KINETIC THEORY OF NORMAL QUANTUM FLUIDS

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— and the cold angels, the abstractions.

Sylvia Plath

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ABSTRACT

Close to equilibrium, a normal Bose or Fermi fluid can be described by an exact kinetic equation whose kernel is nonlocal in space and time. The general expression derived for the kernel is evaluated to second order in the interparticle potential. The result is a wavevector- and frequency-dependent generalization of the linear Uehling-Uhlenbeck kernel with the Born approximation cross section.

The theory is formulated in terms of second-quantized phase space operators whose equilibrium averages are the n-particle Wigner distribution functions. Convenient expressions for the commutators and anticommutators of the phase space operators are obtained. The two-particle equilibrium distribution function is analyzed in terms of momentum-dependent quantum generalizations of the classical pair distribution function $h(k)$ and direct correlation function $c(k)$. The kinetic equation is presented as the equation of motion of a two-particle correlation function, the phase space density-density anticommutator, and is derived by a formal closure of the quantum BBGKY hierarchy. An alternative derivation using a projection operator is also given. It is shown that the method used for approximating the kernel by a second order expansion preserves all the sum rules to the same order, and that the second-order kernel satisfies the appropriate positivity and symmetry conditions.

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I. INTRODUCTION

The classical Boltzmann equation occupies a uniquely successful position in nonequilibrium statistical mechanics. Intermediary between the microscopic and macroscopic worlds, it serves as a model whose intuitive appeal and wide applicability have not been equaled by any other method of description.[1] Although it is limited to dilute gases, similar equations have been developed for denser fluids. A Boltzmann-like kinetic theory for quantum mechanical fluids has long been an attractive possibility, but the problems involved in its formulation are much more severe than in the classical case. A quantum kinetic equation known as the Uehling-Uhlenbeck equation can be obtained from the Boltzmann equation by the substitution of the quantum mechanical cross section for the classical one and the insertion of statistical factors to reproduce the Bose or Fermi ideal gas distributions at equilibrium.[2,3] Several derivations have been given for the Uehling-Uhlenbeck equation,[4-6] and corrections to it have been suggested,[7-9] but systematic attempts to improve upon it have generally not gone beyond the formal stage.[10,11] An exception is the transport equation derived by Kadanoff and Baym for systems slowly varying in space and time,[12] but, as discussed below, there remains a need for a quantum kinetic theory valid on all scales of length and time.

The present approach to this problem was stimulated by certain recent developments in classical kinetic theory. It has been known for some time that a liquid or dense gas can truly be described by a Boltzmann-like kinetic equation only if the kinetic kernel is made

nonlocal in time and space to account for the duration and spatial extent of the collision process.[13, 14] Indeed, the first attempt to treat such effects was made by Enskog more than 50 years ago.[15] Although nonlocal kernels have subsequently appeared in many derivations, it is only in the last few years that systematic and explicit approximations have been obtained. For small deviations from equilibrium, a classical fluid can be described by an exact linear kinetic equation, whose kernel has now been evaluated to second order in the interparticle potential,[16, 17] and to first[18, 19] and second[20] order in a density expansion. Other techniques have been used for the special case of a hard sphere gas.[21, 22] There have also been several methods proposed for obtaining a kernel valid at liquid densities.[23-28]

An important aspect of these new kinetic theories is that they are derived without reference to any length or time scale, and therefore may be useful for the full range of fluid phenomena from the molecular to the hydrodynamic regime. Support for this notion comes from an analysis of the weak coupling equation by Forster and Martin,[17] who showed that it gives consistent predictions of the sum rules and the transport coefficients, reflecting a balanced treatment of the short-time and the long-time behavior. A similar result holds for the low-density equations.[20, 29] From the work of Forster and Martin and of Résibois,[30, 31] it follows that to determine the transport coefficients exactly, the kinetic kernel must be correct through second order in space and time derivatives. The quantum transport equation derived by Kadanoff and Baym was explicitly limited to the

long-time, large-distance regime by the omission of terms higher than first order in the gradients, and it is therefore insufficient even for a complete description of linear hydrodynamics.

The object of this thesis is to demonstrate that a linear kinetic theory for normal quantum fluids with Bose or Fermi statistics can be formulated with the same conceptual simplicity and consistency as has now been attained in the classical case, and, specifically, to calculate the nonlocal kernel to second order in a potential expansion. In the classical limit this second-order kernel properly reduces to the classical one, and in the limit of large times and distances it reduces to the linear Uehling-Uhlenbeck kernel with the Born approximation cross section.

The organization of the thesis is as follows. Sections II, III, and IV introduce the operators, distribution functions, and correlation functions needed for the calculation. Section V contains the derivation of the kinetic equation and a discussion of the method of approximation. An alternative derivation is given in Appendix C. The evaluation of the kernel to second order is carried out in Section VI. Section VII contains a brief discussion of the results and of possibilities for future work.

II. PHASE SPACE OPERATORS

Classical kinetic theory is based on the study of the one-particle phase space distribution function $\rho(rp,t)$, which can be expressed as the ensemble average of the classical phase space density

$$f_c(rp,t) = \sum_i \delta(r-r_i(t))\delta(p-p_i(t)) , \qquad (2.1)$$

where the summation extends over all the particles in the system. In quantum kinetic theory, it is useful to express the Wigner distribution function as the ensemble average of a second-quantized phase space operator $f(rp,t)$. The operator $f(rp,t)$ and its multiparticle analogs are studied in this section. Properties of the distribution functions and time-displaced correlation functions obtained from them are discussed in Sections II and III.

The one-particle phase space density operator $f(rp,t)$ is defined by

$$f(rp,t) = (2\pi\hbar)^{-3}\int dr' e^{-ip\cdot r'/\hbar}\psi^+(r-\tfrac{1}{2}r',t)\psi(r+\tfrac{1}{2}r',t) , \qquad (2.2)$$

where $\psi(r,t)$ and $\psi^+(r',t')$ are the Heisenberg field operators satisfying the commutation or anticommutation relations

$$\psi(r)\psi^+(r') - \eta\psi^+(r')\psi(r) = \delta(r-r') \qquad (2.3a)$$

and

$$\psi(r)\psi(r') - \eta\psi(r')\psi(r) = 0 \qquad (2.3b)$$

at equal times. The factor η equals $+1$ for bosons and -1 for fermions. Throughout this paper, the letters k, r, and p represent vector quantities. When they are needed, the components of a vector are indicated by a Greek superscript.

In terms of $f(rp,t)$, the ordinary number and momentum density operators are given by

$$\hat{n}(r,t) = \psi^+(r,t)\psi(r,t) = \int dp\, f(rp,t) \quad , \tag{2.4a}$$

$$J^\alpha(r,t) = \frac{i\hbar}{2}\left[\left(\frac{\partial}{\partial r^\alpha}\psi^+\right)\psi - \psi^+\left(\frac{\partial}{\partial r^\alpha}\psi\right)\right] = \int dp\, p^\alpha f(rp,t) \quad . \tag{2.4b}$$

These equations provide a first indication of the considerable formal similarity between $f(rp,t)$ and the classical phase space density $f_c(rp,t)$.

The multiparticle phase space operators are defined by

$$f(12..n,t) = (2\pi\hbar)^{-3}\int dr_n'\, e^{-ip_n\cdot r_n'/\hbar} \times \psi^+(r_n - \tfrac{1}{2}r_n', t) f(12..n-1,t)\psi(r_n + \tfrac{1}{2}r_n', t) \quad , \tag{2.5}$$

where 1 stands for the pair of variables $r_1 p_1$, and so forth. The ordering of the operators in Eq. (2.5) corresponds classically to the requirement that all the particles be distinct. The two-particle operator $f(12,t)$, for example, is analogous to the classical density

$$f_c(12,t) = \sum_{i\neq j} \delta(r_1 - r_i(t))\delta(p_1 - p_i(t))\delta(r_2 - r_j(t))\delta(p_2 - p_j(t)) \quad . \tag{2.6}$$

It should be noted that the phase space operators are Hermitian, and that $f(1..i..j..n,t)$ is symmetric under permutations (i,j) for both Bose and Fermi statistics.

We consider a system of unit mass point particles interacting through a central potential $v(12) = v(|r_1 - r_2|)$. In terms of the phase space operators $f(1)$ and $f(12)$, the Hamiltonian is

$$\hat{H} = \frac{1}{2}\int d1\, p_1^2 f(1) + \frac{1}{2}\int d1 d2\, v(12) f(12) \quad , \tag{2.7}$$

where $d1$ stands for $dr_1 dp_1$. For the purpose of carrying out a formal perturbation expansion, later, it is assumed that $v(r)$ has a Fourier transform.

As shown in Appendix A, the equal-time commutation relations of the first few phase space operators can be expressed as

$$[f(1), f(2)] = \delta(1-2) S(1) f(1) \quad , \tag{2.8a}$$

$$[f(1), f(23)] = \delta(1-2) S(1) f(13) + \delta(1-3) S(1) f(12) \quad , \tag{2.8b}$$

$$\begin{aligned}[f(12), f(34)] = {} & \delta(1-3) S(1) f(124) + \delta(1-4) S(1) f(123) \\ & + \delta(2-3) S(2) f(124) + \delta(2-4) S(2) f(123) \\ & + [\delta(1-3)\delta(2-4) + \delta(1-4)\delta(2-3)] S(12) f(12) \quad ,\end{aligned} \tag{2.8c}$$

where $\delta(1-2) = \delta(r_1 - r_2)\delta(p_1 - p_2)$ and

$$S(1) = 2i \sin[\tfrac{1}{2}\hbar D(1)] \quad ,$$

$$S(12) = 2i \sin[\tfrac{1}{2}\hbar D(1) + \tfrac{1}{2}\hbar D(2)] \quad ,$$

$$D(1) = \overleftarrow{\nabla}_{r_1} \cdot \vec{\nabla}_{p_1} - \overleftarrow{\nabla}_{p_1} \cdot \vec{\nabla}_{r_1} \quad .$$

The gradients in the Poisson bracket operator D act to the left or right as indicated by the arrows. If x and y are two functions of the phase space variables rp, for example, then $x(rp)\exp[iD(rp)]y(rp)$ is defined as the formal power series

$$\begin{aligned} x e^{iD} y = {} & xy + i\left[\frac{\partial x}{\partial r} \cdot \frac{\partial y}{\partial p} - \frac{\partial x}{\partial p} \cdot \frac{\partial y}{\partial r}\right] \\ & - \frac{1}{2!}\left[\frac{\partial^2 x}{\partial r^\alpha \partial r^\beta}\frac{\partial^2 y}{\partial p^\alpha \partial p^\beta} - 2\frac{\partial^2 x}{\partial r^\alpha \partial p^\beta}\frac{\partial^2 y}{\partial p^\alpha \partial r^\beta} + \frac{\partial^2 x}{\partial p^\alpha \partial p^\beta}\frac{\partial^2 y}{\partial r^\alpha \partial r^\beta}\right] + \cdots \end{aligned}$$

The first few equal-time anticommutation relations are

$$\frac{1}{2}\{f(1), f(2)\} = f(12) + \delta(1-2)C(1)f(1) , \tag{2.9a}$$

$$\frac{1}{2}\{f(1), f(23)\} = f(123) + \delta(1-2)C(1)f(13) + \delta(1-3)C(1)f(12) , \tag{2.9b}$$

where

$$C(1) = \cos[\tfrac{1}{2}\hbar D(1)] .$$

Except for the presence of higher-order operators on the right-hand side, the anticommutation formulas follow the same pattern as Eqs. (2.8). The relations (2.8) and (2.9), which are new, are a convenient restatement of the commutation and anticommutation relations of pairs $\psi^+(r')\psi(r)$ of the field operators. It should be emphasized that both Eqs. (2.8) and (2.9) are true for both Bose and Fermi statistics.

The occurrence of operators like $S(1)$ is typical of formulas involving the Wigner distribution.[32-37] Expanded in powers of $\hbar$, such formulas give quantum corrections to classical results. The classical expression corresponding to the first term in the expansion of Eq. (2.8a), for example, is the Poisson bracket formula

$$[f_c(1), f_c(2)]_{PB} = \delta(1-2)\left(\overleftarrow{\nabla}_{r_1}\cdot\vec{\nabla}_{p_1} - \overleftarrow{\nabla}_{p_1}\cdot\vec{\nabla}_{r_1}\right)f_c(1) .$$

In this thesis, however, I do not make use of an expansion in $\hbar$ except to compare a quantum mechanical result with its classical limit.

The manipulation of expressions involving $S(1)$ and $S(12)$ is aided by the fact that $D(1)$ commutes with itself and with $D(2)$. It should also be noted that after a Fourier transformation with respect

to r_1, an operator like $\exp\left(-\frac{1}{2}i\hbar\overleftarrow{\nabla}_{r_1}\cdot\vec{\nabla}_{p_1}\right)$ acts on the functions to its right to produce a displacement in momentum:

$$\exp\left(\tfrac{1}{2}\hbar k\cdot\frac{\partial}{\partial p}\right)x(p) = x(p+\tfrac{1}{2}\hbar k) \quad .$$

It is primarily in this form that operators like S(1) and S(12) are used in later sections.

The commutators in the equations of motion

$$\frac{\partial f}{\partial t} = \frac{1}{i\hbar}[f,\hat{H}]$$

for the phase space operators can be rewritten through an application of Eqs. (2.8); the method is illustrated in the derivation of Eq. (2.14) below. The result is the coupled system of equations

$$\left[\frac{\partial}{\partial t}+iL(1)\right]f(1,t) = -\int d2\, iL_1(12)f(12,t) \ , \tag{2.10a}$$

$$\left[\frac{\partial}{\partial t}+iL(12)\right]f(12,t) = -\int d3[iL_1(13)+iL_1(23)]f(123,t) \ , \tag{2.10b}$$

and so forth, where

$$L(1) = L_o(1) = -ip_1\cdot\frac{\partial}{\partial r_1} \ , \tag{2.11a}$$

$$L(12) = L_o(1)+L_o(2)+iv(12)\frac{2}{\hbar}\sin\left(\frac{\hbar}{2}\overleftarrow{\nabla}_{r_1}\cdot\vec{\nabla}_{p_1}+\frac{\hbar}{2}\overleftarrow{\nabla}_{r_2}\cdot\vec{\nabla}_{p_2}\right), \tag{2.11b}$$

$$L_1(12) = iv(12)\frac{2}{\hbar}\sin\left(\frac{\hbar}{2}\overleftarrow{\nabla}_{r_1}\cdot\vec{\nabla}_{p_1}\right) \ . \tag{2.11c}$$

Except for the definition of the interaction operators in Eqs. (2.11b) and (2.11c), this system has the same form as the classical BBGKY hierarchy. These operator equations are analogous to the equations of motion of the reduced Wigner distribution functions in the form first given by Irving and Zwanzig.[33] Equations (2.10) - (2.11) provide

the starting point for the derivation of the correlation-function kinetic equation in Section V.

This section concludes with an application of the commutation relations (2.8) to the operator counterparts of the hydrodynamic variables, namely the number and current density operators $\hat{n}(r,t)$ and $J(r,t)$ given by Eqs. (2.4) and the energy density $E(r,t)$ given by

$$E(r,t) = \int dp\, \mathcal{E}(rp,t) \ , \tag{2.12a}$$

where

$$\mathcal{E}(rp,t) = \frac{1}{2}p^2 f(rp,t) + \frac{1}{2}\int d2\, v(12) f(12) \ . \tag{2.12b}$$

We obtain illustrative formulas for some of the commutators of these operators, as well as expressions for the stress tensor and energy current operators that appear in the differential form of the operator conservation laws. These results are not used elsewhere in this thesis, but they will be required in future work on the conservation laws and transport coefficients predicted by the kinetic equation.

It should be noted, first, that the density operator commutes with itself,

$$[\hat{n}(r_1), \hat{n}(r_2)] = 0 \ . \tag{2.13a}$$

This property is shared by the multiparticle densities such as $\hat{n}(r_1 r_2) = \int dp_1\, dp_2\, f(12)$,

$$[\hat{n}(r_1 r_2), \hat{n}(r_3 r_4)] = 0 \ , \tag{2.13b}$$

and by the combinations like

$$[\hat{n}(r_1), \hat{n}(r_2 r_3)] = 0 \ . \tag{2.13c}$$

One verifies these identities by expanding the S operator in Eqs. (2.8) and integrating by parts with respect to the moment. The procedure is illustrated in the following calculation of the density-current commutator. We write

$$\begin{aligned}[\hat{n}(r_1), J^{\alpha}(r_2)] &= \int dp_1 dp_2 p_2^{\alpha}\Big\{\delta(r_1-r_2)\delta(p_1-p_2) \\ &\quad \times 2i \sin\Big[\tfrac{1}{2}\hbar\Big(\overleftarrow{\nabla}_{r_1}\cdot\vec{\nabla}_{p_1} - \overleftarrow{\nabla}_{p_1}\cdot\vec{\nabla}_{r_1}\Big)\Big] f(r_1 p_1)\Big\} \\ &= -\int dp_1 dp_2\, \delta(r_1-r_2)\delta(p_1-p_2) \\ &\quad \times 2i \sin\Big[\tfrac{1}{2}\hbar\overleftarrow{\nabla}_{p_1}\cdot\Big(\overleftarrow{\nabla}_{r_1}+\vec{\nabla}_{r_1}\Big)\Big] p_2^{\alpha} f(r_1 p_1) \ .\end{aligned}$$

Only the first term in the expansion of the sine survives the integration, and it gives

$$[\hat{n}(r_1), J^{\alpha}(r_2)] = -i\hbar\frac{\partial}{\partial r_1^{\alpha}}[\delta(r_1-r_2)\hat{n}(r_1)] \ . \qquad (2.14)$$

Similar calculations give, for example, the number density-kinetic energy density commutator

$$[\hat{n}(r_1), E_o(r_2)] = -i\hbar\frac{\partial}{\partial r_1^{\alpha}}[\delta(r_1-r_2)J^{\alpha}(r_1)] \ , \qquad (2.15)$$

and the current-current commutator

$$\Big[J^{\alpha}(r_1), J^{\beta}(r_2)\Big] = -i\hbar\Big\{\frac{\partial}{\partial r_1^{\beta}}[\delta(r_1-r_2)J^{\alpha}(r_1)] - \frac{\partial}{\partial r_2^{\alpha}}[\delta(r_1-r_2)J^{\beta}(r_2)]\Big\}. \qquad (2.16)$$

We obtain the differential conservation laws by working out the commutators in the equations of motion $\partial/\partial t = (i\hbar)^{-1}[\ \ , \hat{H}]$ for the number, current, and energy densities. Because of Eq. (2.13c), the potential energy does not contribute to the equation for $\hat{n}(r)$, which is simply the number conservation law

$$\frac{\partial}{\partial t}\hat{n}(r,t) + \frac{\partial}{\partial r^{\alpha}} J^{\alpha}(r,t) = 0 \quad . \tag{2.17a}$$

The momentum and energy conservation laws are written as

$$\frac{\partial}{\partial t} J^{\beta}(r,t) + \frac{\partial}{\partial r^{\alpha}} T^{\alpha\beta}(r,t) = 0 \ , \tag{2.17b}$$

$$\frac{\partial}{\partial t} E(r,t) + \frac{\partial}{\partial r^{\alpha}} J_e^{\alpha}(r,t) = 0 \ , \tag{2.17c}$$

in terms of the stress density and energy current operators

$$T^{\alpha\beta}(r,t) = \int dp\left[p^{\alpha} p^{\beta} f(rp,t) + \tau_{pot}^{\alpha\beta}(rp,t)\right] \ , \tag{2.18}$$

$$J_e^{\beta}(r,t) = \int dp\left[p^{\beta} \mathcal{E}(rp,t) + p^{\alpha} \tau_{pot}^{\alpha\beta}(rp,t)\right] \quad . \tag{2.19}$$

The first terms of Eqs. (2.18) and (2.19) are straightforward to obtain. The second terms, containing the operator $\tau_{pot}^{\alpha\beta}(rp,t)$, are more difficult; they arise from the commutators involving the potential energy part of the Hamiltonian. In terms of the Fourier transform

$$\tau_{pot}^{\alpha\beta}(kp,t) = \int dr\, e^{-ik\cdot r} \tau_{pot}^{\alpha\beta}(rp,t) \ , \tag{2.20}$$

the result for the operator $\tau_{pot}^{\alpha\beta}$ can be expressed as

$$\tau_{pot}^{\alpha\beta}(kp,t) = \tfrac{1}{2}(2\pi)^{-3} \int d\bar{k} d\bar{p}\, \Phi^{\alpha\beta}(k,\bar{k}) f(k-\bar{k}, p, \bar{k}\,\bar{p}, t) \ , \tag{2.21}$$

where $f(kp, k'p', t)$ is the Fourier transform

$$\int dr dr' e^{-i(k\cdot r + k'\cdot r')} f(rp, r'p', t)$$

The function $\Phi^{\alpha\beta}(k,\bar{k})$ satisfies

$$k^{\alpha} \Phi^{\alpha\beta}(k,\bar{k}) = \bar{k}^{\beta} v(\bar{k}) - (\bar{k}^{\beta} - k^{\beta}) v(\bar{k} - k) \ , \tag{2.22}$$

where $v(k)$ is the Fourier transform of the potential. An explicit representation for it is[17]

$$\Phi^{\alpha\beta}(k, \bar{k}) = \int_0^1 ds \left[\frac{(\bar{k}-sk)^{\alpha}(\bar{k}-sk)^{\beta}}{|\bar{k}-sk|} v'(\bar{k}-sk) + \delta_{\alpha\beta} v(\bar{k}-sk) \right] , \quad (2.23)$$

where

$$v'(k) = \frac{dv(k)}{d|k|} .$$

Equations (2.18) - (2.23) are equivalent to the somewhat bulkier expressions for the quantum mechanical stress tensor and energy current given by Puff and Gillis in terms of the operators $\psi(r)$ and $\psi^{+}(r)$.[38]

III. DISTRIBUTION FUNCTIONS

The one- and two-particle Wigner distributions are

$$n(1) = \langle f(1) \rangle \ , \tag{3.1a}$$

$$n(12) = \langle f(12) \rangle \ , \tag{3.1b}$$

where the angular brackets indicate an average in the grand canonical ensemble with inverse temperature β and chemical potential μ. For $\hbar \to 0$, these functions reduce to the classical one- and two-particle phase space distribution functions. Because of translational invariance in the equilibrium ensemble, the one-particle function is simply the momentum distribution $n(p)$, which is normalized to the density by $\int dp\, n(p) = n$. For free particles, it is the Bose or Fermi distribution

$$n_o(p) = (2\pi\hbar)^{-3}\left[e^{\beta(\frac{1}{2}p^2-\mu)}-\eta\right]^{-1} \ . \tag{3.2}$$

This normalization ensures that the $\hbar \to 0$ limit of $n(p)$ is $n\phi(p)$, where

$$\phi(p) = (2\pi/\beta)^{-\frac{3}{2}} e^{-\frac{1}{2}\beta p^2} \tag{3.3}$$

is the Maxwellian. Similarly, the classical limit of $n(12)$ is

$$\lim_{\hbar \to 0} n(12) = n^2 g_c(r_1 - r_2)\phi(p_1)\phi(p_2) \ , \tag{3.4}$$

where $g_c(r)$ is the classical pair distribution function. As will be seen below, the momentum and position variables in the quantum $n(12)$ do not separate in this way, but the pair distribution $g(r)$ is nevertheless given by

$$n^2 g(r_1 - r_2) = \int dp_1 dp_2 n(12) \qquad (3.5)$$

as in the classical case. Though $n(12)$ is real, it is not necessarily nonnegative for all values of its variables. This is characteristic of the Wigner representation. The function $n(12)$ is best regarded as a particular off-diagonal Fourier transform of the two-particle density matrix. Since an integration over all momenta as in (3.5) gives the diagonal part, the pair distribution $g(r)$ is nonnegative, as it must be.

To investigate $n(12)$ in more detail, we can employ perturbation theory.[39] The notation and diagrammatic rules are summarized in Appendix B. Here it is sufficient to note that the Fourier transform of $f(12)$, Eq. (2.5), is given in terms of the operators

$$\hat{\varphi}(\hbar k) = \int dr\, e^{-ik\cdot r} \psi(r)$$

by

$$f(k_1 p_1, k_2 p_2) = (2\pi\hbar)^{-6} \hat{\varphi}^+(1-)\hat{\varphi}^+(2-)\hat{\varphi}(2+)\hat{\varphi}(1+) , \qquad (3.6)$$

where $1\pm = p_1 \pm \frac{1}{2}\hbar k_1$, $2\pm = p_2 \pm \frac{1}{2}\hbar k_2$, and that $n(k_1 p_1, k_2 p_2)$ is given by the sum of imaginary-time ordered momentum space diagrams indicated in Fig. 1. Diagrams 1a and 1b contain the fully interacting one-particle propagator, and diagram 1c stands for the sum of all two-particle connected diagrams, so that Fig. 1 provides a structural decomposition of $n(12)$ that does not yet involve a perturbation expansion. Diagram 1a, in which particles 1 and 2 are uncorrelated, stands for

$$(2\pi)^6 \delta(k_1)\delta(k_2) n(p_1) n(p_2) \quad . \qquad (3.7a)$$

Diagram 1b, in which particles 1 and 2 are correlated only by exchange, gives

$$(2\pi)^3\delta(k_1+k_2)\delta(p_1-p_2)\gamma n(1+)n(1-)\ , \tag{3.7b}$$

where $\gamma=(2\pi\hbar)^3\eta$. As we would expect, this term is of purely quantum mechanical origin, and vanishes for $\hbar\to 0$. Diagram 1c contains the effects of correlations due to the interparticle potential, and can be represented by

$$(2\pi)^3\delta(k_1+k_2)H(k_1p_1p_2)\ , \tag{3.7c}$$

where $H(k_1p_1p_2)$ is a special form of the function $\mathcal{H}(p_1p_2p_3p_4)$ discussed below. In summary, $n(12)$ is given by

$$n(12)=n(p_1)n(p_2)+\int\frac{dk}{(2\pi)^3}e^{ik\cdot(r_1-r_2)}$$
$$\times\left[\delta(p_1-p_2)\gamma n(p_1-\tfrac{1}{2}\hbar k)n(p_1+\tfrac{1}{2}\hbar k)+H(kp_1p_2)\right]\ . \tag{3.8}$$

Comparing this with Eq. (3.4), we see that the classical limit of $H(kpp')$ is given by

$$\lim_{\hbar\to 0}H(kpp')=h_c(k)n\phi(p)n\phi(p')\ , \tag{3.9}$$

where $h_c(k)$ is the Fourier transform of $g_c(r)-1$.

It will be useful to define a quantum generalization $h(kpp')$ of $h_c(k)$ by

$$H(kpp')=h(kpp')N(kp)N(kp')\ , \tag{3.10}$$

where

$$N(kp)\equiv\tfrac{1}{2}n(p+\tfrac{1}{2}\hbar k)\tilde{n}(p-\tfrac{1}{2}\hbar k)+\tfrac{1}{2}n(p-\tfrac{1}{2}\hbar k)\tilde{n}(p+\tfrac{1}{2}\hbar k)\ , \tag{3.11}$$

with

$$\tilde{n}(p) = 1 + \gamma n(p) \quad .$$

Obviously, there are many functions besides N(kp) which reduce to $n\phi(p)$ in the classical limit; the reason for the particular definitions (3. 10) and (3. 11) will be apparent in Section IV. Like H(kpp′), h(kpp′) is real, even under $k \leftrightarrow -k$, and symmetric in p and p′. It vanishes for an ideal gas. The notation should not be interpreted to suggest too close an analogy with the classical distribution functions, however. It should be noted, for example, that the quantum g(r)-1 is <u>not</u> equal to the Fourier transform of $\int dpdp'h(kpp')$, as the exchange term is not included in the definition of h(kpp′). Rather, g(r)-1 is obtained from Eqs. (3. 5 and (3. 8). For an ideal gas, all the correlations come from the exchange term, so that $g_o(r)$ is given by the standard result[40,41]

$$g_o(r) = 1 + \eta w^2(r) \quad , \tag{3. 12}$$

where

$$w(r) = \frac{1}{n_o} \int dp\, e^{ip\cdot r/\hbar} n_o(p) \quad .$$

The calculation of H(kpp′) is in general an exceedingly complicated problem. In addition to all the difficulties involved in a calculation of the quantum mechanical pair distribution function, one must deal with the coupling of the space and momentum variables. The first term in the perturbation expansion of H(kpp′) is not difficult to obtain, however, and serves to illustrate something of the general structure of h(kpp′) and of its relationship to the classical $h_c(k)$. The result for the sum of the general two-particle connected diagram with the momentum labeling of Fig. 2 is written as

$$(2\pi\hbar)^3 \delta(p_1+p_2-p_3-p_4)\mathcal{K}(p_1, p_2, p_3, p_4) \quad . \tag{3.13}$$

A short calculation of the two diagrams on the right hand side of Fig. 2 gives the first-order result

$$\mathcal{K}_1(p_1, p_2, p_3, p_4) = \beta[\hat{v}(p_1-p_3) + \eta\hat{v}(p_1-p_4)]$$

$$\times A_o(p_1, p_2, p_3, p_4) \frac{\tanh\left[\frac{1}{2}\beta\left(p_1^2+p_2^2-p_3^2-p_4^2\right)\right]}{\frac{1}{2}\beta\left(p_1^2+p_2^2-p_3^2-p_4^2\right)} \quad , \tag{3.14}$$

where

$$A_o(p_1, p_2, p_3, p_4) = \frac{1}{2} n_o(p_1) n_o(p_2) \tilde{n}_o(p_3) \tilde{n}_o(p_4)$$

$$+ \frac{1}{2} \tilde{n}_o(p_1) \tilde{n}_o(p_2) n_o(p_3) n_o(p_4) \tag{3.15}$$

and

$$\hat{v}(\hbar k) = v(k) = \int dr\, e^{-ik\cdot r} v(r) \quad .$$

Comparing Fig. 1c and Fig. 2, we see that Eq. (3.7c) defines $H(kpp')$ in terms of $\mathcal{K}(p_1p_2p_3p_4)$ as

$$H(kpp') = \mathcal{K}(p-\tfrac{1}{2}\hbar k, p'+\tfrac{1}{2}\hbar k, p+\tfrac{1}{2}\hbar k, p'-\tfrac{1}{2}\hbar k) \quad . \tag{3.16}$$

To put the result for $H_1(kpp')$ in the form

$$H_1(kpp') = h_1(kpp') N_o(kp) N_o(kp') \quad ,$$

we can use the identity

$$n_o(p-\tfrac{1}{2}\hbar k)\tilde{n}_o(p+\tfrac{1}{2}\hbar k) = n_o(p+\tfrac{1}{2}\hbar k)\tilde{n}_o(p-\tfrac{1}{2}\hbar k) e^{\beta\hbar k\cdot p} \tag{3.17}$$

to extract a factor $N_o(kp)N_o(kp')$ from A_o. The final expression for $h_1(kpp')$ can then be written as

$$h_1(kpp') = -\beta[v(k)+\eta\hat{v}(p-p')] \frac{\tanh(\frac{1}{2}\beta\hbar k\cdot p) - \tanh(\frac{1}{2}\beta\hbar k\cdot p')}{\frac{1}{2}\beta\hbar k\cdot(p-p')} \quad . \tag{3.18}$$

In the limit $\hbar \to 0$, the momentum dependence vanishes and we recover the first-order classical result, $h_c(k) = -\beta v(k)$. The second-order term of $H(kpp')$ is much more complicated. Although it can also be calculated by a straightforward application of perturbation theory, it is obtained more easily from a relationship given in Section V.

IV. CORRELATION FUNCTIONS

The kinetic equation derived in Section V is an equation of motion for the equilibrium correlation function $F(1, 1'|t)$, defined below. Traditional kinetic theories describe the time evolution of the nonequilibrium average of $f(rp, t)$. The connection between these two functions is provided by linear response theory. For small deviations from equilibrium produced by an external potential $u(rp)$, introduced adiabatically in the distant past and turned off at $t = 0$, the subsequent evolution of the nonequilibrium average of $f(rp, t)$ is given by

$$\langle f(rp, t)\rangle_u - \langle f(rp)\rangle = \beta\int dr'dp' L(rp, r'p'|t)u(r'p') + O(u^2) . \quad (4.1)$$

For sufficiently small disturbances, therefore, $\langle f(rp, t)\rangle_u - \langle f(rp)\rangle$ obeys the same kinetic equation as the linear response function $L(rp, r'p'|t)$, which is an equilibrium two-particle correlation function. As is well known, the linear response regime is sufficient to account for many of the important properties of a fluid system, including its full neutron scattering and light scattering spectra as well as its transport coefficients.[42-44]

Closely related to L is the anticommutator correlation function defined by

$$F(1, 1'|t-t') = \langle \tfrac{1}{2}\{f(1, t), f(1', t')\}\rangle - \langle f(1)\rangle\langle f(1')\rangle , \quad (4.2)$$

which also obeys a kinetic equation and which contains equivalent information. Although the formal development of a kinetic equation for L would be identical to that given in Section IV for F, the evaluation of the theory to obtain an approximate but explicit kinetic equation

is easier to carry out for F. In particular, a calculation of the initial value of L would require an analysis of time- or frequency-dependent diagrams rather than equal-time diagrams as in the case of F.

The explicit connection between L and F is given in terms of the Fourier transform

$$S(k\omega pp') = \int d(r-r') e^{-ik\cdot(r-r')} \int_{-\infty}^{\infty} dt\, e^{i\omega t} F(rp, r'p'|t) \qquad (4.3)$$

by

$$L(k\omega pp') = S(k\omega pp')\ \tau(\beta\hbar\omega)\ ,$$

where $\tau(x) = (\frac{1}{2}x)^{-1}\tanh(\frac{1}{2}x)$. [44] It can be seen that the distinction between them vanishes in the classical limit. The letter S serves as a reminder that integration over the momenta reduces $S(k\omega pp')$ to the symmetrized scattering function $S(k\omega)$,

$$S(k\omega) = \int dp dp'\, S(k\omega pp') \quad . \qquad (4.5)$$

The symmetrized function $S(k\omega)$ is related to the Van Hove scattering function $S_{VH}(k\omega)$ by

$$S(k\omega) = \frac{1}{2}(1+e^{-\beta\hbar\omega}) S_{VH}(k\omega) \qquad (4.6)$$

From the definitions (4.2) and (4.3), it can be shown that $S(k\omega pp')$ is real, and that its symmetric integrals over an arbitrary function of the momentum are nonnegative:

$$\int dp dp' g^*(p)\, S(k\omega pp') g(p') \geq 0 \quad . \qquad (4.7)$$

In particular, this guarantees the nonnegativity of $S(k\omega)$. It can also

be shown that $S(k\omega pp')$ is even under $k,\omega \leftrightarrow -k,-\omega$ and symmetric in p and p'.

For discussing the kinetic equation, it is convenient to use the function of complex argument z defined by

$$F(kzpp') = -\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{S(k\omega pp')}{\omega - z} \quad . \tag{4.8}$$

Conversely, S is obtained from F(z) by

$$S(k\omega pp') = -2 \lim_{\epsilon \to 0+} \operatorname{Im} F(k, \omega + i\epsilon, pp') \quad .$$

For $\operatorname{Im} z > 0$, $F(kzpp')$ is the Laplace transform of $F(kpp'|t)$, with the convention

$$F(z) = -i\int_{0}^{\infty} dt\, e^{izt} F(t) \quad . \tag{4.9}$$

We will also use the r-space form $F(1,1'|z)$. In terms of $F(kzpp')$, the basic properties of the anticommutator correlation function may be summarized as

$$F(k, z^*; pp') = [F(k, z; pp')]^* \quad , \tag{4.10a}$$

$$\lim_{\epsilon \to 0+} \operatorname{Im} \int dp dp' g^*(p) F(k, \omega + i\epsilon; pp') g(p') \leq 0 \quad , \tag{4.10b}$$

$$F(-k, -z; pp') = -F(k, z; pp') \quad , \tag{4.10c}$$

$$F(k, z; pp') = F(k, z; p'p) \quad . \tag{4.10d}$$

The importance of preserving these relations in an approximate theory for $F(kzpp')$ has been indicated in the classical case.[17]

We turn now to an examination of the initial value $F(1,1') \equiv F(1,1'|t=0)$, which is an equal-time or static correlation function. Its spatial Fourier transform is indicated by $F(kpp')$.

The structure of $F(1,1')$ can be seen from a diagrammatic analysis like the one given in Section III for $n(11')$. We can obtain the same result more simply, however, by exploiting the properties of the anticommutator: the equilibrium average of Eq. (2.9a) expresses $F(1,1')$ in terms of the one- and two-particle distribution functions as

$$F(1,1') = n(11') - n(1)n(1') + \delta(1-1')\cos\left(\frac{\hbar}{2}\overleftarrow{\nabla}_{r_1}\cdot\vec{\nabla}_{p_1}\right)n(1) \quad .$$

After a Fourier transformation with respect to $r_1 - r_1'$, the last term becomes

$$\delta(p-p')\cosh\left(\tfrac{1}{2}\hbar k\cdot\frac{\partial}{\partial p}\right)n(p) = \delta(p-p')\left[\tfrac{1}{2}n(p+\tfrac{1}{2}\hbar k) + \tfrac{1}{2}n(p-\tfrac{1}{2}\hbar k)\right] \quad .$$

Combining this with expressions (3.8) and (3.10) - (3.11), we obtain the important result

$$F(kpp') = \delta(p-p')N(kp) + h(kpp')N(kp)N(kp') \quad . \qquad (4.11)$$

This can be compared to the classical formula for $F(kpp')$, which is

$$\lim_{\hbar\to 0} F(kpp') = \delta(p-p')n\phi(p) + h_c(k)n^2\phi(p)\phi(p') \quad . \qquad (4.12)$$

The reason for the definition (3.11) can now be seen: $N(kp)$ is the coefficient of $\delta(p-p')$ in Eq. (4.11). In this context, $N(kp)$ can be thought of as the quantum generalization of $n\phi(p)$. Since $h(kpp')$ starts at first order in the potential, the ideal gas result for $F(kpp')$ is

$$F_o(kpp') = \delta(p-p')N_o(kp) \qquad (4.13)$$

A crucial property of $F(kpp')$ is the fact that it has an inverse $F^{-1}(kpp')$ in the sense that

$$\int d\bar{p}\; F(kp\bar{p})F^{-1}(k\bar{p}p') = \delta(p-p') \tag{4.14}$$

for all k. In the classical case, the inverse is given by

$$\lim_{\hbar\to 0} F(kpp') = \frac{\delta(p-p')}{n\phi(p)} - c_c(k)\ , \tag{4.15}$$

where $c_c(k)$ is the classical direct correlation function defined in terms of $h_c(k)$ by the Ornstein-Zernike relation

$$h_c(k) = [1+nh_c(k)]\; c_c(k)\ . \tag{4.16}$$

Analogously, we define a quantum generalization of $c_c(k)$ by

$$h(kpp') = c(kpp') + \int d\bar{p}\; h(kp\bar{p})N(k\bar{p})c(k\bar{p}p')\ . \tag{4.17}$$

It is easy to verify that the quantum static inverse $F^{-1}(kpp')$ is given by

$$F^{-1}(kpp') = \frac{\delta(p-p')}{N(kp)} - c(kpp')\ . \tag{4.18}$$

Like $h(kpp')$, the function $c(kpp')$ vanishes for free particles. The first-order term $c_1(kpp')$ is identical to $h_1(kpp')$, Eq. (3.18).

In addition to the static inverse $F^{-1}(kpp')$, the derivation of the kinetic equation given in Section V makes essential use of the z-dependent inverse $F^{-1}(kzpp')$ satisfying

$$\int d\bar{p}\; F(kzp\bar{p})F^{-1}(kz\bar{p}p') = \delta(p-p') \tag{4.19}$$

for all k and z. Although there has been no explicit proof, the existence of this z-dependent inverse seems well established in the classical case.[17, 19, 20, 24] For a normal quantum fluid, the properties of $F^{-1}(kzpp')$ are similar to the classical ones. In the ideal gas limit,

the quantum inverse

$$F_o^{-1}(kzpp') = [z - k\cdot p]\,\frac{\delta(p-p')}{N_o(kp)} \tag{4.20a}$$

is obtained by inspection from

$$F_o(kzpp') = \frac{\delta(p-p')N_o(kp)}{[z-k\cdot p]} \quad . \tag{4.20b}$$

For an interacting system the inverse can be generated formally through the large-z expansion

$$F^{-1}(1,1'|z) = zF^{-1}(1,1') - i\int d2d2' F^{-1}(1,2)\dot{F}(2,2')F^{-1}(2',1') + O(z^{-1}) , \tag{4.21}$$

where $\dot{F}(1,1')$ is the time derivative of $F(1,1'|t)$ at $t=0$. Clearly, the existence of $F^{-1}(1,1'|z)$ is dependent on the static inverse $F^{-1}(1,1')$. It may be noted here that Eq. (4.20a) is the only explicit result for $F^{-1}(kzpp')$ that is required for the evaluation of the second-order kernel in Section V.

The existence of the static and z-dependent inverses is a special property of the anticommutator function, and is not shared by every correlation function of interest. A counterexample is provided by the commutator function

$$\chi(1,1'|t-t') = (2\hbar)^{-1}\langle [f(1,t), f(1',t')]\rangle \quad . \tag{4.22}$$

From Eq. (2.8a) it can be seen that the Fourier transform of the initial value $\chi(1,1')$ is given by

$$\chi(kpp') = \tfrac{1}{2}\beta M(kp)\delta(p-p') , \tag{4.23}$$

where

$$M(kp) = (\beta\hbar)^{-1}[n(p-\tfrac{1}{2}\hbar k) - n(p+\tfrac{1}{2}\hbar k)] \quad . \tag{4.24}$$

The classical limit of $M(kp)$ is

$$\lim_{\hbar \to 0} M(kp) = k \cdot p \, n\phi(p) \quad . \tag{4.25}$$

Since $\chi(kpp')$ vanishes for $k = 0$, χ does not have a well behaved static inverse, and, consequently, also does not have a z-dependent inverse. The method used in the next section for deriving a kinetic equation for F can therefore not be applied to χ. In fact, it can be shown that χ does not satisfy a kinetic equation of the same form as the one for F. This point is discussed at the end of Appendix C.

V. QUANTUM KINETIC EQUATION

In part A of this Section, the kinetic equation for $F(1,1'|z)$ is derived by a formal closure of the BBGKY hierarchy. An alternative derivation is given in Appendix C. In both cases, the nonlocal kernel is expressed in terms of correlation functions involving two, three, and four particles. A scheme for approximating the kernel in a way that preserves the symmetries of $F(1,1'|z)$ is discussed in part B. It is shown that this scheme also preserves all the sum rules of $S(k\omega pp')$ to the same order of approximation.

A. The Nonlocal Kernel.

From the operator equations of motion (2.10), we obtain a hierarchy of correlation-function equations beginning with

$$[z-L(1)]F(1,1'|z) = F(1,1') + \int d2\, L_1(12)F(12,1'|z)\,, \tag{5.1a}$$

$$[z-L(12)]F(12,1'|z) = F(12,1') + \int d3[L_1(13)+L_1(23)]F(123,1'|z)\,, \tag{5.1b}$$

together with the complementary sequence

$$[z+L(1')]F(1,1'|z) = F(1,1') - \int d2'\, L_1(1'2')F(1,1'2'|z)\,, \tag{5.2a}$$

$$[z+L(1')]F(12,1'|z) = F(12,1') - \int d2'\, L_1(1'2')F(12,1'2'|z)\,, \tag{5.2b}$$

where the higher-order correlation functions analogous to $F(1,1'|t)$ are defined by

$$F(1..n,1'..n'|t-t') = \langle \tfrac{1}{2}\{f(1..n,t), f(1'..n',t')\}\rangle - \langle f(1..n)\rangle\langle f(1'..n')\rangle\,. \tag{5.3}$$

The first equation of the hierarchy, Eq. (5.1a) or Eq. (5.2a), provides an equation of motion for $F(1,1'|z)$, but this equation contains the three-particle correlation function $F(12,1'|z)$, which is dependent

on a four-particle correlation function through Eq. (5. 1a) or (5. 2b), and so on. Our goal is to obtain a closed kinetic equation for $F(1, 1'|z)$ in the form

$$[z-L(1)]F(1, 1'|z) = F(1, 1') + \int d2\ \Sigma(1, 2|z)F(2, 1'|z) \quad . \qquad (5.4)$$

A comparison of Eqs. (5. 1a) and (5. 4) shows that the kinetic kernel or memory function $\Sigma(1, 1'|z)$ must satisfy

$$\int d2\ \Sigma(1, 2|z)F(2, 1'|z) = \int d2\ L_1(12)F(12, 1'|z) \quad . \qquad (5.5)$$

Together with the z-dependent inverse discussed in Section IV, Eq. (5. 5) defines $\Sigma(1, 1'|z)$ uniquely. Thus, an application of Eq. (4. 19) to Eq. (5. 5) gives

$$\Sigma(1, 1'|z) = \int d2d3\ L_1(12)F(12, 3|z)F^{-1}(3, 1'|z) \quad . \qquad (5.6)$$

An equivalent expression that is better suited for the evaluations in part V is obtained below.

It should be noted here that a kinetic equation of the form (5. 4) can be derived with the use of a projection operator, as is done in Appendix C. In this method, the z-dependent inverse is not required; instead, the kernel is expressed in terms of correlation functions containing the modified propagator $\exp[it(1-P)L]$. It is not obvious, however, what conditions are required to guarantee that expressions containing the modified propagator are well behaved. This point is discussed in the appendix. Since both methods lead to a kinetic equation of the form (5. 4), it appears that the use of the modified-propagator expressions is tantamount to assuming the existence of the z-dependent inverse. In the absence of a general proof in either case, the

assertion that $F(1,1'|z)$ is governed by a kinetic equation of the form (5.4) is mainly justified by the well-behaved explicit results that are obtained for the kernel.

We now proceed to express the kinetic kernel in a more convenient form than Eq. (5.6). This derivation is similar to one given in the classical case by Mazenko.[24] It will be useful to define a new kernel $K(kzpp')$ by multiplying $\Sigma(kzpp')$ on the right by the initial value $F(kpp')$,

$$K(kzpp') = \int d\bar{p}\ \Sigma(kzp\bar{p})F(k\bar{p}p') \quad . \tag{5.7}$$

Since $F(kpp')$ and the static inverse $F^{-1}(kpp')$ are known quantities, the kernels Σ and K are completely equivalent. Applying $[z+L(1')]$ to Eq. (5.5) and using Eqs. (5.2), we have

$$\begin{aligned} &K(1,1'|z) - \int d2'd3'\Sigma(1,3'|z)L_1(1'2')F(3',1'2'|z) \\ &\quad = \int d2\, L_1(12)\Big(F(12,1') - \int d2' L_1(1'2')F(12,1'2'|z)\Big) \quad . \end{aligned} \tag{5.8}$$

Now rewriting $\Sigma(1,3'|z)$ on the left hand side of Eq. (5.8) in the form of Eq. (5.6), we obtain the desired expression for $K(1,1'|z)$ as the sum of a static part $K^{(s)}(1,1')$ and a dynamic part $K^{(d)}(1,1'|z)$,

$$K(1,1'|z) = K^{(s)}(1,1') + K^{(d)}(1,1'|z) \quad . \tag{5.9a}$$

The static part

$$K^{(s)}(1,1') = \int d2\ L_1(12)F(12,1') \tag{5.9b}$$

is independent of z and represents a mean-field or modified Vlasov contribution to the equation of motion, while the dynamic part

$$K^{(d)}(1, 1'|z) = -\int d2d2' L_1(12) L_1(1'2') G(12, 1'2'|z) , \qquad (5.9c)$$

$$G(12, 1'2'|z) = F(12, 1'2'|z) - \int d3d3' F(12, 3|z) F^{-1}(3, 3'|z) F(3', 1'2'|z) , \qquad (5.10)$$

starts at order z^{-1} and describes the Boltzmann-like effect of collisions. Equations (5.9) and (5.10) are the expressions that are used in obtaining the explicit results for the second order kernel in Section V. The method of approximation is discussed in the next part of this section.

Through the equation of motion (5.4), the positivity and symmetry properties (4.10) of $F(kzpp')$ determine corresponding properties of the kernel.[45] Conversely, if $F(kzpp')$ is obtained as the solution of the kinetic equation (5.4) with an approximate kernel having these properties, then it will automatically satisfy the requirements of Eqs. (4.10). In terms of $K(kzpp')$, the properties of the kernel are summarized as

$$K(k, z^*; pp') = [K(k, z; pp')]^* , \qquad (5.11a)$$

$$\lim_{\epsilon \to 0+} \mathrm{Im} \int dp dp' g^*(p) K(k, \omega + i\epsilon; pp') g(p') \leq 0 , \qquad (5.11b)$$

$$K(-k, -z; pp') = -K(k, z; pp') . \qquad (5.11c)$$

$$K^{(d)}(k, z; pp') = K^{(d)}(k, z; p'p) . \qquad (5.11d)$$

The static part is real, and odd under $k \to -k$, but by itself it is not symmetric under $p \leftrightarrow p'$; rather, it is the sum of the static part and the streaming term

$$K^{(s)}(kpp') + k \cdot p\, F(kpp') = K^{(s)}(kp'p) + k \cdot p' F(kp'p) \qquad (5.11e)$$

which has this property. This combination is simply $i\dot{F}(kpp')$, where $\dot{F}(kpp')$ is the initial time derivative of $F(kpp'|t)$.

There is an additional general property of the kernel that can be mentioned here, namely, that the static kernel $K^{(s)}(kpp')$ is closely related to the connected part $H(kpp')$ of the two-particle distribution function. Subtracting the terms of order $1/z$ in the large-z expansions of Eqs. (5.1a) and (5.2a), we find

$$[L(1)+L(1')]F(1,1') = -\int d2[L_1(12)F(12,1')+L_1(1'2)F(1'2,1)] ,$$

or

$$k\cdot(p-p')H(kpp') = -K^{(s)}(kpp') + K^{(s)}(kp'p) . \qquad (5.12)$$

This equation can be used to determine $H(kpp')$ through second order from the result given in Section VI for the second-order static kernel. In the classical case, Eq. (5.12) can be inverted to give an expression for $K^{(s)}$. In the classical limit, $H(kpp')$ becomes even in each momentum variable, while $K^{(s)}(kpp')$ becomes odd in p and even in p'. The sum of Eq. (4.12) and its form with $p' \to -p'$ therefore gives

$$\lim_{\hbar\to 0} K^{(s)}(kpp') = -k\cdot p\, n^2 h_c(k)\phi(p)\phi(p') , \qquad (5.13)$$

which is equivalent to the well-known potential-independent expression for the classical $\Sigma^{(s)}$ in terms of the direct correlation function.[46,47] No analogous expression for $K^{(s)}$ is apparent in the quantum mechanical case.[48]

B. Method of Approximation.

Equation (5.12) is an example of a relationship between statics and dynamics that should be maintained in any consistent theory, as

should the symmetry properties (5.11). In this thesis we are concerned with approximating the kinetic kernel by means of a perturbation expansion. To accomplish this in a consistent way, we first write the solution to the kinetic equation (5.4) as

$$F(z) = [z - L_o - \Sigma(z)]^{-1} F \ , \tag{5.14}$$

using an abbreviated notation in which $F(z)$ stands for the "matrix" $F(kzpp')$ with indices p and p'. Similarly, $(z - L_o)$ is the matrix with components $(z - k\cdot p)\delta(p - p')$. Now we "multiply" Eq. (5.14) by FF^{-1} from the left, and obtain

$$F(z) = F[(z - L_o)F - K(z)]^{-1} F \ . \tag{5.15}$$

The advantage of writing $F(z)$ in this form is that the term in brackets is symmetric in its momentum indices.[26] Equation (5.15) is still exact. The method of approximation is to truncate F and $K(z)$ in Eq. (5.15) at second order. Thus, writing $\tilde{F}(z)$ for the solution, we have

$$\tilde{F}(z) = F_{(2)}[(z - L_o)F_{(2)} - K_{(2)}(z)]^{-1} F_{(2)} \ , \tag{5.16}$$

which can be rearranged in the form of an approximate kinetic equation

$$[z - L_o - \tilde{\Sigma}(z)]\tilde{F}(z) = F_{(2)} \ , \tag{5.17}$$

where

$$\tilde{\Sigma}(z) = K_{(2)}(z)[F_{(2)}]^{-1} \ . \tag{5.18}$$

It should be noted that the initial condition used in this approximation is the truncation of the exact initial condition.

Equation (5. 16) can also be written

$$\widetilde{F}(z) = F_{(2)}\{[FF^{-1}(z)F]_{(2)}\}^{-1}F_{(2)} \quad . \tag{5.19}$$

This can be compared to another symmetric approximation, namely

$$\overline{\overline{F}}(z) = \{[F^{-1}(z)]_{(2)}\}^{-1} \quad , \tag{5.20}$$

the inversion of the truncation of the inverse. This is the approximation used by Forster and Martin in the classical case.[17] In this scheme the approximate kinetic equation has the kernel

$$\overline{\Sigma}(z) = [(F^{-1})_{(2)}]^{-1}[F^{-1}\Sigma(z)]_{(2)} \tag{5.21}$$

and initial condition

$$\overline{F} = [(F^{-1})_{(2)}]^{-1} \quad . \tag{5.22}$$

In the classical case, the approximation (5. 21) is equivalent to a direct truncation of $\Sigma(z)$, because of the special form of the classical F. This is not true for the quantum $\overline{\Sigma}(z)$. It should be noted, moreover, that a direct truncation of the quantum mechanical $\Sigma(z)$ does not lead to a symmetric approximation.

The two approximation schemes defined by (5. 16) and (5. 20) have essentially the same physical content; they differ only in technical detail. In the classical limit, the difference can be simply described as follows. In the first scheme, the initial condition and the static part of the kernel are given in terms of the truncated $h_c(k)$; in the second, they are given in terms of the truncated $c_c(k)$. The dynamic part of the kernel is the same in both. In terms of an expansion with constant n, rather than constant μ as employed for the quantum

mechanical calculations, the classical limits are given explicitly by

$$\lim_{\hbar\to 0} \tilde{F}(kpp') = n\phi(p)\delta(p-p') + n^2\phi(p)\phi(p')h_{(2)}(k) \tag{5.23a}$$

$$\lim_{\hbar\to 0} \tilde{\Sigma}^{(s)}(kpp') = -n\phi(p)k\cdot p\,\frac{h_{(2)}(k)}{1+nh_{(2)}(k)} \tag{5.23b}$$

$$\lim_{\hbar\to 0} \tilde{\Sigma}^{(d)}(kzpp') = \lim_{\hbar\to 0}\left[\Sigma^{(d)}(kzpp')\right]_{(2)} \tag{5.23c}$$

and

$$\lim_{\hbar\to 0} \overline{F}(kpp') = n\phi(p)\delta(p-p') + n^2\phi(p)\phi(p')\,\frac{c_{(2)}(k)}{1-nc_{(2)}(k)} \tag{5.24a}$$

$$\lim_{\hbar\to 0} \overline{\Sigma}^{(s)}(kpp') = -n\phi(p)k\cdot p\,c_{(2)}(k) \tag{5.24b}$$

$$\lim_{\hbar\to 0} \overline{\Sigma}^{(d)}(kzpp') = \lim_{\hbar\to 0}\left[\Sigma^{(d)}(kzpp')\right]_{(2)} \tag{5.24c}$$

It can be seen that in the classical case, the two schemes are equally tractable. Quantum mechanically, however, the first scheme is by far the simpler procedure because the static quantites it requires can be obtained more directly.

To conclude the discussion of the approximation scheme given by Eq. (5.16), we can examine its effect on the sum rules of $S(k\omega pp')$. A similar analysis can be applied to Eq. (5.20). For comparison, the large-z expansion of the exact $F(kzpp')$ is given in terms of the frequency moments of $S(k\omega pp')$ by

$$F(kzpp') = \sum_{j=0}^{\infty} z^{-j-1} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi}\,\omega^j S(k\omega pp') \tag{5.25}$$

or, equivalently, by

$$F(z) = z^{-1}F + iz^{-2}\dot{F} - z^{-3}\ddot{F} + \ldots \qquad (5.26)$$

Now expanding the right-hand side of Eq. (4.19), we obtain

$$\widetilde{F}(z) = z^{-1}F_{(2)} + iz^{-2}\dot{F}_{(2)} - z^{-3}[\ddot{F}_{(2)} - (\dot{F}F^{-1}\dot{F})_{(2)} + \dot{F}_{(2)}(F_{(2)})^{-1}\dot{F}_{(2)}] + \ldots \qquad (5.27)$$

If each factor in (5.27) could be evaluated exactly, instead of being truncated at second order as indicated, we would recover the expansion of the exact $F(z)$, but, as given, the third and higher coefficients in the expansion of $\widetilde{F}(z)$ contain terms that are not present in the expansion of $F(z)$. It is not difficult to see, however, that the net contribution of these terms always starts at third order, so that all the frequency moments of $\widetilde{S}(k\omega pp')$ will in fact be correct to second order.

It should be apparent that the considerations of this section are not limited to the second-order potential expansion, but apply to any well-defined expansion to arbitrary order.

VI. THE SECOND-ORDER KERNEL

A. Static Part.

This subsection contains the evaluation of the static kernel $K^{(s)}$ to second order in the potential. We begin by rewriting Eq. (5.9b), Fourier transformed with respect to both r and r′, as

$$(2\pi)^3\delta(k+k')K^{(s)}(kpp') = -(2\pi)^{-3}\int d\bar{k}d\bar{p}\, V(\bar{k}p)F(k-\bar{k}, p, \bar{k}\,\bar{p}; k'p') \ , \qquad (6.1)$$

$$V(kp) = v(k)\frac{2}{\hbar}\sinh\left(\frac{\hbar}{2}k\cdot\frac{\partial}{\partial p}\right) \ . \qquad (6.2)$$

Since the right-hand side contains an explicit factor v(k), our task is to calculate the zero- and first-order terms of F(12, 3). Rather than attack the perturbative calculation directly, it is convenient to analyze the diagrams in terms of fully interacting components, as in the discussion of n(12) in Section III. The diagrams for F(12, 3) are classified as unconnected, two-connected, and three-connected. The unconnected diagrams are shown in Fig. 3a, the two-connected diagrams in Figs. 3a and 3b. The three-connected diagrams are not needed, since they start at second order in the potential.

It should be noted that the diagrams drawn in Fig. 3 show the momentum labels of the particles but not their relative times. For each diagram in Fig. 3 there are two terms to be evaluated, with infinitesimal times corresponding to the order of the field operators in the two terms of the anticommutator in

$$F(12, 3) = \langle \tfrac{1}{2}\{f(12), f(3)\}\rangle - n(12)n(3) \ .$$

It should also be noted that the diagrams for $\langle \frac{1}{2}\{f(12), f(3)\}\rangle$ that cancel with those for $n(12)n(3)$ have been omitted from Fig. 3.

The result for the contribution of the unconnected diagrams, Fig. 3a, is

$$\begin{aligned} F_a(k_1p_1, k_2p_2; k_3p_3) = {} & (2\pi)^6 \delta(k_1)\delta(k_2+k_3)\delta(p_2-p_3)n(p_1)N(k_3p_3) \\ & + (2\pi)^6 \delta(k_2)\delta(k_1+k_3)\delta(p_1-p_3)n(p_2)N(k_3p_3) \\ & + (2\pi)^3 \delta(k_1+k_2+k_3)[\,\delta(2+1-)\delta(3+2-)\gamma n(1-) \\ & + \delta(1+2-)\delta(2+3-)\gamma n(1+)]N(k_3p_3)\,, \end{aligned} \tag{6.3}$$

where $\delta(2+1-) = \delta[(2+)-(1-)]$ with $2+ = p_2+\frac{1}{2}\hbar k_2$, etc. Substituting (6.3) in Eq. (6.1) and writing out the effect of the V operator as a difference of displacements of p, we obtain

$$\begin{aligned} K_a^{(s)}(kpp') = {} & \beta[\,v(k)+\eta\hat{v}(p-p')]M(kp)N(kp') \\ & - \eta\delta(p-p')\int d\bar{p}\,\beta\,\hat{v}(p-\bar{p})M(k\bar{p})N(kp')\,, \end{aligned} \tag{6.4a}$$

where M and N are the one-particle functions defined in Eqs. (4.24) and (3.11). It is equally straightforward to obtain the results for the two-connected diagrams of F(12,3) and substitute in Eq. (6.1) to obtain their contribution to $K^{(s)}$. The diagrams of Fig. 3b give

$$\begin{aligned} K_b^{(s)}(kpp') = {} & \int d\bar{p}\,\beta\,[\,v(k)+\eta\hat{v}(p-\bar{p})]M(kp)H(k\bar{p}p') \\ & - \eta\delta(p-p')\int d\bar{p}\,\beta\,\hat{v}(p-\bar{p})M(k\bar{p})H(kpp')\,, \end{aligned} \tag{6.4b}$$

and the diagrams of Fig. 3c give

$$K_c^{(s)}(kpp') = (2\pi\hbar)^{-3}\int dp_1 dp_2 dp_3\ \delta(p_1+p_2-p_3-p')[X(k)-X(-k)]$$
$$\times\left\{\hat{v}(p_1-p_3)[\delta(p-p_1)-\delta(p-p_3)]+\eta\hat{v}(p_1-p')[\delta(p-p_1)-\delta(p-p')]\right\}, \tag{6.4c}$$

where

$$X(k) = [\tfrac{1}{2}+\gamma n(p'+\tfrac{1}{2}\hbar k)]\mathcal{K}(p_1-\tfrac{1}{2}\hbar k, p_2+\tfrac{1}{2}\hbar k, p_3+\tfrac{1}{2}\hbar k, p'-\tfrac{1}{2}\hbar k)\ . \tag{6.5}$$

$\mathcal{K}$ and H are the forms of the general two-particle connected diagram defined by Eqs. (3.13) and (3.7c).

The combination $K_a^{(s)}+K_b^{(s)}$, taken by itself, is equivalent to a Hartree-Fock approximation for $\Sigma^{(s)}$:

$$\Sigma_{HF}^{(s)}(kpp') = \beta[v(k)+\eta\hat{v}(p-p')]M(kp)-\eta\delta(p-p')\int d\bar{p}\,\beta\,\hat{v}(p-\bar{p})M(k\bar{p})\ , \tag{6.6}$$

which has been used to discuss zero sound in a Fermi liquid.[12] One can also obtain Eq. (4.9) by factoring the nonequilibrium average $\langle f(12)\rangle_{ne}$ in the BBGKY equation connecting $\langle f(1)\rangle_{ne}$ and $\langle f(12)\rangle_{ne}$ and then linearizing the resulting collisionless kinetic equation for $\langle f(1)\rangle_{ne}$.[49]

The expressions (6.4) - (6.5) are written in terms of exact one- and two-particle distribution functions; truncated at second order, they give the full second-order expansion of the static kernel

$$K_{(2)}^{(s)} = K_1^{(s)} + K_2^{(s)}$$

in terms of the zero- and first-order static functions we have already calculated plus the first-order term in the expansion of n(p), which is

$$n_1(p) = n_o(p) + n_o(p)\sigma_1(p)\tilde{n}_o(p)\ , \tag{6.7}$$

where

$$\sigma_1(p) = -\int d\bar{p}\,\beta\,[\hat{v}(0)+\eta\hat{v}(p-\bar{p})]n_o(\bar{p}) \quad . \tag{6.8}$$

The first order kernel is obtained entirely from the unconnected part $K_a^{(s)}$ and has the Hartree-Fock form:

$$K_1^{(s)}(kpp') = \left\{\beta[v(k)+\eta\hat{v}(p-p')]M_o(kp)-\eta\delta(p-p')\int d\bar{p}\,\beta\,\hat{v}(p-\bar{p})M_o(k\bar{p})\right\}N_o(kp') \quad . \tag{6.9a}$$

The second order term contains contributions from both $K_a^{(s)}$ and the two-connected parts $K_b^{(s)}$ and $K_c^{(s)}$, and is given by

$$\begin{aligned} K_2^{(s)}(kpp') = {} & \int d\bar{p}\,\beta[v(k)+\eta\hat{v}(p-\bar{p})][M_o(kp)F_1(k\bar{p}p')+M_1(kp)F_o(k\bar{p}p')] \\ & - \eta\int d\bar{p}\,\beta\,\hat{v}(p-\bar{p})[M_o(k\bar{p})F_1(kpp')+M_1(k\bar{p})F_o(kpp')] \\ & + (2\pi\hbar)^{-3}\int dp_1 dp_2 dp_3\,\delta(p_1+p_2-p_3-p')[X_1(k)-X_1(-k)] \\ & \times\left\{\hat{v}(p_1-p_3)[\delta(p-p_1)-\delta(p-p_3)]+\eta\hat{v}(p_1-p')[\delta(p-p_1)-\delta(p-p')]\right\} , \end{aligned} \tag{6.9b}$$

where

$$X_1(k) = [\tfrac{1}{2}+\gamma n_o(p'+\tfrac{1}{2}\hbar k)]\,\mathcal{K}_1(p_1-\tfrac{1}{2}\hbar k, p_2+\tfrac{1}{2}\hbar k, p_3+\tfrac{1}{2}\hbar k, p'-\tfrac{1}{2}\hbar k) \quad .$$

We note that $K^s_{(2)}$ is odd in k, in accord with Eqs. (5.11), and that its $\hbar\to 0$ limit gives the correct second-order expansion of the classical result, Eq. (5.13).

To complete the list of static quantities appearing in the initial condition $F_{(2)}(kpp')$, we give the second-order term of n(p), which is

$$n_2(p) = n_o(p)\left[\sigma_1(p)\tfrac{1}{2}\coth^{\eta}\left(\tfrac{1}{4}\beta p^2\right)\sigma_1(p)+\sigma_2(p)\right]\tilde{n}_o(p) \quad , \tag{6.10}$$

where

$$\sigma_2(p) = -\int d\bar{p}\,\beta\,[\hat{v}(0)+\eta\hat{v}(p-\bar{p})]n_1(\bar{p})$$

$$+\frac{1}{2}\int\frac{d\bar{k}d\bar{p}}{(2\pi)^3}\beta^2[v(\bar{k})+\eta\hat{v}(p')]^2\Big[\tilde{n}_o(p-\hbar k)n_o(\bar{p})\tilde{n}_o(\bar{p}+\hbar\bar{k})E_2(\beta\hbar\bar{k}\cdot p')$$

$$+\gamma n_o(p-\hbar\bar{k})\tilde{n}_o(\bar{p})n_o(\bar{p}+\hbar\bar{k})E_2(-\beta\hbar\bar{k}\cdot p')\Big] \qquad (6.11)$$

and

$$p' = p-\bar{p}-\hbar\bar{k}\ , \quad E_2(x) = x^{-2}(e^x-1-x)\ .$$

The second order term of $H(kpp')$ is given in terms of $K_2^{(s)}$ by Eq. (5.12). This is not a circular definition, because $K_2^{(s)}$ contains the first order term H_1 but does not contain H_2.

B. Dynamic Part.

Up to this point we have dealt with the diagrammatic analysis of equal-time correlation functions, for which the calculations are relatively straightforward. To obtain the dynamic part of the kinetic kernel from Eq. (5.9c), we must analyze the z-dependent function $G(12,1'2'|z)$, and the calculations will in general be more complicated. To obtain the dynamic part to second order, however, we need only the free-particle function $G_o(12,1'2'|z)$. This simplifies our work considerably. It should be noted that there is no first-order contribution to the dynamic part.

Using Eqs. (4.20) and (5.1), we find

$$G_o(12,1'2'|z) = [z-L_o(1)-L_o(2)]^{-1}G_o(12,1'2')\ , \qquad (6.12)$$

where

$$G_o(12,1'2') = F_o(12,1'2') - \int d3d3'F_o(12,3)F_o^{-1}(3,3')F_o(3',1'2')\ , \qquad (6.13)$$

so that our task is reduced to the evaluation of the zero-order static

functions on the right-hand side of Eq. (5.10). The last term, which can be obtained from Eqs. (4.20) and (6.3), cancels the contribution of twenty of the twenty-four diagrams for $F_o(12, 1'2')$. The remaining four diagrams, Fig. 4, give

$$G_o(k_1p_1, k_2p_2; k_3p_3, k_4p_4) = \Big\{(2\pi)^6 \delta(k_1+k_3)\delta(k_2+k_4)\delta(p_1-p_3)\delta(p_2-p_4)$$
$$+(2\pi)^6 \delta(k_1+k_4)\delta(k_2+k_3)\delta(p_1-p_4)\delta(p_2-p_3)$$
$$+\gamma(2\pi)^3 \delta(k_1+k_2+k_3+k_4)[\delta(3+1-)\delta(4+2-)\delta(1+4-)$$
$$+\delta(1+3-)\delta(2+4-)\delta(4+1-)]\Big\} a(k_1p_1, k_2p_2), \tag{6.14}$$

where

$$a(k_1p_1, k_2p_2) = \frac{1}{2}\left[n_o(1+)n_o(2+)\tilde{n}_o(1-)\tilde{n}_o(2-)+n_o(1-)n_o(2-)\tilde{n}_o(1+)\tilde{n}_o(2+)\right]. \tag{6.15}$$

Using Eq. (3.17), we can also write $a(k_1p_1, k_2p_2)$ as

$$a(k_1p_1, k_2p_2) = N_o(k_1p_1)N_o(k_2p_2)\frac{\cosh[\frac{1}{2}\beta\hbar(k_1\cdot p_1+k_2\cdot p_2)]}{\cosh(\frac{1}{2}\beta\hbar k_1\cdot p_1)\cosh(\frac{1}{2}\beta\hbar k_2\cdot p_2)}. \tag{6.16}$$

We note in passing that in the classical limit, $G_o(12, 1'2')$ reduces to

$$\lim_{\hbar\to 0} G_o(12, 1'2') = n^2\phi(p_1)\phi(p_2)[\delta(1-1')\delta(2-2') + \delta(1-2')\delta(2-1')],$$

in agreement with a direct classical calculation.

Now substituting (6.12) and (6.14) in Eq. (5.9c) and performing several integrations, we obtain the second order dynamic kernel in the form

$$K_2^{(d)}(kzpp') = \int \frac{d\bar{k}d\bar{p}}{(2\pi)^3} V(\bar{k}, p)\Big\{V(\bar{k}, p')\delta(p-p') - V(\bar{k}-k, p')\delta(\bar{p}-p')$$

$$+\eta V\left(\frac{p-\bar{p}}{\hbar}+\frac{k}{2}, p'\right)\delta\left(\frac{p+\bar{p}}{2}-p'-\frac{\hbar k}{4}+\frac{\hbar\bar{k}}{2}\right)$$

$$-\eta V\left(\frac{p-\bar{p}}{\hbar}-\frac{k}{2}, p'\right)\delta\left(\frac{p+\bar{p}}{2}-p'+\frac{\hbar k}{4}-\frac{\hbar\bar{k}}{2}\right)\Big\}\frac{a(k-\bar{k}, p;\bar{k}\,\bar{p})}{z-(k-\bar{k})\cdot p-\bar{k}\cdot\bar{p}} \quad . \qquad (6.17)$$

The operator $V(k, p)$, defined in Eq. (6.2), acts on everything to its right in Eq. (6.17).

It is instructive to examine the classical limit of Eq. (6.17). We obtain the classical expression for $[\Sigma^{(d)}(kzpp')n\phi(p)]_{(2)}$ by using

$$\lim_{\hbar\to 0} a(k-\bar{k}, p;\bar{k}\,\bar{p}) = n^2\phi(p)\phi(\bar{p}) \ , \qquad (6.18)$$

$$\lim_{\hbar\to 0} V(kp) = v(k)k\cdot\frac{\partial}{\partial p} \ , \qquad (6.19)$$

and noting that the third term in the braces in Eq. (6.17) cancels the fourth. In terms of an expansion with constant n, the result is simply[17]

$$\lim_{\hbar\to 0} K^{(d)}(kzpp') = \int \frac{d\bar{k}d\bar{p}}{(2\pi)^3} v(\bar{k})\bar{k}\cdot\frac{\partial}{\partial p}\Big\{v(\bar{k})\bar{k}\cdot\frac{\partial}{\partial p}\delta(p-p')$$

$$-v(\bar{k}-k)(\bar{k}-k)\cdot\frac{\partial}{\partial p}\delta(\bar{p}-p')\Big\}\frac{n^2\phi(p)\phi(\bar{p})}{z-(k-\bar{k})\cdot p-\bar{k}\cdot\bar{p}} \quad . \qquad (6.20)$$

It should be noted that the statistical factor $a(kp, k'p')$ reduces to its classical value (6.18) in the high temperature or low density limit, $\beta\mu\to-\infty$, but the kinematic exchange and wave diffraction terms of Eq. (6.17) are unchanged.

While the classical weak coupling kernel is naturally expressed as a generalized Fokker-Planck operator, the quantum weak coupling kernel actually has a Boltzmann-like collisional structure, although this is not at all apparent from (6.17). We now proceed to transform the second-order kernel to such a form, beginning by writing explicitly the displacements in p and p' indicated by the V operators. The result has two types of terms, characterized by the sign in $a(k-\overline{k}, p\pm\frac{1}{2}\overline{k};\overline{k}\,\overline{p})$. Corresponding to this sign, we change the variables of integration by

$$\overline{k} = \pm(p_3-p), \quad \overline{p} = p_4+\tfrac{1}{2}(p_3-p\mp k)$$

and insert $\int dp_2\, \delta(p+p_2-p_3-p_4\pm k)$. As we have no further need to refer to the classical limit, we have set $\hbar = 1$. Finally, we add the above to its version with p_3 and p_4 interchanged, and obtain the principal result of this section,

$$K_2^{(d)}(kzpp') = (2\pi)^{-3}\int dp_2 dp_3 dp_4 [\,v(p-p_3)+\eta v(p-p_4)]\, W(pp_2p_3p_4, p')$$
$$\times\, [\hat{A}(pp_2p_3p_4|k,z) - \hat{A}(pp_2p_3p_4|-k,-z)] \qquad (6.21)$$

where

$$\begin{aligned} W(p_1p_2p_3p_4, p') = {} & [v(p_1-p_3)+\eta v(p_1-p_4)]\,\delta(p_1-p') \\ & +[v(p_2-p_4)+\eta v(p_2-p_3)]\,\delta(p_2-p') \\ & -[v(p_3-p_1)+\eta v(p_3-p_2)]\,\delta(p_3-p') \\ & -[v(p_4-p_2)+\eta v(p_4-p_1)]\,\delta(p_4-p') , \end{aligned} \qquad (6.22)$$

$$\hat{A}(p_1p_2p_3p_4|k,z) = \tfrac{1}{2}\delta(p_1+p_2-p_3-p_4+k)$$

$$\times A_o(p_1+\tfrac{1}{2}k, p_2+\tfrac{1}{2}k, p_3-\tfrac{1}{2}k, p_4-\tfrac{1}{2}k|z)\ , \qquad (6.23)$$

$$A_o(p_1p_2p_3p_4|z) = \frac{\tfrac{1}{2}n_o(p_1)n_o(p_2)\tilde{n}_o(p_3)\tilde{n}_o(p_4)+\tfrac{1}{2}\tilde{n}_o(p_1)\tilde{n}_o(p_2)n_o(p_3)n_o(p_4)}{z-\tfrac{1}{2}\left(p_1^2+p_2^2-p_3^2-p_4^2\right)} \ . \qquad (6.24)$$

To clarify the structure of the dynamic kernel as given by Eq. (6.21), it is useful to examine the following limits. For $k=0$, the δ-function in $\hat{A}$ may be used to reduce the W factor to

$$[v(p-p_3)+\eta v(p-p_4)][\delta(p-p')+\delta(p_2-p')-\delta(p_3-p')-\delta(p_4-p')];$$

for $k=0$, $z\to\omega+i0^+$ the denominators of the $\hat{A}$ factors produce

$$\delta\left(\omega\pm\tfrac{1}{2}\left[p_1^2+p_2^2-p_3^2-p_4^2\right]\right)$$

and the numerators then differ only by a factor of $e^{\beta\omega}$. For k and ω equal to zero, therefore, the second-order dynamic kernel reduces to the linear Uehling-Uhlenbeck collision kernel with the Born approximation cross section, in the form

$$\lim_{\epsilon\to 0} K_2^{(d)}(0,i\epsilon;pp') = -i\pi(2\pi)^{-3}\int dp_2dp_3dp_4[v(p-p_3)+\eta v(p-p_4)]^2$$

$$\times[\delta(p-p')+\delta(p_2-p')-\delta(p_3-p')-\delta(p_4-p')]\,\delta(p+p_2-p_3-p_4)$$

$$\times\delta\left(\tfrac{1}{2}\left[p^2+p_2^2-p_3^2-p_4^2\right]\right)n_o(p)n_o(p_2)\tilde{n}_o(p_3)\tilde{n}_o(p_4)\ . \qquad (6.25)$$

The Uehling-Uhlenbeck kernel can be interpreted in terms of energy and momentum conserving collisions between free particles with incoming momenta p and p_2 and outgoing momenta p_3 and p_4.

Correspondingly, the k, z-dependent kernel involves collisions in the presence of a medium of other particles, whose collective effect is represented by a momentum k and an energy $\omega = \mathrm{Re}\, z$. Except at $k = 0$, however, the collisions are not simply described by a cross section.

The dynamic kernel may be rewritten in yet another form, one which clearly displays its full symmetry. After inserting $\int dp_1 \delta(p-p_1)$ in Eq. (6.21), we obtain three additional formulas for $K^{(d)}$ by performing the changes of variable $(1 \leftrightarrow 2, 3 \leftrightarrow 4)$, $(1 \leftrightarrow 3, 2 \leftrightarrow 4)$, and $(1 \leftrightarrow 4, 2 \leftrightarrow 3)$, where 1 stands for p_1, etc. Using the symmetries

$$W(1234, p') = - W(3412, p') = \eta W(2134, p') , \tag{6.26}$$

$$\hat{A}(1234|k, z) = - \hat{A}(3412|-k, -z) = \hat{A}(2134|k, z) , \tag{6.27}$$

we then write the sum of these four formulas as

$$K_2^{(d)}(kzpp') = \frac{1}{4} \int \frac{d1d2d3d4}{(2\pi)^3} W(1234, p) W(1234, p') \times [\hat{A}(1234|k, z) - \hat{A}(1234|-k, -z)] . \tag{6.28}$$

From this expression, it follows immediately that the second order kernel satisfies the positivity and symmetry conditions (5.11).

Finally, it may be noted that if we had worked with the linear response function $L(1, 1'|z)$, we would have obtained an approximate kinetic equation similar in form to the one for $F(1, 1'|z)$ but differing by detailed-balancing factors corresponding to the factor $\tau(x)$ in Eq. (4.4). The second-order dynamic kernel, for example, would have the same form as (6.21) but the function $A_o(p_1 p_2 p_3 p_4|z)$ in

(6.24) would be multiplied by $\tau[\frac{1}{2}\beta(p_1^2+p_2^2-p_3^2-p_4^2)]$. Similarly, the first-order term (6.9a) of the static kernel would be multiplied by $\tau(\beta\hbar k\cdot p')$. In the long-time, large-distance limit the effect of these factors would disappear and we would again recover the Uehling-Uhlenbeck kernel (6.25).

VII. CONCLUSION

This thesis presents what is believed to be the first explicit equation for a quantum mechanical fluid that is meaningful on all scales of length and time. Although the second-order kernel is not directly applicable to a real fluid with a strong repulsive interaction, it provides a model kinetic equation containing features which should also appear in any improved theory. The symmetries of the kernel, which are related to the conservation laws, and the positivity or stability condition, which ensures that $S(k\omega)$ and the transport coefficients are positive, are maintained exactly. The short-time limit reflected in the sum rules, and the long-time, large-distance limit reflected in the Uehling-Uhlenbeck kernel are correctly reproduced to the order of the approximation.

While the approach to quantum kinetic theory developed here is limited to the linear response domain, it is independent of any appeal to coarse-graining in space or time and of assumptions such as the Bogoliubov functional ansatz.[4, 50] It is clear a priori that assumptions of the former kind preclude an accurate description of the short-time behavior. Likewise, the Bogoliubov theory does not attempt to describe the short-time behavior, and in fact it has been shown in the classical case that the ansatz is correct only for vanishing wave vector and frequency.[51]

This work may be applied or extended in several ways. A detailed examination of the conservation laws and transport coefficients determined by the second order equation is in progress. It should be

possible to derive a weak-coupling equation for the condensed Bose gas, as a model for the study of superfluidity. The expressions for the kernel and the method of approximation given in Section V are suitable for a density or fugacity expansion, the first term of which defines an approximate kernel containing all effects of binary collisions. This would provide a kinetic equation applicable to a real quantum gas at densities for which a two-term virial expansion is the appropriate description of the equation of state. Applied to a molecular system, the density expansion would produce a wavelength- and frequency-dependent generalization of the Waldmann-Snider equation that could be useful for the study of intermolecular forces and collisional effects in moderately dense molecular gases.

APPENDIX A

The commutation and anticommutation relations (2.8) and (2.9) can all be obtained from the identity

$$(2\pi\hbar)^{-6}\int dr_1'\int dr_2' e^{-i(p_1\cdot r_1' + p_2\cdot r_2')/\hbar}$$

$$\times\left\{\delta(r_1+\tfrac{1}{2}r_1'-r_2+\tfrac{1}{2}r_2')\psi^+(r_1-\tfrac{1}{2}r_1')\psi(r_2+\tfrac{1}{2}r_2')\right\} = \delta(1-2)e^{\frac{1}{2}i\hbar D(1)}f(1)\ , \qquad (A.1)$$

which is derived below. Following that is the derivation of Eqs. (2.8a) and (2.9a), which is sufficient to indicate the general procedure.

We begin by rewriting the definition of $f(r_1p_1)$ in terms of the Fourier transformed field operators

$$\varphi(k) = \int dr\, e^{-ik\cdot r}\psi(r)\ ,\quad \varphi^+(k) = \int dr\, e^{+ik\cdot r}\psi^+(r)\ ,$$

as

$$f(r_1p_1) \equiv (2\pi)^{-3}\int dr_1'\, e^{-ip_1\cdot r_1'}\psi^+(r_1-\tfrac{1}{2}r_1')\psi(r_1+\tfrac{1}{2}r_1')$$

$$= (2\pi)^{-9}\int dr_1'dk_1dk_2 e^{-ir_1\cdot(k_1-k_2)}e^{ir_1'\cdot(\frac{1}{2}k_1+\frac{1}{2}k_2-p_1)}\varphi^+(k_1)\varphi(k_2). \qquad (A.2)$$

For convenience, $\hbar$ is set equal to unity. The left-hand side of Eq. (A.1), called I in what follows, is similarly represented as

$$I = (2\pi)^{-15}\int dr_1'dr_2'dkdk_1dk_2\, e^{-i(p_1\cdot r_1' + p_2\cdot r_2')}$$

$$\times e^{-ik\cdot(r_1+\frac{1}{2}r_1'-r_2+\frac{1}{2}r_2')}e^{-ik_1\cdot(r_1-\frac{1}{2}r_1')}e^{ik_2\cdot(r_2+\frac{1}{2}r_2')}\varphi^+(k_1)\varphi(k_2)\ . \qquad (A.3)$$

Adding and subtracting terms in the exponents of Eq. (A.3), we bring to the right the factors for $f(r_1p_1)$ appearing in Eq. (A.2) and change

the variable k to $k-k_2$, obtaining

$$I = (2\pi)^{-15}\int dr'_1 dr'_2 dk dk_1 dk_2 e^{-ik\cdot(r_1-r_2)}$$

$$\times\left[e^{-ik\cdot(\frac{1}{2}r'_1+\frac{1}{2}r'_2)} e^{-ir'_2\cdot(\frac{1}{2}k_1-\frac{1}{2}k_2)}\right]$$

$$\times e^{-ir'_2\cdot(\frac{1}{2}k_1+\frac{1}{2}k_2-p_2)} e^{-ir_1\cdot(k_1-k_2)} e^{ir'_1\cdot(\frac{1}{2}k_1+\frac{1}{2}k_2-p_1)} \varphi^+(k_1)\varphi(k_2). \quad (A.4)$$

The next step is to rewrite the term in square brackets in Eq. (A.4) as

$$\left[e^{\frac{1}{2}i\overleftarrow{\nabla}_{r_1}\cdot\left(\vec{\nabla}_{p_1}+\vec{\nabla}_{p_2}\right)} e^{\frac{1}{2}i\vec{\nabla}_{r_1}\cdot\vec{\nabla}_{p_2}}\right].$$

This requires attention to the order of the factors in subsequent expressions, but allows us to perform the integrations over k, k_1, and k_2 to obtain

$$I = \delta(r_1-r_2)\left(e^{\frac{1}{2}i\overleftarrow{\nabla}_{r_1}\cdot\left(\vec{\nabla}_{p_1}+\vec{\nabla}_{p_2}\right)} e^{\frac{1}{2}i\vec{\nabla}_{r_1}\cdot\vec{\nabla}_{p_2}}\right)\delta(p_1-p_2)f(r_1p_1)$$

$$= \delta(r_1-r_2)e^{\frac{1}{2}i\overleftarrow{\nabla}_{r_1}\cdot\vec{\nabla}_{p_2}} e^{\frac{1}{2}i\vec{\nabla}_{r_1}\cdot\vec{\nabla}_{p_2}}\left[e^{\frac{1}{2}i\overleftarrow{\nabla}_{r_1}\cdot\vec{\nabla}_{p_1}}\delta(p_1-p_2)f(r_1p_1)\right]. \quad (A.5)$$

In Eq. (A.5), the gradient $\vec{\nabla}_{p_1}$ acts on both the functions to its right; the term in square brackets can be written more explicitly as

$$\left\{e^{\frac{1}{2}i\overleftarrow{\nabla}_{r_1}\cdot\vec{\nabla}_{p_1}}\delta(p_1-p_2)\right\}\left\{e^{\frac{1}{2}i\overleftarrow{\nabla}_{r_1}\cdot\vec{\nabla}_{p_1}}f(r_1p_1)\right\}$$

where the momentum gradient acts only on the function within the braces. The spatial gradient is not restricted. With this convention, Eq. (A.5) becomes

$$I = \delta(r_1-r_2)\left\{e^{\frac{1}{2}i\overleftarrow{\nabla}_{r_1}\cdot\vec{\nabla}_{p_2}} e^{\frac{1}{2}i\vec{\nabla}_{r_1}\cdot\vec{\nabla}_{p_2}} e^{\frac{1}{2}\overleftarrow{\nabla}_{r_1}\cdot\vec{\nabla}_{p_1}} \delta(p_1-p_2)\right\}$$

$$\times e^{\frac{1}{2}i\overleftarrow{\nabla}_{r_1}\cdot\vec{\nabla}_{p_1}} f(r_1p_1) \quad . \tag{A.6}$$

Replacing $\vec{\nabla}_{p_2}$ by $-\vec{\nabla}_{p_1}$ within the braces in Eq. (A.6), we obtain

$$I = \delta(r_1-r_2)\left\{e^{-\frac{1}{2}i\vec{\nabla}_{r_1}\cdot\vec{\nabla}_{p_1}} \delta(p_1-p_2)\right\} e^{\frac{1}{2}i\overleftarrow{\nabla}_{r_1}\cdot\vec{\nabla}_{p_1}} f(r_1p_1) \ ,$$

or

$$I = \delta(r_1-r_2)\delta(p_1-p_2) e^{\frac{1}{2}i\left(\overleftarrow{\nabla}_{r_1}\cdot\vec{\nabla}_{p_1} - \overleftarrow{\nabla}_{p_1}\cdot\vec{\nabla}_{r_1}\right)} f(r_1p_1) \quad .$$

This proves the identity, Eq. (A. 1).

To calculate the commutator and anticommutator

$$f(1)f(2) \mp f(2)f(1) \ ,$$

it is sufficient to focus on the term $f(1)f(2)$, which is expressed in terms of the field operators as

$$f(1)f(2) = (2\pi\hbar)^{-6}\int dr_1' dr_2' \, e^{-i(r_1'\cdot p_1 + r_2'\cdot p_2)/\hbar} J \ , \tag{A.7}$$

where

$$J = \psi^+(r_1-\tfrac{1}{2}r_1')\psi(r_1+\tfrac{1}{2}r_1')\psi^+(r_2-\tfrac{1}{2}r_2')\psi(r_2+\tfrac{1}{2}r_2') \quad .$$

The first step is to convert J to a sum of terms in normal form, with all the creation operators on the left. Using the commutation relations of the field operators, Eqs. (2. 3), we obtain

$$J = \psi^{+}(r_1-\tfrac{1}{2}r'_1)\psi^{+}(r_2-\tfrac{1}{2}r'_2)\psi(r_2+\tfrac{1}{2}r'_2)\psi(r_1+\tfrac{1}{2}r'_1)$$

$$+ \delta(r_1+\tfrac{1}{2}r'_1-r_2+\tfrac{1}{2}r'_2)\psi^{+}(r_1-\tfrac{1}{2}r'_1)\psi(r_2+\tfrac{1}{2}r'_2) \quad . \qquad \text{(A. 8)}$$

The first term of Eq. (A. 8) is just the combination of operators that appears in the definition of f(12), while the second term is the combination that appears in the identity (A. 1), so substitution of Eq. (A. 8) in Eq. (A. 7) gives

$$f(1)f(2) = f(12) + \delta(1-2)e^{\frac{1}{2}i\hbar D(1)}f(1) \quad . \qquad \text{(A. 9)}$$

Since the phase space operators are Hermitian, f(2)f(1) is given by

$$f(2)f(1) = [f(1)f(2)]^{+} = f(12) + \delta(1-2)e^{-\frac{1}{2}i\hbar D(1)}f(1) \quad . \qquad \text{(A. 10)}$$

Combining (A. 9) and (A. 10), we obtain

$$[f(1), f(2)] = \delta(1-2)2i\sin[\tfrac{1}{2}i\hbar D(1)]f(1) \qquad \text{(2. 8a)}$$

and

$$\tfrac{1}{2}\{f(1), f(2)\} = f(12) + \delta(1-2)\cos[\tfrac{1}{2}i\hbar D(1)]f(1) \quad , \qquad \text{(2. 9a)}$$

which are the desired formulas. The method for obtaining the commutation and anticommutation relations involving the multiparticle operators is identical. The additional terms in (2. 8c), for example, arise in the permutations needed to put the operators in f(12)f(34) in normal form. Once that is done, Eq. (A. 1) is applicable with no further difficulty.

APPENDIX B

The evaluation of the diagrams displayed in the figures follows standard rules of many-body perturbation theory, with minor exceptions.[39] This appendix is not intended as a complete account of the method, but rather as a summary of the notation and the special conventions that are employed here.

The basic object of the theory is taken to be the imaginary-time-ordered n-particle momentum-space Green's function defined by

$$\mathcal{G}_n(12\ldots n, 1'2'\ldots n') = \langle T[\varphi_1\varphi_2\ldots\varphi_n\varphi^+_{n'}\ldots\varphi^+_{2'}\varphi^+_{1'}]\rangle \ , \qquad \text{(B. 1)}$$

where 1 and $1'$ stand for the combination of wavevector and time variables

$$1 = (\tfrac{1}{\hbar}p_1 - \tfrac{1}{2}k_1, \tau_1) \ , \quad 1' = (\tfrac{1}{\hbar}p_1 + \tfrac{1}{2}k_1, \tau_{1'}) \ ,$$

and so forth. T is the time-ordering operator that rearranges the field operators from right to left in ascending order of their τ arguments and inserts a factor of η^{π}, where π is the signature of the required permutation. The field operators $\varphi^+_i = \varphi^+(i)$ are defined by

$$\varphi^+(k,\tau) = \int dr\, e^{ikr}\left[e^{\hat{K}\tau/\hbar}\psi^+(r)e^{-\hat{K}\tau/\hbar}\right] ,$$

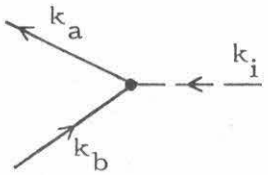
where $\hat{K} = \hat{H} - \mu\hat{N}$. The variables τ_i are restricted to the range $0 \le \tau_i \le \beta\hbar$. In general, it is important to exploit the periodicity of $\mathcal{G}_n$ in its τ variables to define a discrete-frequency Fourier representation for it. For the low-order perturbation theory calculations required here, however, it is more convenient to remain in the imaginary-time representation.

Terms in the perturbation expansion of G_n are represented by diagrams consisting of points, particle lines $\longrightarrow$, and interaction lines ----. Each n-particle diagram has 2n exterior points: n creation points at the bottom, labeled $\tau_{1'} \ldots \tau_{n'}$, and n annihilation points at the top, labeled $\tau_1 \ldots \tau_n$. Entering each annihilation point and leaving each creation point is a particle line carrying the appropriate wavevector, which is $\frac{1}{\hbar}p_{1'}-\frac{1}{2}k_{1'}$ for 1', $\frac{1}{\hbar}p_1+\frac{1}{2}k_1$ for 1, etc. The direction of positive momentum on these lines is indicated by an arrow pointing upwards. A line of wavevector $\frac{1}{\hbar}p$, running from point a to point b, represents the free propagator $\mathcal{G}_1^o(p, \tau_b - \tau_a)$,

$$\mathcal{G}_1^o(p,\tau) = \begin{cases} \gamma n_o(p) e^{-\Omega(p)\tau} & \text{for } \tau < 0 \ , \\ \tilde{n}_o(p) e^{-\Omega(p)\tau} & \text{for } \tau > 0 \ , \end{cases} \tag{B.2}$$

where $\gamma = (2\pi\hbar)^3 \eta$, $\tilde{n}_o(p) = 1 + \gamma n_o(p)$, and $\hbar\Omega(p) = \frac{1}{2}p^2 - \mu$. If both a and b are exterior points, $\mathcal{G}_1^o$ is multiplied by a momentum-conserving factor $(2\pi\hbar)^3 \delta(p_b - p_a)$.

An interaction line of wavevector k_i, assigned an arbitrary direction, represents the potential $v(k_i)$. It connects two interior points, or vertices, which are given a single imaginary-time label τ_i. In addition to the interaction line, one particle line enters the vertex and one leaves it. A particle line connecting two interior points is assigned a momentum label p_j. Conservation of momentum at a vertex



is maintained by a factor $(2\pi)^3\delta(k_a - k_b - k_i)$. It should be noted that the arrows on the particle lines serve to guarantee conservation of particle number at a vertex as well as to keep track of the signs of the momenta. There is an integral

$$-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau_i \int \frac{dk_i}{(2\pi)^3}$$

for each interaction and an integral $(2\pi\hbar)^{-3}\int dp_j$ for each internal particle line. A factor η is inserted for each crossing of two external particle lines and for each closed particle loop. The propagator for a closed loop is interpreted as $\lim_{\epsilon \to 0-} \mathcal{G}_1^0(p_j, \epsilon)$.

A linked diagram is one in which every interior point is connected to an exterior point by a continuous sequence of particle or interaction lines. The complete perturbation expansion of $\mathcal{G}_n$ is represented by the set of topologically distinct linked n-particle diagrams. To evaluate the terms in the expansion of the functions $n(12..n)$ and $F(1..i, 2..j)$, $i+j=n$, in which the creation operator φ_1^+, always occurs to the left of the annihilation operator φ_1, etc., we simply label the exterior points of the diagram with the appropriate infinitesimal time values and multiply the result for $\mathcal{G}_n$ by the factor γ^{-n}.

APPENDIX C

This appendix contains an alternative derivation of the kinetic equation for $F(1,1'|z)$, based on the use of a projection operator. A projection operator derivation of a kinetic equation in the classical case was given by Akcasu and Duderstadt,[16] who used the generalized Langevin equation approach of Mori.[52] Since we are interested here in obtaining an equation for a correlation function rather than for a dynamical variable, Mori's argument is not necessary, and we can obtain the kinetic equation in a more straightforward way.

We define a statistical projection operator P acting on a phase-space operator $x(t)$ by

$$Px(t) = \langle \tfrac{1}{2}\{x(t), \delta f(\overline{2})\} \rangle F^{-1}(\overline{2},\overline{3})\delta f(\overline{3}) , \qquad (C.1)$$

where

$$\delta f(1) = f(1, t=0) - n(1) .$$

An integration over each barred variable is implicit. P may be pictured geometrically as a projection onto the one-particle operator subspace spanned by $\delta f(rp,t)$ at $t = 0$. It can be verified directly that

$$P\delta f(rp) = \delta f(rp) , \qquad (C.2a)$$

$$Q\delta f(rp) = 0 , \qquad (C.2b)$$

where $Q = 1 - P$, and that $P^2 = P$ and $Q^2 = Q$.

We now apply Zwanzig's procedure[53] to

$$\frac{\partial}{\partial t}\delta f(1,t) = iL\delta f(1,t) ,$$

where $iL = (i\hbar)^{-1}[\ ,\hat{H}]$, to obtain the equation of motion for the projected quantity $P\delta f(1,t)$ in the form

$$\frac{\partial}{\partial t} P\delta f(1,t) = PiLP\delta f(1,t) + \int_0^t d\tau\, PiLe^{QiL\tau}QiLP\delta f(1,t-\tau)$$

$$+ PiLe^{QiLt}QiLQ\delta f(1,t=0) \quad . \tag{C. 3}$$

The last term in (C. 3), corresponding to the random force term in the generalized Langevin equation, vanishes because of Eq. (C. 2). The other terms may be written out explicitly as follows. The left hand side is simply

$$\frac{\partial}{\partial t} P\delta f(1,t) = \left[\frac{\partial}{\partial t} F(1,\overline{2}|t)\right] F^{-1}(\overline{2},\overline{3})\delta f(\overline{3})$$

The first term on the right-hand side is

$$PiLP\delta f(1,t) = F(1,\overline{2}|t)F^{-1}(\overline{2},\overline{3})\langle \tfrac{1}{2}\{iL\delta f(\overline{3}), \delta f(\overline{4})\}\rangle F^{-1}(\overline{4},\overline{6})\delta f(\overline{6})$$

$$= \delta f(\overline{4})F^{-1}(\overline{4},\overline{2})iL_o(\overline{2})F(1,\overline{2}|t)$$

$$+ \delta f(\overline{6})F^{-1}(\overline{6},\overline{4})iL_1(\overline{4}\,\overline{5})F(\overline{4}\,\overline{5},\overline{3})F^{-1}(\overline{3},\overline{2})F(1,\overline{2})|t) \ ,$$

where the second line is obtained using

$$\langle\{x, iLy\}\rangle = -\langle\{iLx, y\}\rangle \tag{C. 4}$$

and Eq. (2. 10a). The remaining term of Eq. (C. 3) is

$$\int_0^t d\tau PiLe^{QiL\tau}QiLP\delta f(1,t-\tau) =$$

$$\int_0^t d\tau\, \delta f(\overline{5})F^{-1}(\overline{5},\overline{4})\langle \tfrac{1}{2}\{\delta f(\overline{4}), iLe^{QiL\tau}QiL\delta f(\overline{3})\}\rangle F^{-1}(\overline{3},\overline{2})F(1,\overline{2}|t-\tau).$$

Now applying $\langle \frac{1}{2}\{\delta f(1'),\ \ \}\rangle$ to the equation, we obtain

$$\left[\frac{\partial}{\partial t} - iL_o(1')\right]F(1, 1'|t) = i\Sigma^{(s)}(1', \overline{2})F(1, \overline{2}|t) - \int_o^t d\tau \Sigma^{(d)}(1', \overline{2}|-\tau)F(1, \overline{2}|t-\tau) \tag{C. 5}$$

where

$$\Sigma^{(s)}(1, 1') = L_1(1\,\overline{2})F(1\,\overline{2}, \overline{3})F^{-1}(\overline{3}, 1') \tag{C. 6a}$$

and

$$\Sigma^{(d)}(1, 1'|t) = -\langle \tfrac{1}{2}\{\delta f(1), iLe^{-QiLt}QiL\delta f(\overline{2})\}\rangle F^{-1}(\overline{2}, 1') \ . \tag{C. 6b}$$

Equation (C. 5) is not yet in the form we want. To convert it, we interchange the labels 1 and 1′, let $t \to -t$ and $\tau \to -\tau$, and use $F(1, 1'|t) = F(1', 1|-t)$. This gives

$$\left[\frac{\partial}{\partial t} + iL_o(1)\right]F(1, 1'|t) = -i\Sigma^{(s)}(1, \overline{2})F(\overline{2}, 1'|t) - \int_0^t d\tau\, \Sigma^{(d)}(1, \overline{2}|\tau)F(\overline{2}, 1'|t-\tau) \ , \tag{C. 7}$$

which, with the transform convention (4. 9), is equivalent to the kinetic equation (5. 4). The static kernel (C. 6a) is the same as given by Eqs. (5. 7) and (5. 9b). The dynamic kernel is not in a form comparable to Eq. (5. 9c), but it can be rearranged as follows. Using Eq. (C. 2), we have

$$K^{(d)}(1, 1'|t) = \langle \tfrac{1}{2}\{iL\delta f(1), e^{-QiLt}QiL\delta f(1')\}\rangle \ ,$$

where $K^{(d)}(1, 1'|t) = \Sigma^{(d)}(1, \overline{2}|t)F(\overline{2}, 1')$ as in Eq. (5. 7). We now insert a redundant factor Q to the left of $e^{-QiLt}Q$ and move it to the other side of the anticommutator using

$$\langle\{x, Py\}\rangle = \langle\{Px, y\}\rangle \ , \tag{C. 8a}$$

$$\langle\{x, Qy\}\rangle = \langle\{Qx, y\}\rangle \ , \tag{C. 8b}$$

to obtain

$$K^{(d)}(1, 1'|t) = \langle \tfrac{1}{2}\{QiL\delta f(1), e^{-QiLt} QiL\delta f(1')\}\rangle \ . \tag{C. 9}$$

Since

$$iL\delta f(1) = - iL_o(1)\delta f(1) - iL_1(1\bar{2})\delta f(1\bar{2}) \ ,$$

where $\delta f(12) = f(12) - n(12)$, and since $Q\delta f(1) = 0$, Eq. (C. 9) becomes

$$K^{(d)}(1, 1'|t) = - L_1(1\bar{2})L_1(1'\bar{2}')\langle \tfrac{1}{2}\{Q\delta f(1\bar{2}), e^{-QiLt} Q\delta f(1'\bar{2}')\}\rangle \ . \tag{C. 10}$$

The Q in front of $\delta f(1\bar{2})$ can now be removed. Writing out the effect of the Q in front of $\delta f(1'\bar{2}')$ and using

$$\langle\{x, e^{-QiLt} y\}\rangle = \langle\{e^{QiLt} x, y\}\rangle \ , \tag{C. 11}$$

we finally obtain

$$K^{(d)}(1, 1'|t) = -L_1(1\bar{2})L_1(1\bar{2}')\left[\overset{*}{F}(1\bar{2}, 1'\bar{2}'|t) - \overset{*}{F}(1\bar{2}, \bar{3}|t)F^{-1}(\bar{3}, \bar{3}')F(\bar{3}', 1'\bar{2}')\right] , \tag{C. 12}$$

where

$$\overset{*}{F}(12, 1'2'|t) = \langle \tfrac{1}{2}\{e^{QiLt}\delta f(12), \delta f(1'2')\}\rangle \ , \tag{C.13a}$$

$$\overset{*}{F}(12, 3|t) = \langle \tfrac{1}{2}\{e^{QiLt}\delta f(12), \delta f(3)\}\rangle \ . \tag{C.13b}$$

The expression (C. 12) for $K^{(d)}(1, 1'|t)$ is analogous to Eqs. (5. 9c) - (5. 10). The differences are that the time dependence of the $\overset{*}{F}$ functions is governed by the modified propagator e^{QiLt}, and that the last two factors in the second term of Eq. (C. 12) are independent of time.

In a practical evaluation of Eq. (C. 12), one proceeds by re-expressing the modified-propagator correlation functions in terms of the standard ones. This is illustrated by the following evaluation of $K^{(d)}$ to second order in the interaction potential. It is convenient to begin with Eq. (C. 10). Using Eq. (C. 11) and the convention (4. 9), we write the second order dynamic kernel as

$$K_2^{(d)}(1, 1'|z) = - L_1(1\overline{2})L_1(1'\overline{2}')G_o(1\overline{2}, 1'\overline{2}'|z) , \qquad \text{(C. 14a)}$$

where

$$G_o(12, 1'2'|z) = \langle \tfrac{1}{2}\{\frac{1}{z+QL_o} Q\delta f(12), Q\delta f(1'2')\}\rangle_o . \qquad \text{(C. 14b)}$$

An application of the operator identity

$$[A-B]^{-1} = A^{-1} + A^{-1}B[A-B]^{-1}$$

to $[z+QL_o]^{-1}Q = Q[z+QL_o]^{-1}Q$ with $A = z+L_o$ and $B = PL_o$ gives

$$\frac{1}{z+QL_o} Q = \frac{1}{z+L_o} Q + \frac{1}{z+L_o} PL_o Q \frac{1}{z+QL_o} Q . \qquad \text{(C. 15)}$$

Since $PL_o = L_o P$, the second term of (C. 15) vanishes, and we obtain

$$\begin{aligned} G_o(12, 1'2'|z) &= \langle \tfrac{1}{2}\{\frac{1}{z+L_o} Q\delta f(12), Q\delta f(1'2')\}\rangle_o \\ &= \langle \tfrac{1}{2}\{\frac{1}{z+L_o} \delta f(12), Q\delta f(1'2')\}\rangle_o \\ &= \frac{1}{z-L_o(1)-L_o(2)}[F_o(12, 1'2') - F_o(12, \overline{3})F_o^{-1}(\overline{3}, \overline{3}')F_o(\overline{3}', 1'2')] \end{aligned} \qquad \text{(C. 16)}$$

This is identical to Eqs. (6. 12) - (6. 13).

We turn now to the question of the mathematical behavior of the expressions containing the modified propagator. Since no approximations have been made, Eq. (C. 7) is a formal identity; the projection operator method therefore appears to provide an unambiguous derivation of an exact kinetic equation for $F(1, 1'|z)$ of the form (5. 4). We cannot accept this equation as physically meaningful, however, unless we have some assurance that the projection operator expressions for the kinetic kernel do not hide important singularities. As emphasized previously, we do obtain well-behaved results for the kernel of the equation for $F(1, 1'|z)$, but we do not know what conditions on the projection operator are required to guarantee this in general. As the following example shows, the projection operator expressions sometimes can be exceedingly ill-behaved.

The example we consider is the problem of finding a kinetic equation for the commutator correlation function $\chi(1, 1'|t)$, Eq. (4. 22). To this end, we define a projection operation $\mathcal{P}$ by

$$\mathcal{P}x(t) = \langle \frac{1}{2\hbar}[x(t), \delta f(\overline{2})] \rangle \chi^{-1}(\overline{2}, \overline{3}) \delta f(\overline{3}) \qquad \text{(C. 17)}$$

where $\chi^{-1}(\overline{2}, \overline{3})$ is assumed to be the static inverse satisfying

$$\chi(1, \overline{2})\chi^{-1}(\overline{2}, 1') = \delta(1-1') \ . \qquad \text{(C. 18)}$$

As discussed in Section III, $\chi(kpp')$ vanishes at $k = 0$. If we ignore this, however, and proceed formally in the same way as above, we obtain an equation

$$\left[\frac{\partial}{\partial t}+iL_o(1)\right]\chi(1,1'|t) = -i\Gamma^{(s)}(1,\bar{2})\chi(\bar{2},1'|t)$$

$$-\int_0^t d\tau\Gamma^{(d)}(1,\bar{2}|\tau)\chi(\bar{2},1'|t-\tau) \ , \qquad \text{(C. 19)}$$

with the kernels $\Gamma^{(s)}$ and $\Gamma^{(d)}$ defined by expressions analogous to Eqs. (C. 6), containing the projector $\mathcal{P}$ instead of P. Thus, this derivation encourages us to believe that the commutator function $\chi(1,1'|t)$ satisfies a kinetic equation of the same form as the one satisfied by $F(1,1'|t)$. This is not true, however, as is shown by the following. The Fourier transforms of the commutator and anticommutator functions are related by the fluctuation-dissipation formula

$$\chi(1,1'|\omega) = S(1,1'|\omega)\frac{1}{2\hbar}\tanh(\tfrac{1}{2}\beta\hbar\omega) \ . \qquad \text{(C. 20)}$$

Given the kinetic equation (C. 7) for F, we can therefore obtain an equation for χ by applying Eq. (C. 20). It is sufficient for the present purpose to do this in the classical limit, where Eq. (C. 20) gives

$$\chi_c(1,1'|t) = \tfrac{1}{2}i\beta\frac{\partial}{\partial t}F_c(1,1'|t) \ . \qquad \text{(C. 21)}$$

Applying this to the classical limit of Eq. (C. 7), we obtain

$$\left[\frac{\partial}{\partial t}+iL_o(1)\right]\chi_c(1,1'|t) = -i\Sigma_c^{(s)}(1,\bar{2})\chi(\bar{2},1'|t) - \int_0^t d\tau\Sigma_c^{(d)}(1,\bar{2}|\tau)\chi(\bar{2},1'|t-\tau)$$

$$-\tfrac{1}{2}i\beta\Sigma_c^{(d)}(1,\bar{2}|t)F(\bar{2},1') \qquad \text{(C. 22)}$$

The last term in Eq. (C. 22) is a feature which is entirely absent from Eq. (C. 19). Since the classical kernels $\Sigma_c^{(s)}$ and $\Sigma_c^{(d)}$ are well-studied and well-behaved objects, there can be no doubt that the

kernels $\Gamma^{(s)}$ and $\Gamma^{(d)}$ in Eq. (C. 19) are exceedingly ill-behaved, if indeed they have any meaning at all. In the quantum mechanical case, Eqs. (C. 7) and (C. 20) formally determine an equation for $\chi(1, 1'|t)$ having an infinite number of terms. It is difficult to imagine, therefore, that the projection operator expressions for the kernels in Eq. (C. 19) are a useful starting point for physical approximations.

This example is admittedly extreme, since it is obvious that the projection operator $\mathcal{P}$ is poorly defined. It is nevertheless surprising that the vanishing of $\chi(kpp')$ at the point $k = 0$ leads to such a severe derangement in the projection operator formulas for the equation of motion of $\chi(kzpp')$. This may be a warning that subtler features of the projection operator may also produce difficulties.

FIGURE CAPTIONS

Figure 1. Diagrams for n(12). The lines in (a) and (b) represent the fully interacting propagator. Part (c) represents the sum of all two-particle connected diagrams.

Figure 2. First-order terms of the two-particle connected diagram.

Figure 3. Unconnected and two-connected diagrams for F(12, 3).

Figure 4. Zero-order diagrams for G(12, 34).

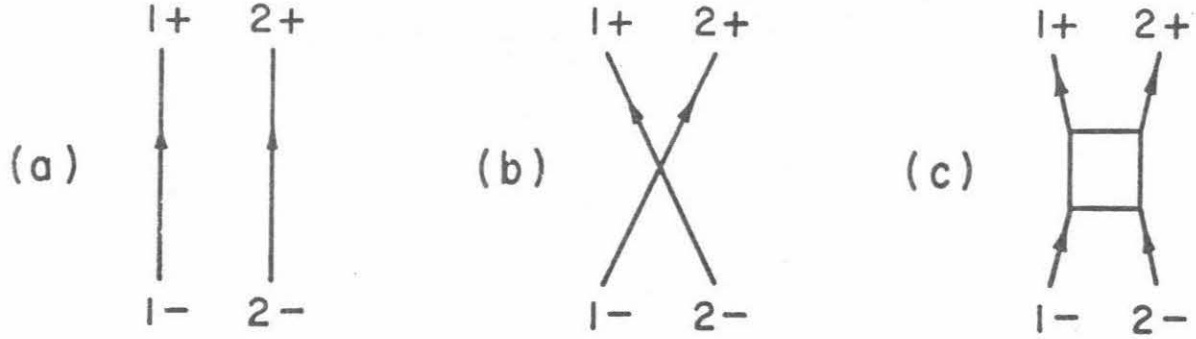


Figure 1

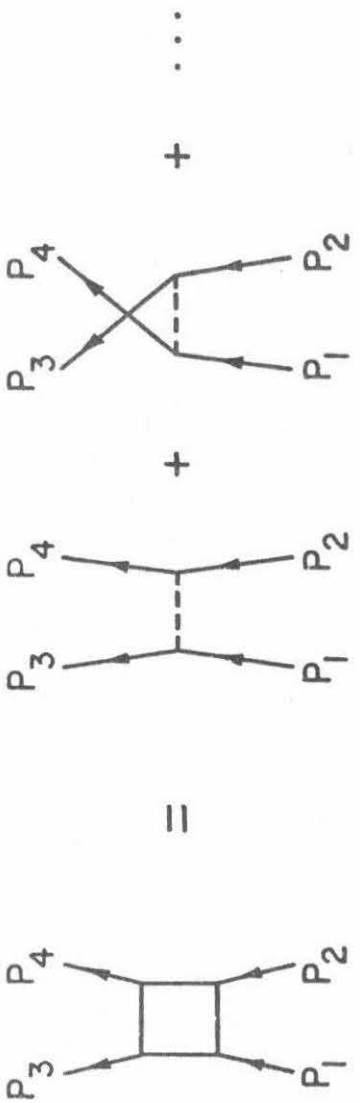


Figure 2

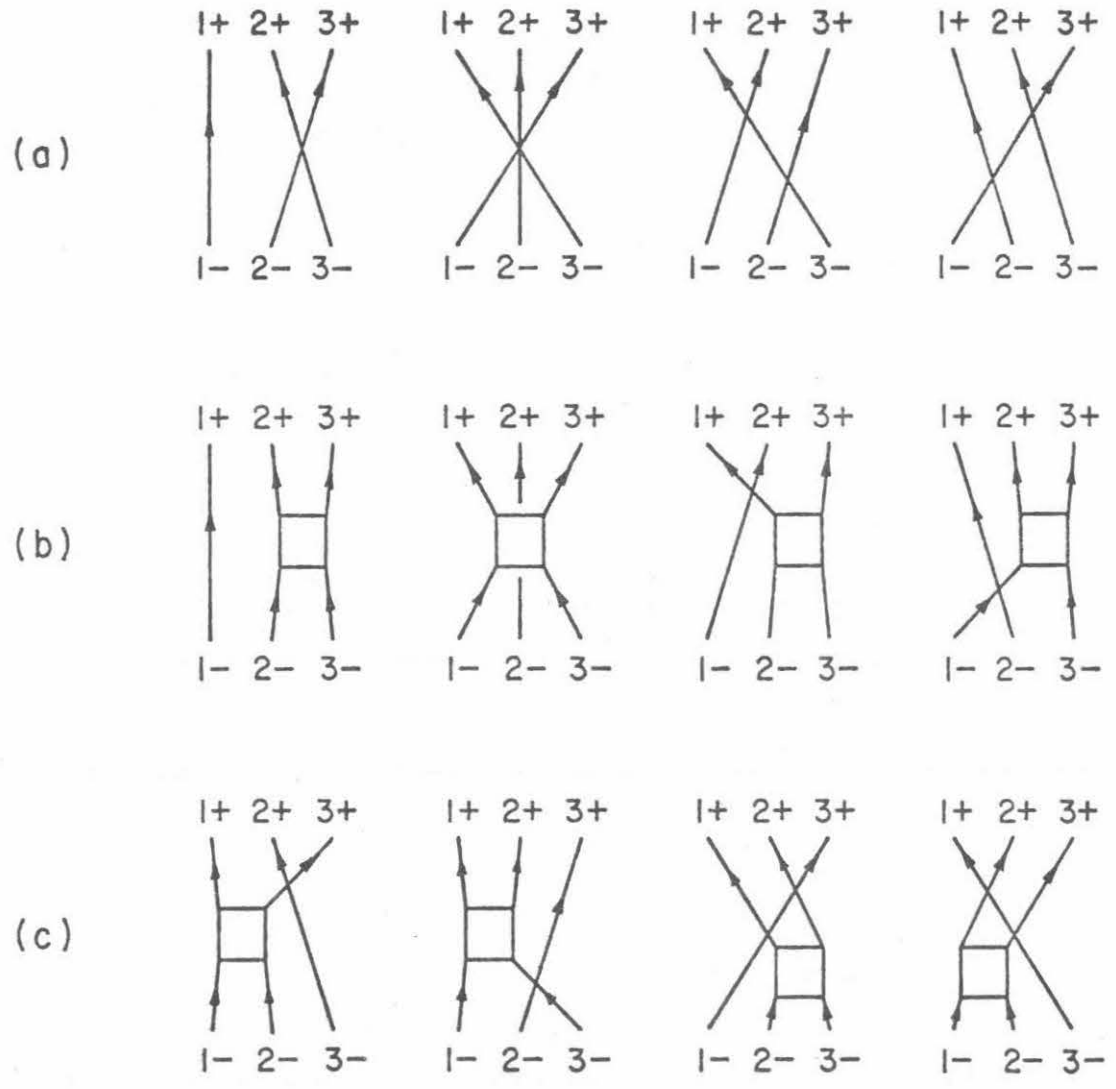


Figure 3

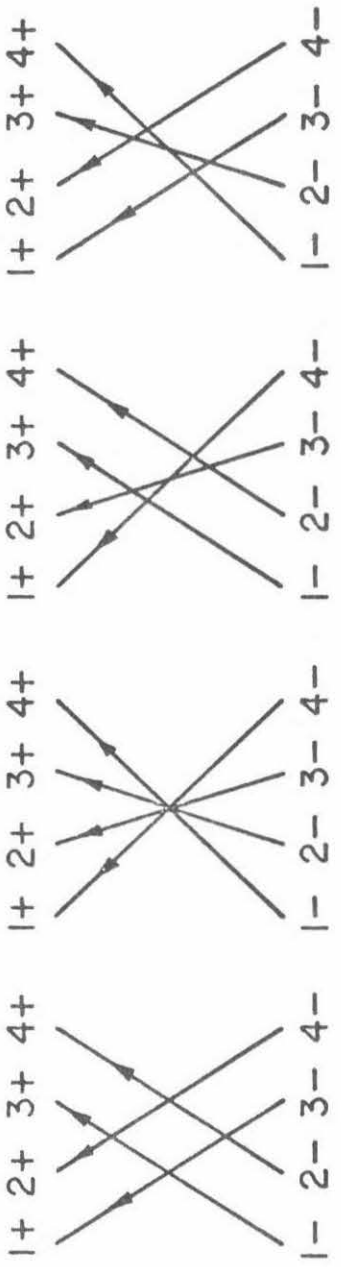


Figure 4

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