(\vec{r},\vec{p},t\,|\,\vec{r}',\vec{p}') . \tag{2.21}$$

These equations also hold separately for the self-part $f_s$ and the distinct part $f_d$. In particular Eq. (2.21) when applied to the self-part expresses the fact that the probability for a particle to go from $\vec{r}'$ to $\vec{r}$ in a time $t$ equals the probability of the flight from $\vec{r}$ to $\vec{r}'$ in a time $t$ if the directions of the initial and final momenta are reversed.

In concluding this section we note that the method of fictitious potentials is clearly not limited to potentials which couple only to single-particle quantities. Thus one may deduce from a given kinetic equation any correlation function of the form

$$\langle D(\vec{r},\vec{p},t) Q(0)\rangle ,$$

where $Q$ is any function of the internal variables. Thus an approximate kinetic equation not only allows the calculation of transport coefficients involving single-particle quantities, but also the off diagonal transport coefficients such as those which occur when both particle and heat currents are present.

## III. KINETIC EQUATIONS

From its definition in Eq. (2.16), the equation of motion for $f$ may be directly computed to be

$$\left(\frac{\partial}{\partial t}+\frac{\vec{p}}{m}\cdot\frac{\partial}{\partial\vec{r}}\right)f(\vec{r},\vec{p},t\,|\,\vec{r}\,',\vec{p}\,')=\Omega^{-1}\langle[iL_1D(\vec{r},\vec{p})]e^{-iLt}D(\vec{r}\,',\vec{p}\,')\rangle\,,$$

where $iL_1=-\sum_{j=1}^{N}\frac{\partial U}{\partial\vec{r}_j}\cdot\frac{\partial}{\partial\vec{p}_j}$

is the interaction part of the Liouville operator.

We find it more convenient to work with the Fourier-Laplace transform of $f$ defined by

$$F(\vec{k},\vec{p},s\,|\,\vec{p}\,')\equiv\Omega^{-1}\int e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')}d^3(\vec{r}-\vec{r}\,')\int_0^\infty e^{-st}f(\vec{r},\vec{p},t\,|\,\vec{r}\,',\vec{p}\,')dt$$

$$=\Omega^{-1}\langle D(-\vec{k},\vec{p})(s+iL)^{-1}D(\vec{k},\vec{p}\,')\rangle\,,\tag{3.1}$$

where $$D(\vec{k},\vec{p})=\sum_{j=1}^{N}e^{-i\vec{k}\cdot\vec{r}_j}\delta(\vec{p}-\vec{p}_j)\,.\tag{3.2}$$

The equation of motion for $F$ is

$$sF(\vec{k},\vec{p},s\,|\,\vec{p}\,')=f(\vec{k},\vec{p},t=0\,|\,\vec{p}\,')+i\langle[LD(-\vec{k},\vec{p})](s+iL)^{-1}D(\vec{k},\vec{p}\,')\rangle\,.\tag{3.3}$$

Separating $L$ into its kinetic and potential parts (3.3) becomes

$$(s-im^{-1}\vec{k}\circ\vec{p})F(\vec{k},\vec{p},s\,|\,\vec{p}\,')=f(\vec{k},\vec{p},t=0\,|\,\vec{p}\,')+A(\vec{k},\vec{p},s\,|\,\vec{p}\,')\,,\tag{3.4}$$

where $$A(\vec{k},\vec{p},s\,|\,\vec{p}\,')=-\Omega^{-1}\left\langle\sum_j\left(\frac{\partial U}{\partial\vec{r}_j}\cdot\frac{\partial D(-\vec{k},\vec{p})}{\partial\vec{p}_j}\right)(s+iL)^{-1}D(\vec{k},\vec{p}\,')\right\rangle\,.\tag{3.5}$$

In Eqs. (3.3) and (3.4)

$$f(\vec{k},\vec{p},t=0\,|\,\vec{p}\,')=\Omega^{-1}\int e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')}d^3(\vec{r}-\vec{r}\,')f(\vec{r},\vec{p},t=0\,|\,\vec{r}\,',\vec{p}\,')\,.\tag{3.6}$$

Integrating by parts the explicit appearance of $U(r_1,r_2,\ldots,r_N)$ may be eliminated from Eq. (3.5) to give

$$A(\vec{k},\vec{p},s\,|\,\vec{p}\,')=-\frac{1}{\beta\Omega}\left\langle\sum_{j=1}^{N}\frac{\partial}{\partial r_j}\cdot\left(\frac{\partial D(-\vec{k},\vec{p})}{\partial\vec{p}_j}\,\frac{1}{s+iL}\,D(\vec{k},\vec{p}\,')\right)\right\rangle\,.\tag{3.7}$$

To illustrate the use of this formalism we consider a simple collective approximation. The best known such approximation is the linearized Vlasov equation which is the classical limit of the random phase approximation. This is not a sensible approximation, however, for short-range forces. Its natural generalization to the case of short-range forces is to approximate $A(\vec{k},\vec{p},s\,|\,\vec{p}\,')$ as a linear functional of the excess density.

$$A(\vec{k},\vec{p},s\,|\,\vec{p}\,')=K(\vec{k},\vec{p},s\,|\,\vec{p}\,')\int d^3p''F(\vec{k},\vec{p}\,'',s\,|\,\vec{p}\,')\,.\tag{3.8}$$

In order to use the ansatz (3.8) we must evaluate $K$, which can be done approximately by comparing term by term the expansions in powers of $s^{-1}$ of Eqs. (3.7) and (3.8). The lowest-order term in the expansion of $K$ is given by

$$K_0 = i\vec{k}\cdot \frac{\partial f_M(\vec{p})}{\partial \vec{p}} \, \frac{(S_{\vec{k}}-1)}{\beta S_{\vec{k}}} \ . \tag{3.9}$$

The calculation is similar to that of de Gennes[6] for the moments of $S(\vec{k},\omega)$, and will not be presented here.

If we combine the ansatz (3.8) with the lowest-order approximation (3.9) for $K$, and substitute into Eq. (3.4), we obtain

$$\left(s-\frac{i\vec{k}\cdot\vec{p}}{m}\right) F(\vec{k}',\vec{p},s\,|\,\vec{p}\,') = f(\vec{k},\vec{p},t=0\,|\,\vec{p}\,') + i\vec{k}\cdot \frac{\partial f_M(\vec{p})}{\partial \vec{p}} \, \frac{(S_{\vec{k}}-1)}{\beta S_{\vec{k}}} \int d^3p''F(\vec{k},\vec{p}\,'',s\,|\,\vec{p}\,') \ . \tag{3.10}$$

This is just the linearized Vlasov equation with the Fourier transform of the intermolecular potential replaced by

$$-\beta^{-1}c(\vec{k}) = -\beta^{-1}[(S_{\vec{k}}-1)/S_{\vec{k}}]\,\Omega/N \ .$$

If one integrates out the dependence on $\vec{p}\,'$ in Eq. (3.10), one obtains the equation used by Nelkin and Ranganathan[3] for the calculation of $S(\vec{k},\omega)$ in liquids. They obtained this equation phenomenologically by modifying the linearized Vlasov equation to give the correct short-time behavior of the desired correlation function. In the discussion given here we see that the essential feature of this approximation is the assumption of a linear functional dependence on the density as stated in Eq. (3.8).

In an earlier derivation[4] we obtained the integral of Eq. (3.10) over $\vec{p}\,'$ by working with the functional derivative of the one-particle distribution function with respect to a momentum independent external potential. This gives the same result for $S(\vec{k},\omega)$, but it does not allow the calculation of other one particle quantities such as the transverse current-current correlation function. In the present derivation we see readily that Eq. (3.10) leads to the ideal-gas result for the transverse current-current correlation function, a result in rather poor agreement with Rahman's molecular dynamics calculations of this quantity.[7]

It is possible to calculate more terms in the high-frequency expansion of the kernel $K$, retaining the functional ansatz of Eq. (3.8). Because of the importance of the transverse modes in dense fluids, it seems clear that improvements on the theory should rather be made by improving the functional ansatz. This is discussed briefly at the end of the paper.

## IV. EIGENFUNCTIONS OF THE LIOUVILLE OPERATOR

Classical correlation functions of the form $\langle A(t)B(0)\rangle$ may be expressed in a form suitable for calculation with approximate sets of eigenfunctions of the Liouville operator. In particular we will consider $F(\vec{k},\vec{p},s\,|\,\vec{p}\,')$.

The most convenient starting point is the second line of Eq. (3.1) which gives an exact formal expression for the Fourier-Laplace transform of $f$. It is convenient to view this expression as a matrix element of the resolvent operator $(s+iL)^{-1}$ between two elements in a space of functions of $6N$ variables. An inner product of two functions in this space is defined by

$$\langle \phi_1 | \phi_2 \rangle = \langle \phi_1^* \phi_2 \rangle \ , \tag{4.1}$$

where $\langle\ \rangle$ is a thermodynamic average which we have taken over a classical canonical ensemble. If sets of orthonormal basis functions are known, one may write out the usual expansion theorems. In the problems considered here, however, such a set of functions is not known. A more limited expansion theorem for a subspace spanned by some set of functions is sufficient for the present calculation. Thus for any function $|\,\phi\rangle$ in a subspace spanned by the set of functions $|n\rangle$ (not necessarily orthogonal)

$$|\,\phi\rangle = \int_n a(n)\,|n\rangle \ , \tag{4.2}$$

where $\int_n$ denotes a sum and/or integral over the range of the labeling index $n$.

For the calculation of $f(\vec{r},\vec{p},t\,|\,\vec{r}\,',\vec{p}\,')$, we work in the subspace $V_S$ of all functions of the form

$$\Psi = \sum_{j=1}^{N} \psi(\vec{r}_j,\vec{p}_j) \ . \tag{4.3}$$

Zwanzig[5] has constructed a set of approximate eigenfunctions of the Liouville operator of the form (4.3). (We refer to this paper as Z1.) The functions determined in Z1 may be slightly modified to have the desired completeness property over the subspace $V_S$. Our first step is to construct this set of functions spanning $V_S$. It should be emphasized that this is a mathematical construction which is entirely independent of any dynamical approximations. Once this set has been constructed it will be applied to the equation of motion for $F(\vec{k},\vec{p},s\,|\,\vec{p}\,')$. An approximate equation of motion is obtained in closed form under the approximation that the basis functions we have constructed are eigenfunctions of the Liouville operator. They will be solutions of the approximate eigenvalue equation given in Z1. An important simplification of the results in Z1 is obtained in that the explicit appearance of the eigenvalues and eigenfunctions is eliminated.

If functions of the form (4.3) are chosen to make

$$\lambda \equiv \langle \Psi | L | \Psi \rangle / \langle \Psi | \Psi \rangle \tag{4.4}$$

an extremum, then for translationally invariant systems

$$\psi_{\vec{u},\vec{k}}(\vec{r},\vec{p}) = \gamma_{\vec{u},\vec{k}}(\vec{v})\, e^{i\vec{k}\cdot\vec{r}} , \tag{4.5}$$

where the function $\gamma_{\vec{u},\vec{k}}$ is taken as a function of the velocity $\vec{v}=\vec{p}/m$ for convenience, and $\vec{u}$ and $\vec{k}$ label the eigenfunctions. Letting $\mu$ and $\nu$ be the components of $\vec{u}$ and $\vec{v}$, respectively, in the direction of $\vec{k}$, it is shown in Z1 that $\gamma_{\vec{u},\vec{k}}$ satisfies

$$\vec{k}\circ[\vec{v}-\vec{u}]\,\gamma_{\vec{u},\vec{k}}(\vec{v}) = \vec{k}\circ\vec{u}\,[S_{\vec{k}}-1]\int d^3v'\,\phi_M(\vec{v}\,')\,\gamma_{\vec{u},\vec{k}}(\vec{v}\,') , \tag{4.6}$$

when $\gamma_{\vec{u},\vec{k}}$ is chosen to make Eq. (4.4) an extremum. The approximate eigenvalue $\lambda_{\vec{u},\vec{k}}$ has been written $\lambda=\vec{u}\cdot\vec{k}$, for convenience. $\phi_M(\vec{v}\,')$ in Eq. (4.6) is a unit normalized Maxwellian distribution of velocities, and $S_{\vec{k}}$ is the usual structure factor. In Z1 Eq. (4.6) was shown to have solutions for all real numbers $\mu$ by expressing $\gamma$ in terms of the usual van Kampen-Case eigenfunctions of the Vlasov equation.[8] The transverse velocity components play no role in this development. For our purposes, however, it is necessary to include the dependence on the transverse components in order that we have a set of functions which spans $V_S$.

The solution of Eq. (4.6) may be studied by a slight extension of the results of van Kampen and Case. Since the equation is homogeneous in $\gamma_{\vec{u},\vec{k}}$ the arbitrary normalization may be chosen such that the integral on the right-hand side of Eq. (4.6) is one. The solution is then seen to be $\mu(S_{\vec{k}}-1)(\nu-\mu)^{-1}$ plus an arbitrary function of the velocity $\vec{v}$ times $\delta(\mu-\nu)$. In order to treat the velocity components in a symmetric way and to construct a set of functions in which $D(\vec{k},\vec{p})$ may be expanded, we have chosen the arbitrary function to be proportional to a $\delta$ function of the transverse velocities. With this choice, application of the normalization condition gives the solution in the following form

$$\gamma_{\vec{u},\vec{k}}(\vec{v}) = \mu(S_{\vec{k}}-1)\{P(\nu-\mu)^{-1} + \pi[e_1(\mu)/E_2(\vec{u})]\,\delta(\vec{v}-\vec{u})\} , \tag{4.7}$$

where $e_1(\mu) = 1 + \mu(S_{\vec{k}}-1)P\int_{-\infty}^{\infty}[\phi_M(\nu)/(\mu-\nu)]\,d\nu$ ,

$$e_2(\mu) = \mu(S_{\vec{k}}-1)\phi_M(\mu), \quad E_2(\vec{u}) = \phi_M(\mu_1)\phi_M(\mu_2)e_2(\mu) . \tag{4.8}$$

$P$ denotes a Cauchy principal value, and $\mu_1$ and $\mu_2$ are the transverse components of $\vec{u}$. The eigenfunction $|\vec{u},\vec{k}\rangle$ thus has an eigenvalue $\lambda_{\vec{u},\vec{k}}=\vec{k}\cdot\vec{u}$ which is infinitely degenerate in the transverse components of the labeling vector $\vec{u}$. In the Appendix these functions are shown to be complete on the single-particle subspace $V_S$.

Because of the completeness of the $|\vec{u},\vec{k}\rangle$ on $V_S$, one may write

$$|D(\vec{k},\vec{p})\rangle\!\rangle = \int d^3u\,\mathfrak{D}(\vec{p},\vec{u})\,|\vec{u}-\vec{k}\rangle . \tag{4.9}$$

We are now in a position to obtain an approximate kinetic equation for $F$. The equation of motion (3.3) for $F(\vec{k},\vec{p},s\,|\,\vec{p}\,')$ can be written in the form

$$sF(\vec{k},\vec{p},s\,|\,\vec{p}\,') = f(\vec{k},\vec{p},t=0\,|\,\vec{p}\,') - \int d^3u\,\Omega^{-1}\langle D(\vec{k},\vec{p})\,|\,iL/(s+iL)\,|\,\vec{u},-\vec{k}\rangle\,\mathfrak{D}(\vec{p}\,',\vec{u}) \tag{4.10}$$

If we now make the approximation that the $|\vec{u},\vec{k}\,\rangle$ are eigenfunctions, i.e.,

$$L|\vec{u},\vec{k}\,\rangle \cong \lambda_{\vec{u},\vec{k}}|\vec{u},\vec{k}\,\rangle\ , \tag{4.11}$$

we have

$$sF(\vec{k},\vec{p},s|\vec{p}\,') = f(\vec{k},\vec{p},t=0|\vec{p}\,') - i\int\frac{d^3u}{\Omega}\ \frac{\lambda_{\vec{u},-\vec{k}}\langle D(\vec{k},\vec{p})|\vec{u},-\vec{k}\rangle}{(s+i\lambda_{\vec{u},-\vec{k}})}\ \mathfrak{D}(\vec{p}\,',\vec{u})\ . \tag{4.12}$$

Also in this approximation $F$ may be written

$$F(\vec{k},\vec{p},s|\vec{p}\,') = \int d^3u\,\Omega^{-1}\langle D(\vec{k},\vec{p})|\vec{u},-\vec{k}\rangle\ \mathfrak{D}(\vec{p}\,',\vec{u})(s+i\lambda_{\vec{u},-\vec{k}})^{-1}\ . \tag{4.13}$$

The appearance of the eigenvalues in (4.12) will now be eliminated by first computing $\lambda_{\vec{u},-\vec{k}} \times\langle D(\vec{k},\vec{p})|\vec{u},-\vec{k}\,\rangle$ by using the eigenvalue equation for $\gamma_{\vec{u},\vec{k}}$ and then regrouping terms to be simple operations on $F$. The result will be a closed equation in $F$.

By a straightforward calculation

$$\langle D(\vec{k},\vec{p})|\vec{u},-\vec{k}\,\rangle = Nf_M(\vec{p})[\gamma_{\vec{u},-\vec{k}}(\vec{p}/m) + (S_{\vec{k}}-1)\int d^3v''\phi_M(\vec{v}\,'')\gamma_{\vec{u},-\vec{k}}(\vec{v}\,'')]\ . \tag{4.14}$$

Using the eigenvalue equation (4.6) for $\gamma_{\vec{u},-\vec{k}}$ yields

$$\lambda_{\vec{u},-\vec{k}}\langle D(\vec{k},\vec{p})|\vec{u},-\vec{k}\rangle = -N(\vec{k}\cdot\vec{p}/m)f_M(\vec{p})\gamma_{\vec{u},-\vec{k}}(\vec{p}/m)\ . \tag{4.15}$$

If this is put into (4.12) it is seen that to this approximation this gives the free-particle streaming term $(i\vec{k}\cdot p/m)F$ if $\gamma_{\vec{u},-\vec{k}}$ were replaced by the term in brackets in (4.14). Making this replacement and subtracting a compensating term yields

$$\frac{i\vec{k}\cdot\vec{p}}{m}\,F(\vec{k},\vec{p},s|\vec{p}\,') - \frac{i\vec{k}\cdot\vec{p}}{m}f_M(\vec{p})(S_{\vec{k}}-1)\int\frac{d^3u}{\Omega}\int d^3v''\phi_M(\vec{v}\,'')\gamma_{\vec{u},-\vec{k}}(\vec{v}\,'')\frac{\mathfrak{D}(\vec{p}\,',\vec{u})}{(s+i\lambda_{\vec{u},-\vec{k}})} \tag{4.16}$$

for the second term on the right-hand side of Eq. (4.12). Using (4.13) to calculate $\int d^3\vec{p}\,F(\vec{k},\vec{p},s|\vec{p}\,')$, the second term in (4.16) is seen to be

$$-(i\vec{k}\cdot\vec{p}/m)f_M(\vec{p})(S_{\vec{k}}-1)S_{\vec{k}}^{-1}\int d^3\vec{p}\,''F(\vec{k},\vec{p}\,'',s|\vec{p}\,')\ .$$

Collecting terms, one has

$$(s-i\vec{k}\cdot\vec{p}/m)F(\vec{k},\vec{p},s|\vec{p}\,') = f(\vec{k},\vec{p},0|\vec{p}\,') - (i\vec{k}\cdot\vec{p}/m)f_M(\vec{p})[(S_{\vec{k}}-1)/S_{\vec{k}}]\int d^3p''F(\vec{k},\vec{p}\,'',s|\vec{p}\,') \tag{4.17}$$

which is a closed equation for $F$. It is easily solved and there is no explicit appearance of the eigenfunctions. [The interchange of the order of integrations in getting to (4.12) and (4.17) has not been verified explicitly since the exact form of $\mathfrak{D}(\vec{p},\vec{u})$ is not known.]

The work of this section has been exact up to and including Eq. (4.10). An expansion scheme with (4.17) as the zeroth approximation may be derived from this equation if $L$ is replaced by $(L-\lambda_{\vec{u},-\vec{k}})+\lambda_{\vec{u},-\vec{k}}$ and considering $(L-\lambda_{\vec{u},-\vec{k}})$ as a perturbation. A deeper analysis of the meaning of such an expansion is, however, necessary.

The above derivation demonstrates the important role of the continuous nature of the eigenvalue spectrum in leading to an expression for $F$ which has phase mixing (or Landau damping). [Note that (4.17) is the same form as the linearized Vlasov equation.] A discrete spectrum would have led to an expression for $F$ in terms of a sum of simple poles located at each eigenvalue. Thus although improved eigenfunctions have been calculated by Nossal and Zwanzig[9,10] (denoted NZ), the discrete nature of their spectrum does not lead to interesting structure in $F$. An improved theory of this type should combine the more relevant dynamical content of the eigenfunctions in NZ with the phase mixing due to particle motion that we have included here.

## REMARKS

Section II has provided a formal method for calculating certain correlation functions. This method is most readily applied when we have a valid kinetic equation such as the appropriately linearized Boltzmann equation for rare gases or the Vlasov equation for plasmas. For a liquid there is of course no generally valid kinetic equation.

In Secs. III and IV we have derived a modified Vlasov equation as an approximate kinetic equation for the high-frequency motions in simple liquids. The same equation was derived by two apparently unrelated methods. The first method assumed that the collision term in the exact equation of motion could be taken proportional to the local excess density. The second method assumed that certain sums of single-particle functions could be taken as eigenfunctions of the Liouville operator. For the problem studied, both methods are closely connected to short-time expansions, and both methods emphasize the importance of high-frequency density oscillations. That they should give similar results is thus not surprising, but that the results are identical is not well understood.

The calculation presented here did not account for the transverse motions in any realistic way nor did it include the dynamical information available in the fourth frequency moment of $S(\vec{k},\omega)$. These features are contained in the improved variational eigenfunctions of NZ, but this calculation does not allow for the important phase mixing associated with the continuous nature of the eigenvalue spectrum.

Clearly the next level of improvement would be to construct eigenfunctions which include the dynamical information in NZ and the continuous spectrum caused by selecting functions from larger regions of function space as in Z1. In NZ high-frequency eigenfunctions were constructed which were linear combinations of the density, the three components of the particle current and the time derivatives of the latter. The seemingly most natural generalization of this which includes more freedom in function space would be

$$\Psi = \Psi_1 + iL\Psi_2 .$$

$\Psi_1$ and $\Psi_2$ are sums of single-particle functions whose form is to be determined by the variational principle. Such functions are presently being considered.

The identity of the results of Secs. III and IV also suggests that the eigenfunctions of NZ may be used as a guide for making an improved ansatz on the collision term. The function space formalism of Sec. IV is presently being applied to expand the collision term as a sum over the high-frequency modes studied in NZ. This is a natural generalization of the density ansatz of Sec. III.

## APPENDIX

If the set of functions $\Psi_{\vec{u},\vec{k}}$ is to be complete on $V_S$, it must be shown that for any

$$Q = \sum_{j=1}^{N} Q(\vec{v}_j)\, e^{i\vec{k}\cdot\vec{r}_j}$$

there must exist a function $q(\vec{u})$ such that

$$Q(\vec{v}) = \int d^3u\, q(\vec{u})\gamma_{\vec{u},\vec{k}}(\vec{v}) . \qquad (\mathrm{A.1})$$

Using the expression (4.8) for $\gamma_{\vec{u},\vec{k}}$ this becomes

$$Q(\vec{v}) = \phi_M(\vec{v})\, e_1(\nu) q(\vec{v}) + (S_{\vec{k}} - 1)\, P \int d^3u\, \mu\, q(\vec{u})\, (\nu - \mu)^{-1} . \qquad (\mathrm{A.2})$$

Multiplying by $\phi_M(\nu_1)\phi_M(\nu_2)$ and integrating over $\nu_1$ and $\nu_2$ (the transverse components of $\vec{v}$) yields

$$\overline{Q}(\nu) = \phi_M^{-1}(\nu) e_1(\nu)\tilde{q}(\nu) + (S_{\vec{k}} - 1) P \int_{-\infty}^{\infty} d\mu\, \mu\, \tilde{q}(\mu)(\nu - \mu)^{-1} , \qquad (\mathrm{A.3})$$

where

$$\overline{Q}(\nu) = \int d\nu_1 d\nu_2\, \phi_M(\nu_1)\phi_M(\nu_2) Q(\vec{v})$$

and

$$\tilde{q}(\mu) = \int d\mu_1 d\mu_2\, q(\vec{u}) .$$

If $\tilde{q}(\mu)$ exists then $q(\vec{u})$ may always be calculated from (A.2). Thus one must show that $\tilde{q}(\mu)$ always exists for a given $\overline{Q}(\nu)$. But this statement of the question through (A.3) is exactly that for the purely longitudinal eigenfunctions set forth in Z1. Since there are in one-to-one correspondence with the complete set of van Kampen-Case functions, as shown in Z1, $\tilde{q}$ always exists (for reasonably well behaved $\overline{Q}$). Hence the set $\Psi_{\vec{u},\vec{k}}$ is complete on $V_S$.

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# Effect of Boundary Conditions on the Stability of a Nonuniform Plasma in a Magnetic Field

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The propagation of high-frequency electrostatic waves is considered in a plasma in which there is a zero-order temperature gradient perpendicular to the uniform magnetic field. The frequency range is such that the ions do not respond to the perturbed fields (this condition is satisfied if $\alpha/\rho_i \ll k_\perp d$ resulting in $\omega \gg \omega_{ci}$, $\omega \gg \omega_{pi}$, where $\omega_{ci}$ and $\omega_{pi}$ are the ion-cyclotron and ion-plasma frequencies and $\alpha, \rho_i, k_\perp$, and $d$ are the scale length of the temperature gradient, the ion Larmor radius, the perpendicular component of the wave vector, and the electron Debye length, respectively). For $\omega \ll \omega_{ce}$, $\rho_e \ll d \ll \lambda_\perp$ and a specific form of the temperature gradient the differential equation for $\varphi$ is reduced to an elementary form where $\omega, \omega_{ce}$ are the wave-and electron-cyclotron frequencies and $\lambda_\perp$ and $\rho_e$ the wavelength perpendicular to the uniform magnetic field and the electron Larmor radius, respectively. $\varphi$ is the electrostatic potential. For $\lambda_\perp \ll \alpha$ the exact solution is very close to the local solution of Mikhailovskii and Pashitskii which neglects the effects of the boundaries. However for $\lambda_\perp \gtrsim \alpha$ the plasma is unstable to shorter axial wavelengths than predicted by the local theory. It is shown that the instability is due to the interaction of a positive energy wave with a negative energy wave. When the phase velocities of the two waves are different the plasma is stable. However, when the nonuniform plasma is adjacent to a cold resistive plasma, instability may again result. This is analogous to the resistive wall amplifier of Birdsall, Brewer and Haeff.
The relevance of these results to the stability of low frequency waves in a nonuniform plasma is pointed out.

## 1. INTRODUCTION

There is a class of plasma instabilities which occur only in a nonuniform plasma in a magnetic field. These instabilities are usually referred to as drift instabilities[1] and are of great importance for research on thermonuclear fusion. If such instabilities are confined to the interior of the plasma due to the unstable wave growing to nonlinear proportions faster than it can propagate a scale length in the direction of the nonuniformity[1] then the effect of the boundaries will be unimportant. The condition for this to be the case is that the wavelength transverse to the magnetic field be much less than the scale length of the nonuniformity.[1] Waves in a cylindrical plasma, of low azimuthal mode number, do not satisfy this condition and Chen[2] has shown that the growth rates obtained from a nonlocal solution (i.e., solution of boundary-value problem) are markedly different from the growth rates obtained from the local solution.

In this paper we consider a high-frequency drift instability discovered by Mikhailovskii and Pashitskii[3] in which only the electrons respond to the wave fields. Whereas Mikhailovskii and Pashitskii made use of the local approximation[1] we obtain the nonlocal dispersion relation taking into account the effect of the boundaries.

In Sec. 2 we derive the dispersion relation for semi-infinite slab geometry and obtain a generalization of Ref. 3. The instability is shown to result from an interaction between a positive energy wave and a negative energy wave. In Sec. 3