The quality of the crystals of zinc sulfide investigated at present is very poor indeed compared with that of, say, the silicon crystals readily available. Addamiano and Aven[25] have reported that the density of the vapor-grown crystals normally investigated is several percent lower than that deduced from crystal spacing and atomic weights, or that obtained for melt-grown crystals. Similarly, most specimens are polytypes or are heavily twinned. Methods of growing more perfect crystals are therefore vital to progress in this field. One approach being made in this laboratory[26] is to grow zinc sulfide epitaxially on silicon. Present results indicate that the first layers of zinc sulfide are almost as perfect as the silicon substrate, suggesting that the use of silicon as a seed may be valuable in the growing of good quality crystals of ZnS.

[25] A. Addamiano and M. Aven, J. Appl. Phys. **31**, 36 (1960).

[26] P. L. Jones, C. N. W. Litting, D. E. Mason, and V. A. Williams (private communication).

REVIEWS OF MODERN PHYSICS VOLUME 37, NUMBER 4 OCTOBER 1965

On the Areas of Equivalence of the Bogoliubov Theory and the Prigogine Theory of Irreversible Processes in Classical Gases*

J. STECKI,† H. S. TAYLOR

Department of Chemistry, University of Southern California, Los Angeles, California

The irreversible equations of evolution of classical gases, as obtained by Prigogine and Résibois from a study of the Liouville equation, in the limit of the system being very large, are examined, and the structure of the Markovian equation of evolution of the velocity distribution function is studied for homogeneous systems. It is then shown that the Markovian equations completely contain the Bogoliubov theory.

I. INTRODUCTION

Much of the recent work on irreversible statistical mechanics has been concerned with derivations of kinetic equations for the probability densities describing the time evolution of the system. For the case of classical systems, the most general kinetic equations ever derived have been given by Prigogine and his collaborators.[1–3] These authors have also shown how the general kinetic equations can be reduced to a set of Markovian equations[4] and how these can be further simplified in the so-called instantaneous collision approximations[5] (ICA). In doing this, these authors have demonstrated, under very general conditions, how the irreversible equations of evolution are obtained by appropriate asymptotic procedures from (reversible) mechanical equations of motion of the system under consideration.

In view of this generality and of the rigor of derivation of the results of Prigogine and his co-workers, it is imperative to compare other approaches with the Prigogine theory. In this paper such a comparison and evaluation is presented, of a kinetic theory of classical gases advanced by Bogoliubov[6] in 1946.

The Bogoliubov theory is worth particular attention for several reasons. It is a strictly statistical-mechanical theory; it does not make recourse to thermodynamic arguments or concepts; and the kinetic equations are obtained by a systematic and well-defined procedure. On the other hand, it does not attempt complete generality nor any discussion of the question of how the irreversible equations can be obtained from the reversible ones; it starts from simplifying assumptions. We also note in passing that recent applications to specific problems have been most often based on either of the two theories, and that in some cases identical kinetic equations were obtained (e.g., for classical electron plasmas.[7–9] The final result of a study of the Bogoliubov theory is presented below; it is shown how the Bogoliubov prescription results in a well-defined approximation to the Markovian kinetic equations of

* Financial support of this work by the U.S. Office of Naval Research, Physics Branch, under contract Norn. 228(23)NR013-307, is gratefully acknowledged.

† On leave from the Polish Academy of Sciences, Institute of Physical Chemistry, Warsaw, Poland.

[1] I. Prigogine, *Non-equilibrium Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1962).

[2] R. Balescu, *Statistical Mechanics of Charged Particles* (John Wiley & Sons, Inc., New York, 1963).

[3] I. Prigogine and P. Résibois, Physica **27**, 629 (1961); Ref. 1 Chap. 11.

[4] No "memory effects"—the time evolution of probabilities at time t depends on values at time t only; in the non-Markovian case it depends on values at earlier times $t' < t$.

[5] F. Henin, P. Résibois, and F. C. Andrews, J. Math. Phys. **2**, 68 (1961); F. C. Andrews, *ibid.* **2**, 91 (1961); Ref. 1, Chap. 11, p. 242, par. 6.

[6] N. N. Bogoliubov, *Problems of a Dynamical Theory in Statistical Physics* (1946). [English translation in *Studies in Statistical Mechanics*, edited by J. de Boer and G. E. Uhlenbeck (North-Holland Publishing Company, Amsterdam, 1962).]

[7] R. Balescu, Phys. Fluids **3**, 52 (1960); R. Balescu and H. S. Taylor, *ibid.* **4**, 85 (1961).

[8] A. Lenard, Ann. Phys. (N. Y.) **10**, 590 (1960); R. L. Guernsey, thesis, University of Michigan (1960) [Office of Naval Research Technical Report Nonr. 1224(15), unpublished].

[9] This led one of us to make a preliminary study of the relationship between these two theories in an unpublished work (H.S.T., 1961).

Prigogine and Résibois,[3] still being more general than the simplified I.C.A. equations.[5]

In Sec. II we recall the customary description of a system in terms of the reduced distribution functions (probability densities) of positions and momenta, and we introduce the Fourier expansion used by Prigogine[1,2]; in Sec. III we summarize the basic procedure used in solving the Liouville equation. In Sec. IV we recall the general kinetic equations of Prigogine and Résibois,[3] and in Sec. V we examine the Markovian equation for the velocity distribution function and we give the recursions which express the Prigogine–Résibois results in the ordinary p, r space. In Sec. VI we outline the Bogoliubov theory in the λ-version as recently reformulated and carried on to all orders in λ by one of us.[10] Finally, in Sec. VII we show the equivalence of Bogoliubov results and the Markovian kinetic equation of Sec. V.

II. DISTRIBUTION FUNCTIONS AND THEIR DECOMPOSITIONS

The usual statistical description of a classical system starts from the specific N-particle probability density $P(x_1, \cdots, x_N)$ of finding the system about a state represented by a point $x_1, \cdots, x_N$ in the phase space—thus, particle 1 about x_1, $\cdots$, particle N about x_N. Each x is a 6-vector p, r. $P(x)$ is conserved along the natural trajectory of the closed system

$$\delta P = 0 \tag{2.1}$$

or

$$\left[\partial_t + \sum_i \left(\dot{p}_i \frac{\partial}{\partial p_i} + \dot{q}_i \frac{\partial}{\partial q_i}\right)\right] P = 0. \tag{2.2}$$

To be specific, consider a system of N spherical structureless particles interacting with conservative forces, with the Hamiltonian

$$H = H_0 + \lambda U, \tag{2.3}$$

$$H_0 = \sum_i p_i^2/(2m), \tag{2.4}$$

$$U = \sum_{i<j} u_{ij}, \qquad u_{ij} = u(|\mathbf{r}_i - \mathbf{r}_j|). \tag{2.5}$$

The Liouville equation [Eq. (2.2)] can be rewritten as

$$(\partial_t + K_N) P = 0 \tag{2.6}$$

with the following definitions:

$$K_s = K_s^0 - \lambda \delta K_s, \qquad 1 \leq s \leq N, \tag{2.7}$$

$$K_s^0 = \sum_{i=1}^{s} K_1^0(i), \tag{2.8}$$

$$K_1^0(i) = \mathbf{v}_i \cdot (\partial/\partial \mathbf{r}_i), \tag{2.9}$$

$$\mathbf{v}_i = m^{-1}\mathbf{p}_i, \tag{2.10}$$

$$\delta K_s = \sum_{i<j\epsilon(s)} \theta_{ij}, \tag{2.11}$$

$$\theta_{ij} = \frac{\partial u_{ij}}{\partial \mathbf{r}_i} \cdot \frac{\partial}{\partial \mathbf{p}_i} + \frac{\partial u_{ij}}{\partial \mathbf{r}_j} \cdot \frac{\partial}{\partial \mathbf{p}_j}. \tag{2.12}$$

[10] J. Stecki, Phys. Fluids **7**, 33 (1964).

Besides P, one introduces a set of generic reduced distribution functions (RDF) $f_s(x_1, \cdots, x_s)$ which are probability densities for finding a set of *any* s particles at $x_1, \cdots, x_s$. Necessarily they are symmetric functions of x, and under the assumption of symmetry of P, the (standard) definition is[11]

$$f_s(x_1, \cdots, x_s) = \frac{N!}{(N-s)!} \int dx_{s+1} \cdots dx_N P(x_1, \cdots, x_N). \tag{2.13}$$

All macroscopic properties of a fluid can be expressed with the aid of a few $f_s (s = 1, 2, \cdots; s \ll N)$. The detailed properties of P are irrelevant insofar as a statistical description is concerned and the evolution of the system may be considered to be fully known if the evolution of f_s is known for $s \ll N$.

Under a weak restriction of P vanishing fast enough at the boundary of the part of the phase space accessible to the system, the Liouville equation is integrated over $N-s$ 6-vectors to give the well-known Bogoliubov–Born–Green–Kirkwood–Yvon (BBGKY) hierarchy of coupled equations:

$$(\partial_t + K_s) f_s = \int dx_{s+1} \sum_{i=1}^{s} \theta_{i,s+1} f_{s+1}. \tag{2.14}$$

The so-called transport or kinetic equations are usually differential equations for the one-particle distribution function f_1. In the Bogoliubov theory, the closure of the system (2.14) is achieved because of the assumption that $f_s (s \geq 2)$ are functionals of f_1. In the Prigogine theory, various components of f_s are separated according to the time scales of their variation, and when those dying-off rapidly are neglected, closed differential equations again result.

We now briefly discuss the Fourier analysis of the r dependence of P and of f_s, as introduced by Prigogine and Balescu.[1,2] Introduce the $3N$-dimensional complete orthonormal set

$$|\{\mathbf{k}\}\rangle = |\{\mathbf{k}_1, \cdots, \mathbf{k}_N\}\rangle = \prod_{j=1}^{N} |\mathbf{k}_j\rangle, \tag{2.15}$$

$$|\{\mathbf{k}_j\}\rangle = V^{-\frac{1}{2}} \exp(i\mathbf{k}_j \cdot \mathbf{r}_j). \tag{2.16}$$

Under periodic boundary conditions

$$\mathbf{k}_j = V^{-\frac{1}{3}} 2\pi \mathbf{n}_j, \tag{2.17}$$

[11] Each f_s is symmetric with respect to permutations of its 6-vector arguments irrespectively of any symmetry properties of P. A fully general definition of RDF has been introduced by Irving and Kirkwood, e.g., f_2 is defined as

$$f(x', x'') = \int dx^N \sum_{i \neq j} \Sigma \delta(x' - x_i) \delta(x'' - x_j) P(x_1, \cdots, x_N).$$

One usually writes $f(x_1, x_2)$ instead of $f(x', x'')$ although really one should distinguish between *specific particle indices* and *generic indices*; the first ones label particles, the latter ones label variables of a function of several 6-vectors. The assumption of symmetry of P does not affect the actual calculations because the Liouville equation is linear and the Hamiltonian symmetric; hence even if P is not symmetric, one can always define a new symmetrized P from which f_s will follow now rigorously as given by Eq. (2.13).

where $\mathbf{n}_j$ is a 3-vector with integer components. Then

$$P=\sum_{\{\mathbf{k}\}}\cdots\sum|\{\mathbf{k}\}\rangle\langle\{\mathbf{k}\}|P\rangle, \tag{2.18}$$

$$\langle\{\mathbf{k}\}|P\rangle=V^{-N/2}\int d\mathbf{r}^N\exp\left(-i\sum_j\mathbf{k}_j\cdot\mathbf{r}_j\right)P. \tag{2.19}$$

One simply integrates P over $\mathbf{r}_j$ whenever in the chosen set $\{\mathbf{k}\}=\{\mathbf{k}_1,\cdots,\mathbf{k}_N\}$ the vector $\mathbf{k}_j$ happens to be zero. In particular

$$V^{+N/2}\langle\{0\}|P\rangle=\int d\mathbf{r}^N P\equiv\rho_0(\mathbf{p}_1,\cdots,\mathbf{p}_N) \tag{2.20}$$

is the N-particle velocity distribution function (VDF). Consider now a Fourier component of a RDF f_s—it can contain up to s nonzero $\mathbf{k}$ vectors chosen from the set $\mathbf{k}_1,\mathbf{k}_2,\cdots,\mathbf{k}_s$. The expansion (2.18) is ordered according to the number of nonzero k vectors[12]; the VDF is expressible in terms of the "all-zero" Fourier component; the one-particle DF is expressible in terms of the Fourier components with one nonzero $\mathbf{k}$ vector and the "all-zero" one; the two-particle DF is expressible in terms of the Fourier component with two, one, and no nonzero $\mathbf{k}$ vectors, etc. An ordering of the expansion of f_s according to the number of nonzero k vectors leads to the following new decomposition of f_s.[1]

Define

$$F_s=c^{-s}f_s,\qquad c\equiv N/V, \tag{2.21}$$

and set

$$F_1=u_1+\Phi_1, \tag{2.22}$$

$$F_2=u_2+u_1(1)\Phi_1(2)+u_1(2)\Phi_1(1)+\Phi_2(1,2), \tag{2.23}$$

and in general

$$F_s=\sum_{r=0}^{s}\sum_{p_r}u_r\Phi_{s-r}. \tag{2.24}$$

The permutations p_r are over the assignments of variable to functions u_r, but not within variables once they are assigned. ϕ_m is the m-particle VDF obtained from f_s upon integration over s positions. Then

$$\langle\{k\}|u_r\rangle\neq 0, \tag{2.25}$$

if and only if the set of nonzero $\mathbf{k}$ vectors present in $\{\mathbf{k}\}$ is identical with the set of r variables of u_r. The Prigogine–Balescu decomposition is different from decompositions of f_s which are generalizations of known decompositions of the equilibrium RDF; this one is made automatically if one works with the Fourier coefficients classified according to the nonzero $\mathbf{k}$ vectors. We shall see below the indications of sound physical meaning of functions u_r.

III. THE RESOLVENT METHOD

The basic problem of statistical mechanics of irreversible phenomena is to formulate an unequivocal, general, and the least restrictive prescription for constructing the kinetic equations describing the time evolution of the system whose microscopic equations of motion are known. The latter are time-reversible and it is one of the basic principles of physics to require that any new equations of motion *be* time reversible. Kinetic equations describe an irreversible time evolution and lead (for a large class of systems) to the equilibrium state as described by Gibbsian statistics.

The Poincaré recurrence theorem proves that any isolated classical system will sooner or later approach as close to a phase point $\mathfrak{X}=\{x_1,\cdots,x_N\}$ as desired even if $\mathfrak{X}$ was realized at some earlier time t_0. This makes irreversibility, strictly speaking, impossible; the only possible answer is that the irreversibility can only appear as an approximate property. The results of Prigogine[1] show that it is an asymptotic property of large systems; one obtains irreversible kinetic equations by considering *causal solutions*[13] *of the Liouville equation in the limit of very large system* $N\to\infty$, $V\to\infty$, N/V finite. Thus a simple reconciliation: irreversibility can be realized strictly in an infinite system and is only approximately realized in finite, but large, systems. The smaller the (closed) system, the worse the approximation, and finally no trace of irreversibility can be found in a mechanical system of several bodies.

Consider now, after Prigogine *et al.*[1–3] the Liouville equation [Eq. (2.6)] and the "initial value" problem: given $P(0)$ find $P(t)$ for $t>0$. A very compact formulation results if one introduces the Laplace transform

$$\tilde{P}(s)=\int_0^\infty dte^{-st}P(t), \tag{3.1}$$

whereupon the Liouville equation gives

$$(s+K_N)\tilde{P}(s)=P(0), \tag{3.2}$$

insofar as

$$\lim_{t\to\infty}e^{-st}P(t)=0. \tag{3.3}$$

This is assumed to be true under a sufficient condition

$$\mathrm{Re}\,s>0. \tag{3.4}$$

[12] When the expansion (2.18) thus ordered is substituted into the definitions of f_s [Eq. (2.13)], important restrictions on the volume dependence of the Fourier components are found resulting from the requirement that in the limit of large system ($N\to\infty$, $V\to\infty$; $N/V=c$ finite) f_s depend only on the ratio c thus remaining finite too. This is called the *postulate of finiteness of the RDF* of Prigogine and Balescu (Refs. 1 and 2).

[13] The important concept of causality is well known in the scattering theory. The following simple example might be helpful. An incoming plane wave with an outgoing radial wave form the causal solution describing the scattering experiment. But the Schrodinger equation allows equally well a solution consisting of an incoming radial wave and an outgoing plane wave; this is the anticausal solution. It does not correspond to the scattering experiment.

The formal solution of the Liouville equation is

$$\tilde{P}(s)=(s+K_N)^{-1}P(0). \tag{3.5}$$

The Laplace transform $\tilde{P}(s)$ can be inverted in a standard way. It is here that the causality principle is satisfied in a very natural way. On inverting the Laplace transform, one finds the causal solution for $t>0$ and formally 0 for $t<0$. Now if one would take a generalized Fourier transform, with $-\infty<t<+\infty$, on inversion one could find either causal or anticausal solutions depending on the choice of the contour of integration. If one starts with the Laplace transform, appropriate for the initial value problem, causal solutions result.

Further complication arises because of the behavior of the resolvent $(s+K_N)^{-1}$, which is of course crucial for the entire theory. For a finite system the resolvent displays isolated singularities on the imaginary axis.[1] In the asymptotic limit N, $V\to\infty$ a finite discontinuity appears. The function $P^+(s)$, analytic in the right half-plane, together with its analytic continuation into the left half-plane, corresponds to the causal solution.[1,2] This function eventually leads to quantities showing irreversible behavior.

IV. GENERAL NONMARKOVIAN EQUATIONS

We outline now very briefly the general results of Prigogine and Résibois.[3] Introducing the new variable

$$z=is \tag{4.1}$$

and Laplace-inverting the Fourier expansion of Eq. (3.5) one expresses the Fourier coefficients of the N-particle DF at time t in terms of all Fourier coefficients at time 0:

$$\langle\{k\}\mid P(t)\rangle=-\frac{1}{2\pi}\int_c dz e^{-izt}\times\sum_{\{\mathbf{k}'\}}\langle\{\mathbf{k}\}\mid(K_N-iz)^{-1}\mid\{k'\}\rangle\langle\{k'\}\mid P(0)\rangle. \tag{4.2}$$

The contour of z integration is now a straight line from right to left just above the real axis, closed by a sufficiently large half-circle in the lower half-plane. The resolvent is expanded in powers of λ,

$$(K_N-iz)^{-1}=\sum_0^\infty\lambda^n(K_N{}^0-iz)^{-1}[\delta K_N(K_N{}^0-iz)^{-1}]^n, \tag{4.3}$$

and this is used in conjunction with the multiple Fourier expansion of each term in the sum (4.3) into the complete set $\mid\{\mathbf{k}\}\rangle$. Then the "free-particle propagator," which is (4.3) with $\lambda=0$, is diagonal. We denote it by $\mathcal{P}(z)$:

$$\langle\{\mathbf{k}\}\mid\mathcal{P}(z)\mid\{\mathbf{k}'\}\rangle\equiv\langle\{\mathbf{k}\}\mid(K_N{}^0-iz)^{-1}\mid\{\mathbf{k}'\}\rangle=-i(\sum_{j=1}^N\mathbf{k}_j\cdot\mathbf{v}_j-z)^{-1}\prod_{l=1}^N\delta^{Kr}(\mathbf{k}_l,\mathbf{k}_l'). \tag{4.4}$$

In view of (2.11), a typical term is of the form

$$\sum_{\{\mathbf{k}'\}}\sum_{\{\mathbf{k}''\}}\langle\{\mathbf{k}\}\mid\mathcal{P}(z)\sum_{i<j}\theta_{ij}\mid\{\mathbf{k}''\}\rangle\times\sum_{\{\mathbf{k}'''\}}\langle\{\mathbf{k}''\}\mid\mathcal{P}(z)\sum_{i<j}\theta_{ij}\mid\{\mathbf{k}'''\}\rangle\cdots\times\sum_{i<j}\theta_{ij}\mathcal{P}(z)\mid\{\mathbf{k}'\}\rangle\langle\{\mathbf{k}'\}\mid P(0)\rangle. \tag{4.5}$$

Each δK_N introduces a pairwise sum of $N(N-1)/2$ terms, each intermediate state $\{\mathbf{k}\}$ introduces a $3N$-tuple sum over $\mathbf{k}$ vectors. The matrix elements of θ_{ij} modify the wave vectors subject to simple conservation laws[14] which follow from the translational invariance of (2.12). One can speak of a *state* $\{\mathbf{k}\}$ which is propagated (from right to left) subject to *transitions* introduced by the matrix elements $\langle\{\mathbf{k}\}\mid\theta_{ij}\mid\{\mathbf{k}'\}\rangle$. In the diagrammatic notation invented by Prigogine and Balescu,[1] the state is symbolized by labeled horizontal lines (nonzero $\mathbf{k}$-vectors) and transitions occur at the vertices at which the lines meet or cross. The terms in (4.2) expanded as indicated in (4.5) are classified and rearranged so that they can be expressed in terms of three functions defined below. Those leading from a "lower state of correlation" (less nonzero $\mathbf{k}$ vectors) at the right to a "higher state of correlation" (more nonzero $\mathbf{k}$ vectors) at the left, thus "creating correlations," are isolated from those representing "diagonal transitions" (the final-left identical with the initial-right $\{k\}$ state), and from those "destroying the correlations." The corresponding general creation, diagonal, and destruction operators are defined:

$$C(\{\mathbf{k}\},\{\mathbf{k}'\};z)=\sum_1^\infty\lambda^n\langle\{\mathbf{k}\}\mid[\mathcal{P}(z)\delta K_N]^n\mid\{\mathbf{k}'\}\rangle, \tag{4.6}$$

$$\psi(\{\mathbf{k}\};z)=\sum_2^\infty\lambda^n\langle\{\mathbf{k}\}\mid\delta K_N[\mathcal{P}(z)\delta K_N]^{n-1}\mid\{\mathbf{k}\}\rangle, \tag{4.7}$$

$$\mathfrak{D}(\{\mathbf{k}\},\{\mathbf{k}'\};z)=\sum_1^\infty\lambda^n\langle\{\mathbf{k}\}\mid[\delta K_N\mathcal{P}(z)]^n\mid\{\mathbf{k}'\}\rangle. \tag{4.8}$$

The multiple Fourier expansion as exemplified by (4.5) is understood. A very important restriction is also implied; no *intermediate* $\{\mathbf{k}\}$ state identical to the initial (right) state is allowed by definition; thus all are finite at Im $z=0$ and it is assumed that their poles in the lower half-plane are all at finite distances from the real axis. This assumption is corroborated by explicit calculations for some simple examples. Their inverse Laplace transforms are then defined and denoted by

[14] $k_l=k_l'$ for all $l\neq i,j$; $k_i+k_j=k_i'+k_j'$; otherwise $\langle\{k\}\mid\theta_{ij}\mid\{k'\}\rangle=0$.

It is a function of $\mathbf{k}$ vectors and a differential operator in the p-space.

$\mathcal{C}(\{k\}, \{k'\}; \tau)$, $G(\{k\}; \tau)$, and $D(\{k\}, \{k'\}; \tau)$, respectively, τ being the resulting auxiliary time variable.

Then Prigogine and Résibois[3] find the following set of general kinetic equations. First, the expression for the all-zero Fourier coefficient (the VDF) at time t yields upon differentiation the following non-Markovian differential equation:

$$\partial_t \rho_0(t) = \int_0^t G_0(\tau)\rho_0(t-\tau)\, d\tau + D_0(t). \tag{4.9}$$

Here G_0 is $G(\{\mathbf{k}\}, \tau)$ with an all-zero final and initial state and D_0 stands for the sum of all destruction terms with a final all-zero state. Thus in D_0 is lodged the dependence on initial correlations.

To conform with the Prigogine–Résibois notation we denote from now on the Fourier coefficients by $\rho_{\mathbf{k}}(t)$ or $\rho(\{\mathbf{k}\}, t)$. For each nonzero $\{\mathbf{k}\}$ Fourier coefficient $\rho_{\mathbf{k}}(t)$, the terms in expanded Eq. (4.2) [cf. Eq. (4.5)] are split into two groups showing entirely different time behavior. The Fourier coefficient $\rho_{\mathbf{k}}(t)$ is correspondingly decomposed

$$\rho_{\mathbf{k}}(t) = \rho_{\mathbf{k}}'(t) + \rho_{\mathbf{k}}''(t). \tag{4.10}$$

The primed part results from propagation and destruction of initial correlations, and is shown to obey a differential equation similar to (4.9):

$$(\partial_t + i\sum_j \mathbf{k}_j \cdot \mathbf{v}_j)\rho'(\{\mathbf{k}\}, t)$$

$$= \int_0^t d\tau G(\{\mathbf{k}\}, \tau)\rho'(\{\mathbf{k}\}, t-\tau) + D_{\mathbf{k}}(t). \tag{4.11}$$

One can prove[3,15] that in the limit of long times ρ' vanishes,

$$\rho_{\mathbf{k}}' \to 0 \qquad t \to \infty. \tag{4.12}$$

The other set of terms which make up the other part, ρ_k'', represents the persistent correlations. These are created by operators $\mathcal{C}(\tau)$ acting, as the detailed calculation shows, on the primed parts of Fourier coefficients of lower state of correlation

$$\rho_k''(t) = \sum_{\text{lower } \{\mathbf{k}'\}} \int_0^t d\tau \mathcal{C}(\{k\}, \{k'\}; \tau)\rho'(\{\mathbf{k}'\}, t-\tau). \tag{4.13}$$

These equations are the most general kinetic equations ever derived for a classical fluid. The remarkable feature is that they are non-Markovian; a memory is extended into the past. The extent of memory is governed by the time dependence of $\mathcal{C}(\tau)$ or $G(\tau)$; if $\mathcal{C}(\tau)$ is virtually zero after some time τ^*, the right-hand side of (4.13) evaluated at t depends upon ρ' in the interval $(t, t-\tau^*)$ and no further into the past. If, therefore, all these operators vanish for τ large enough, say $\tau > \tau^*$, then for time t long enough

$$t \gg \tau^*, \tag{4.14}$$

the integration limits can be extended to infinity without affecting the result. In such a way a Markovian regime results. The set of Markovian kinetic equations is discussed below. It may be noted that all equations result from the solution of the initial value problem, as outlined above; then $\rho''(t)$ are best expressed in an explicit form, whereas the expressions for ρ' and ρ_0 simplify remarkably upon taking the time derivative ∂_t, and accordingly are best expressed as solutions of differential equations (4.9) and (4.11).

Now, as Prigogine and Résibois have shown,[3] for times distant enough from the initial time 0, a Markovian regime is established. Then (4.9) simplifies to

$$\partial_t \rho_0(t) = X\rho_0(t). \tag{4.15}$$

X stands for the time-independent Markovian operator ($\Omega i\psi$ in Résibois notation) which will be examined below. Mathematically, $\psi_0(z) = \psi(\{O\}, z)$ is expanded in powers of z around the origin $z=0$. Similarly one obtains

$$(\partial_t + i\sum \mathbf{k}_j \mathbf{v}_j)\rho_k' = X_{kk}\rho_k' \tag{4.16}$$

which replaces (4.11). Equation (4.13) is left unchanged but now ρ' appearing in the right-hand side are solutions of Markovian differential equations (4.15) and (4.16).

A transparent pattern emerges if one considers an initial state at $t=0$ given in terms of all $\rho_k(0)$ or alternatively of $\rho_0(0)$ and u functions $u_1(0)$, $u_2(0)$, $\cdots$.[16] To solve the Markovian equation for $\rho_0(t)$ all we need is $\rho_0(0)$. Similarly the Markovian differential equations for ρ' will give $u_1'(t)$ in terms of $u_1(0)$, $u_2'(t)$ in terms of $u_2(0)$, etc. On the other hand the double-primed part represents terms which are fully expressible in terms of lower correlations; thus $u_1''(t)$ can be obtained if only $\rho_0(0)$ is known, $u_2''(t)$ can be calculated if only $\rho_0(0)$ and $u_1(0)$ are known, etc. Significantly, in the Markovian regime no term appears expressing a lower u function in terms of a higher one, thus no information about $u_3(0)$ is needed if one wishes to calculate $u_2(t)$. These terms are present in the general non-Markovian equations and are expressed by the destruction operators $D_k(t)$. Hence Eqs. (2.1) to (2.3) coupled with these observations show us that the Markovian scheme, valid for large systems and long times, uncouple the BBGKY equations [cf. (2.14)].

We are in a position now to appreciate the Prigogine–Balescu decomposition of f_s into the u functions, as imposed by the Fourier expansion. It is the u function which is decomposed in turn into two parts (corresponding to ρ' and ρ''). Any typical decomposition using f_s only, such as

$$f_2 = U_2 + f_1 f_1, \text{ etc.}$$

is bound to lump together and mix the primed and double-primed parts which show entirely different time behavior.

[15] Ref. 1, Chap. 12.

[16] Cf. Sec. II. $\langle\{\mathbf{k}\} \mid u_r\rangle \sim \int dp^{N-r}\rho_{\mathbf{k}}$ and there are r specific nonzero $\mathbf{k}$ vectors in $\langle\{\mathbf{k}\}\mid$. Hence u_r are essentially ρ_k expressed in the ordinary p, r space.

V. MARKOVIAN EQUATION OF EVOLUTION OF THE VDF

It is instructive to consider the simplified derivation of the Markovian equation (4.11) as given by Prigogine.[3] Neglect in (4.9) the short-lived destruction term $D_0(t)$ (i.e., $D_0(t)\to 0$ as t gets large), extend the time intergral to infinity, and expand $\rho_0(t-\tau)$ in Taylor series around $\rho_0(t)$; then one can express the moments of G_0 in terms of z derivative at $z=0$ of its Laplace transform, $\psi_0(z)$; the result is

$$\partial_t\rho_0 = i\psi_0(0)\rho_0(t)+\sum_1^\infty (\nu!)^{-1}\psi_0^{(\nu)}(0)\frac{\partial^\nu\rho_0}{\partial t^\nu}. \quad (5.1)$$

This can be solved successively leading to the same operator X in (4.15) as is obtained from a more rigorous Prigogine–Résibois derivation. The first approximation,

$$\partial_t\rho_0 = i\psi_0(0)\rho_0, \quad (5.2)$$

is known as the instantaneous-collision approximation (ICA) introduced by Prigogine. It is only $\psi(0)$ that appears in the general H-theorem.[5,15] As Balescu has shown,[17] the *stationary* current in the electric conductivity problem, is given in terms of $\psi(0)$ only.

Our intention is to express the quantities appearing in the Markovian equation (4.15) in the ordinary p, r space and without the aid of the Laplace variable z. This will make possible an explicit comparison with the results following from the rigorous generalization of the Bogoliubov theory, as made by one of us.[10] Two points are to be made. First, there is a simple connection between the operator $\psi_0(z)$ and the creation operator $C_{k0}=C(\{\mathbf{k}\},\{\mathbf{0}\};z)$ with the initial all-zero state. In the definition of ψ the outmost left θ-vertex can be separated out explicitly:

$$i\psi_0(z) = \langle\{0\}\mid\sum_{i<j}\theta_{ij}\mid\{k_ik_j,0,\cdots\}\rangle \times C(\{\mathbf{k}_i,\mathbf{k}_j,\mathbf{0},\cdots\},\{\mathbf{0}\};z). \quad (5.3)$$

Now take Eq. (4.13) and consider the creation from the all-zero state only, evaluated asymptotically ($t\to\infty$ in the integration limit):

$$\rho_{k,o}''\equiv\rho''(\{k\},\{0\};t)=\int_0^\infty d\tau\,\mathcal{C}(\{k\},\{0\};\tau)\rho_0(t-\tau). \quad (5.4)$$

This can be manipulated identically as the simplified Eq. (4.15) leading to

$$\rho_{k,o}''(t)=C_{ko}(0)\rho_0(t)+\sum_1^\infty\frac{i^\nu}{\nu!}C_{ko}^{(\nu)}\frac{\partial^{(\nu)}\rho_0}{\partial t^\nu}, \quad (5.5)$$

where $C_{ko}^{(\nu)}$ are, in abbreviated notation, again derivatives at $z=0$. Comparison of (5.5) with (5.1) shows that

$$\partial_t\rho_0=\langle\{0\}\mid\delta K_N\mid\{k\}\rangle\rho_{k,o}''. \quad (5.6)$$

[17] R. Balescu, Physica **27**, 693 (1961).

This is a counterpart of the first of BBGKY equations, Eq. (2.13),

$$\partial_t F_1(1;t)=c\int dx_2\theta_{12}F_2(1,2;t). \quad (5.7)$$

Strictly speaking $f_2=c^2F_2$ is a complete two-particle DF; here the ρ' part of it is excluded as it was included into the short-lived term $D_0(t)$, whose contribution is neglected in the Markovian equation (4.11) or (5.1). It follows that *a correct Markovian equation* (4.11) *is obtained even if in the* BBGKY *equation one uses only that part of* $f_2(1,2)$ *which comes from* ρ''. Moreover, it is sufficient to consider creation from the all-zero state only.

Secondly, the free-particle propagator as given by (4.4) is to be evaluated at $z=0$ in (5.2) as well as in (5.1) and (5.5). To be sure that we do not introduce inadvertedly anticausal solutions, we shall approach the origin from the upper half-plane, thus taking the limit $z=+i0$ rather than unspecified $z=0$. Then we can make use of the results by Résibois[18,19] who has shown that for any function $f(\mathbf{p},\mathbf{r})$,

$$\mathcal{P}(+i0)\,f(\mathbf{p},\mathbf{r})\equiv[K_N^0-i(i0)]^{-1}f = \int d\mathbf{r}'\int d\mathbf{p}'G^0(\mathbf{rp}\mid\mathbf{r}'\mathbf{p}')\,f(\mathbf{p}'\mathbf{r}'), \quad (5.8)$$

$$G^0=\lim_{\epsilon\to+0}\int_0^\infty d\tau e^{-\epsilon\tau}\prod_{j=1}^N\delta(\mathbf{p}_j-\mathbf{p}_j')\,\delta(\mathbf{r}_j-\mathbf{r}_j'-\mathbf{v}_j'\tau). \quad (5.9)$$

Thus

$$\mathcal{P}(+i0)\,f(p,r)=\lim_{\epsilon\to+0}\int_0^\infty d\tau e^{-\epsilon\tau}f(p,r-v\tau). \quad (5.10)$$

We see immediately that $\mathcal{P}(+i0)$ can be also identified with the propagator introduced by Bogoliubov and used by Choh and Uhlenbeck,[20] Guernsey,[8] and in Ref. 10,

$$\mathcal{P}(+i0)=\int_0^\infty\exp(-\tau K_N^0)\,d\tau\equiv\int_0^\infty d\tau\,\dot{S}_{-\tau} \quad (5.11)$$

which is further discussed and used in Sec. VI. It averages a given function over the straight-line (unperturbed) trajectory backwards in time.

Now we return to the problem of making the connection with the Bogoliubov theory; we discuss first the instanteneous-collision approximation as expressed in the ordinary space in terms of the distribution functions f_s. Therefore, we take the first term of (5.5); the creation operator is an infinite sum [cf. (4.6)]:

$$C(\{k\},\{0\};+i0)=\sum_1^\infty\lambda^nC_n(\{k\}). \quad (5.12)$$

[18] P. Résibois, *Theorie formelle du scattering classique*, thesis, University of Brussels, 1960 (unpublished).
[19] P. Résibois, J. Math. Phys. **4**, 166 (1963).
[20] S. T. Choh and G. E. Uhlenbeck, U.S. Office of Naval Research Technical Report Nonr. 1224(15), 1958 (unpublished).

Symbolically in an abbreviated notation [cf. (4.6)]

$$C_n \sim (\mathcal{P}\delta K_N)^n, \tag{5.13}$$

the Fourier expansion with given final state, initial all-zero state, and no other all-zero states, and the limit $z=+i0$, being understood. Hence the simple recursion relation:

$$C_n \sim \mathcal{P}\delta K_N C_{n-1}. \tag{5.14}$$

This however cannot be directly inverted into the ordinary p, r space because of the restriction of no all-zero state between δK_N and C_{n-1}. As one of us has shown,[21] one can circumvent this difficulty by following closely the procedure used by Résibois[17] who added and subtracted adequately chosen terms so as to have a full sum ($-\infty<\mathbf{k}<+\infty$ with no restrictions) over each of the $\mathbf{k}$ vectors of interest. This involves the following steps. Define h_s, $s\geq 2$, a set of approximate RDF in which the I.C.A. results:

$$h_s = f_s^{\mathrm{ICA}} = \int dp^{N-s}[\rho_0 + \sum_{\{\mathbf{k}\}} \mid \{k\}> \rho_{\mathbf{k},o}'']. \tag{5.15}$$

Order ρ'' according to the number γ of nonzero $\mathbf{k}$ vectors in the final set $\{\mathbf{k}\}$, and introduce ordered generic indices by collecting terms of the same structure differing only in labeling of the particles, dropping also terms of the order N^{-1}. Then for a homogeneous system ($u_1=0$)

$$h_s = \int dp^{N-s} \times[\rho_0 + \sum_{\gamma=2}^{s} \sum_{p_\gamma} \sum_{\{\mathbf{k}\}} \sum_{\gamma \neq \{0\}_\gamma} C(\{k\}_\gamma)\rho_0(t) \mid \{k\}_\gamma 0\cdots 0]. \tag{5.16}$$

By a careful consideration of terms with $k_j=0$ and $k_j\neq 0$, and by taking advantage of the simplifications introduced by the integral over $\mathbf{N}-\mathbf{s}$ momenta (diagrams with two particle indices "destroyed" simultaneously do not contribute[22]), one arrives after some manipulations to the following result:

$$h_s = h_s^0 + \sum_1^\infty \lambda^n h_s^n, \tag{5.17}$$

$$h_s^0 = \int dp^{N-s}\rho_0, \tag{5.18}$$

$$h_s^n = \int dp^{N-s}\hat{h}_s^n \rho_0(t), \tag{5.19}$$

where the operators $\hat{h}_s^n$ fulfill the following recursion relation[21]:

$$\hat{h}_s^n = \mathcal{P}\delta K_s \hat{h}_s^{n-1} + \mathcal{P}\int dr_{s+1} \sum_{i=1}^{s} \theta_{i,s+1}[\hat{h}_{s+1}^{n-1} - \hat{h}_2^{n-1}(i, s+1)], \tag{5.20}$$

$$\hat{h}_s^0 \equiv 1. \tag{5.21}$$

This expresses the recursion (5.14) in the ordinary space in terms of reduced distribution functions h_s. Clearly this recursion can be carried on in a most straightforward way. An example is given in Sec. VI. Also this recursion forms a basis for the connection with the Bogoliubov theory.

Turning now to a more general problem of general Markovian equation (5.1) in the configuration space, let us stress that, in view of the complexity of the operator X, Eq. (4.15) or Eq. (5.1), there are certainly numerous such representations. One could, for instance, consider $\psi(0)$ as determined by (5.15)–(5.21) with (5.7) and use the expressions of Prigogine and Résibois[3] in which X is an infinite sum of products of ψ and its derivatives at $z=0$. We rather chose to derive recursion relations for the λ expansion of complete X in which all terms belonging to different ψ's are mixed together. The resulting recursion will enable us to make a direct connection with the Bogoliubov theory.

Together with (5.6), Eq. (5.5) also expresses the operator X. Define therefore an operator $\hat{O}$ by

$$\rho''(\{\mathbf{k}\}, t) = \hat{O}(\{\mathbf{k}\})\rho_0(t). \tag{5.22}$$

Comparing with (5.5), the $\{\mathbf{k}\}$ dependence being from now on tacitly understood,

$$\hat{O} = C + \sum_1^\infty \frac{i^\nu}{\nu!} C^{(\nu)} X^\nu, \tag{5.23}$$

where we used

$$\partial^\nu \rho_0 / \partial t^\nu = X\cdots X\rho_0(t) = X^\nu \rho_0(t). \tag{5.24}$$

Now consider the λ expansion of each $\hat{O}$:

$$\hat{O} = \sum_1^\infty \lambda^M \hat{O}_M, \tag{5.25}$$

$$\hat{O}_M = C_M + \sum_{\nu=1}^\infty \frac{i^\nu}{\nu!} \sum_{n=1}^{M} C_{M-n}{}^{(\nu)}[X^\nu]_M. \tag{5.26}$$

All we need to know about X at this stage is that [cf. Eq. (4.7)] its expansion starts with λ^2:

$$X = \sum_2^\infty \lambda^n [X]_n. \tag{5.27}$$

The interpretation of the z derivative of C is quite important. We have shown above the meaning of $\mathcal{P}(z=+i0)$ in the ordinary space [cf. (4.4), (5.8)–

[21] J. Stecki, J. Chem. Phys. **40**, 1197 (1964).
[22] Ref. 1, Chap. 7, p. 161, par. 8.

(5.10)]. Its derivatives in the **k** space are

$$(\partial^\nu/\partial z^\nu)_{z=+i0}(\sum \mathbf{k}_j\mathbf{v}_j-z)^{-1}=\nu!(\sum k_j v_j-z)^{-\nu-1}\,|_{z=+i0}, \tag{5.28}$$

and we notice that

$$\langle\{\mathbf{k}\}\,|\,[\mathcal{P}(+i0)]^\nu\,|\,\{\mathbf{k}\}\rangle=[\langle\{\mathbf{k}\}\,|\,\mathcal{P}(+i0)\,|\,\{\mathbf{k}\}\rangle]^\nu. \tag{5.29}$$

Hence we can interpret the z derivative as

$$\langle\{k\}\,|\,[\mathcal{P}(+i0)]^\nu\,|\,\{k\}\rangle = \frac{(-i)^\nu}{(\nu-1)!}\left(\frac{d^{\nu-1}}{dz^{\nu-1}}\right)_{z=+i0}(\sum \mathbf{k}_j\cdot\mathbf{v}_j-z)^{-1}. \tag{5.30}$$

Using the simplified notation of (5.13) or (5.14), we can write

$$C_1^{(1)}\sim\mathcal{P}\mathcal{P}\delta K_N\ (\nu=1), \tag{5.31}$$

$$C_1^\nu\sim\mathcal{P}^{\nu+1}\delta K_N. \tag{5.32}$$

In general $C_n^{(\nu)}$ can be constructed by following the rules for differentiating a multiple product; however, it verifies the following remarkably simple recursion:

$$C_n^{(\nu)}\sim\mathcal{P}\delta K_N C_{n-1}^{(\nu)}+i\nu\mathcal{P}C_n^{\nu-1},\qquad \nu\geq 1,\ n\geq 2. \tag{5.33}$$

For $n=1$ and $\nu=0$, (5.32) and (5.14) are to be used, respectively. Now taking (5.26), introducing the restrictions $M\geq 2\nu+1$, $[X]^{m\nu}=0$ unless $m\geq 2$, applying the recursion for C's and separating out the **X** farthest to the right, by

$$[X^\nu]_n=[X^{\nu-1}X]_n=\sum_{m=2}^{n-2\nu+2}[X^{\nu-1}]_{n-m}[X]_m, \tag{5.34}$$

we find after some algebra the final recursion relation in the abbreviated notation

$$\hat{O}_M=\mathcal{P}\delta K_N\hat{O}_{M-1}-\mathcal{P}\sum_{m=2}^{M-1}O_{M-m}[X]_m. \tag{5.35}$$

The first term gives the ICA, Eq. (5.14); the second term contains $\hat{O}$ to the lower order and $[X]_m$ which is to be represented by (5.6) in terms of $O_{m-1}(\{k\}_\gamma)$, where $\{k\}_\gamma$ contains two nonzero vectors:

$$[X]_m=\langle\{0\}\,|\,\sum_{i<j}\theta_{ij}\,|\,\{\mathbf{k}_i,\mathbf{k}_j,O,\cdots\}\rangle \times\hat{O}_{m-1}(\{\mathbf{k}_i,\mathbf{k}_j,O,\cdots\}). \tag{5.36}$$

Thus, in principle, the recursion (5.35) enables one to find explicitly X and $O(\{k\})$ to any desired approximation. Now we could consider O_M as a matrix element of a corresponding operator in the ordinary space, thus putting

$$\hat{O}_M(\{k\}_\gamma)\equiv\langle\{k\}_\gamma,O,\cdots\,|\,\hat{O}_M'\,|\,\{0\}\rangle, \tag{5.37}$$

and try to find a recursion relation for $\hat{O}_M'$. However, this will not be done because we show that (5.35) in the ordinary space is exactly the general recursion derived from the Bogoliubov theory.

VI. THE BOGOLIUBOV THEORY

This remarkable theory was proposed as early as in 1946. After having derived the set of BBGKY equations, (2.14), Bogoliubov noted that the macroscopic transport equations are closed differential equations for $F_1(p, r, t)$, where in the set (2.14), $\partial_t F_1$ depends on F_2, $\partial_t F_2$ depends on F_3, etc. Next Bogoliubov considered the simple-minded expansion in powers of t (thus around $t=0$) and demonstrated it to be entirely inappropriate in case one is interested in times of much larger order than the collision time. He then proceeded to formulate his theory in uniquely defined mathematical terms. In the Bogoliubov theory, which is really an algorithm for approximate solution of the BBGKY hierarchy by successive approximations, two basic assumptions are made:

(A) $F_s(t)$ is a functional of $F_1(t)$ and the whole time dependence of F_s is lodged in F_1's.

(B) The "boundary condition" discussed below is satisfied; for homogeneous systems it reads

$$\dot{S}_{-\tau}F_s(x_1,\cdots,x_s;t)\to\prod_1^s F_1(p_j,t)\quad\text{as}\quad\tau\to+\infty. \tag{6.1}$$

As Bogoliubov pointed out, these assumptions depend upon (i) separation of time scales ($t\gg t_{\text{collision}}$ in the simplest case) and (ii) weakening of correlations with the increased spatial distance. By the latter it is meant that as the positions $\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_s$ in $F_s(x_1,\cdots,x_s)$ tend further and further apart, the function F_s becomes "uncorrelated," i.e., it approaches a product $F_1(x_1)F_1(x_2)\cdots$ which represents a probability of independent events. This is a simple and physically quite obvious assumption. It is incorporated into (6.1) as

$$\dot{S}_{-\tau}F_s\equiv\exp(-\tau K^0)F_s(\{\mathbf{p}_j\},\{\mathbf{r}_j\};t) =F_s(\{p_j\},\{r_j-v_j\tau\}). \tag{6.2}$$

Clearly, as τ increases, positions r are separated from one another. The boundary condition also incorporated the causality principle by the choice of signs in $\tau\to\infty$, $\exp(-\tau\cdots)$. As mentioned in Sec. III, the causality principle poses no difficulty in the "initial value problem"; here, however, one is dealing with differential equations and at time t (as we shall see below) already away from $t=0$, and some care has to be exercised.

Bogoliubov actually developed his theory in two versions: either expansions in powers of $c=N/V$ or expansions in powers of λ were used. The c version was used by Bogoliubov to rederive Boltzmann equation, by Choh and Uhlenbeck[20] to derive the next, ternary collision term, and was also considered by Cohen,[23] who simplified the Choh and Uhlenbeck result

[23] E. G. D. Cohen, Physica **28**, 1025, 1045, 1060 (1962).

to an expression which was proven by Résibois[19] to be exactly equivalent to the ternary collision term in the I.C.A. The λ expansion was used in application to plasmas; notably Guernsey[8] showed that it can be used to rederive the Balescu–Lenard kinetic equation for a homogeneous electron plasma in a positive background. The latter was obtained by Balescu[7] from Prigogine theory and independently by Lenard,[8] who solved the integral equation for the screened potential proposed by Bogoliubov. Guernsey[24] also applied the λ version in considering the two-particle correlation function and arrived at the results identical with those obtained from Prigogine theory by Balescu and Taylor.[7] There was one notable attempt at studying the boundary condition[25] in which also general relations for the c version, valid to all powers of c, have been derived.

Having in view an evaluation of the Bogoliubov theory within the framework of the Prigogine–Résibois general kinetic equations, we considered the λ version, expecting the comparison to be easier because the Prigogine theory is based on an infinite λ expansion.

Another aspect of the comparison of these theories should also be explained. As we indicated above, the Prigogine theory is based upon a detailed study of the solutions of the Liouville equation; the resulting multitude of terms is classified and there results a "hierarchy of approximations." Definite mathematical properties of the functions involved are presupposed; however, in dealing with applications one can always generalize a detail of the treatment or use a more general set of equations. And the most general kinetic equations are identities (for large isolated systems) including every possible term in the λ expansion of the causal solution of the Liouville equation.[26] On the other hand, the Bogoliubov theory does not lend itself to generalizations. The basic assumptions (A) and (B) restrict the results, in words of Bogoliubov, to a "particular solution." Once these assumptions are made and the mathematical formalism (unequivocally given by Bogoliubov) is adopted, the final and most general result (in form of kinetic equations) at which one can possibly arrive, is set once and for all.

In view of these differences in the approach as well as in view of the mathematical formulation being so very different, we decided to study the *results* to which Bogoliubov procedure leads, rather than discuss the Bogoliubov assumptions. In the latter case one is led to discuss the physical arguments which Bogoliubov gave to make his assumptions plausible and thus to leave the firm ground of mathematics for more or less vague speculations.[27]

Therefore we derive first the most general results to which the mathematical procedure set by Bogoliubov can lead. We follow closely the treatment in Ref. 10, using the same compact notation. Bogoliubov used the F_s functions defined by (2.21) rather than f_s. Then, with the use of (2.7), the BBGKY hierarchy (2.14) reads

$$(\partial_t+K_s^0)F_s=\lambda\delta K_sF_s+\lambda c\int dx_\alpha\sum_{i=1}^{S}\theta_{i\alpha}F_{s+1}(\{S\},\alpha), \tag{6.3}$$

where the variable labeled α is a dummy variable which is integrated over. The assumption (A) means that one can obtain F_s by an action of an appropriate operator on $F_1(t)$. It might be different for different s. Also, F_1 of different variables: $F_1(x_1, t)$, $F_1(x_2, t)$, $\cdots$ can appear. We can write this down as

$$F_s(t)=\Omega_s'\{F_1(x_j, t)\}. \tag{6.4}$$

Also Ω_s' are time-independent operators. Now the Bogoliubov expansion

$$F_s=F_s^0+\sum_1^\infty\lambda^nF_s^n \tag{6.5}$$

is *the expansion of the time-independent operators* Ω' in powers of λ. For the particular case $s=2$, one obtains automatically from (6.3) a λ expansion of the time derivative ∂_tF_1:

$$\partial_tF_1(j)=A_0(j)+\sum_1^\infty\lambda^nA_n(j), \tag{6.6}$$

$$A_0(j)\equiv-K_1^0(j)F_1(j), \tag{6.7}$$

$$A_n(j)\equiv c\int dx_\alpha\theta_{j\alpha}F_2^{n-1}(j,\alpha), \qquad n\geq1. \tag{6.8}$$

We cannot yet substitute our expansion into (6.3) because the time derivative ∂_tF_s has to be expanded also. Bogoliubov introduced for this purpose his D operators which allow us to write formally

$$\partial_tF_s=\sum_0^\infty\lambda^mD_mF_s, \tag{6.9}$$

where D^m is defined by a description: differentiate (6.4) with respect to t and substitute the λ^m term of (6.6) for $\partial_tF_1(t)$ (for each j). Thus we can write:

$$\partial_tF_s=\sum_0^\infty\sum_0^\infty\lambda^{n+m}D_mF_s^n, \tag{6.10}$$

$$\partial_tF_s^n=\sum_j\frac{\delta F_s^n}{\delta F_1(j)}\cdot\frac{\partial F_1(j)}{\partial t}=\sum_j\frac{\delta F_s^n}{\delta F_1(j)}\sum_0^\infty\lambda^mA_m(j), \tag{6.11}$$

$$D_mF_s^n=\sum_j\frac{\delta F_s^n}{\delta F_1(j)}A_m(j). \tag{6.12}$$

We shall give below explicit expressions for the action

[24] R. L. Guernsey, Boeing Laboratories Technical Report D1-82-D083, 1960 (unpublished).

[25] C. F. Curtiss and H. G. Hollinger, J. Chem. Phys. **32**, 1386 (1960); H. B. Hollinger, *ibid.* **36**, 3208 (1962).

[26] A preliminary study indicates that one also can, for example, study and incorporate fluctuations (by retaining terms of the order N^{-1}) without destroying the framework of the theory.

[27] There has been an abundance of these in published and preprint literature and it is virtually impossible to quote here all comments and remarks about the Bogoliubov theory.

of D operators. Now we can use (6.5) and (6.10) in (6.3); collecting the same powers of λ we arrive at the basic set of equations:

$$(D_0+K_s^0)F_s^0=0, \tag{6.13}$$

$$(D_0+K_s^0)F_s^n=-\sum_{m=1}^{n}D_mF_s^{n-m}+\delta K_sF_s^{n-1}$$

$$+c\int dx_\alpha\sum_{i\epsilon\{s\}}\theta_{i\alpha}F_{s+1}^{n-1}(\{S\},\alpha), \tag{6.14}$$

which are solved successively as follows. Bogoliubov chose as the zeroth approximation the factorized distribution function

$$F_s^0=F_1(x_1,t)F_1(x_2,t)\cdots F_1(x_s,t). \tag{6.15}$$

This is a physical choice which is not necessitated mathematically.[28] Bogoliubov showed that it is a solution of (6.13) consistent with the boundary condition (B), Eq. (6.1). Then he showed that the solution of an equation

$$(D_0+K_s^0)F_s^n=g_s^n, \tag{6.16}$$

where the right-hand side is a functional of F_1, is

$$F_s^n=\int_0^\infty d\tau\,\exp(-\tau K_s^0)g_s^n$$

$$\times(\cdots,\{\exp[+\tau K_1^0(j)]F_1(j)\}) \tag{6.17}$$

under the boundary condition (B); g_s may stand for the right-hand side of (6.14). We now limit ourselves to homogeneous systems in which F_1 depends only on $\mathbf{p}$ and not on $\mathbf{r}$. The general relations can be found in Ref. 10.

Bogoliubov used (6.17) to derive the first approximation which reads

$$F_s'=\int_0^\infty d\tau\,\exp(-\tau K_s^0)\delta K_sF_s^0, \tag{6.18}$$

and can be rewritten on the basis of (5.8)–(5.10) as

$$F_s'=\mathcal{P}\delta K_sF_s^0. \tag{6.19}$$

On the basis of this result and of earlier calculations[8,20] we can assert that the operator Ω_s' in (6.4) operates on a product of F_1's of different variables. The latter falls into two groups; the main set of s variables, $1,\cdots,s$, and a set of l additional dummy variables which are introduced by the integral term of (6.14) or from the action of D operators, with (6.8) and are always integrated over. Because of the factor λc in (6.3) here can be at most $l=n-1$ of them and their number equals the power of c. Hence a combined λ and c expansion results. It was asserted and proved by induction[10] that

$$F_s^n=\sum_{l=0}^{n-1}c^lF_s^{nl} \tag{6.20}$$

$$F_s^{nl}=\Omega_s^{nl}(\{S\},\{l\})\prod_{j\epsilon\{S\}}\prod_{\alpha_i\epsilon\{l\}}F_1(j)F_1(\alpha_i). \tag{6.21}$$

Now the action of the D operators can be written down explicitly. We quote here only an example

$$D_nF_s^0=D_n\prod_{j\epsilon\{S\}}F_1(j)=\sum_{i\epsilon\{S\}}\prod_{j\neq i}F_1(j)A_n(i)$$

$$=\sum_{i\epsilon\{S\}}\prod_{j\neq i}F_1(j)c\int dx_\alpha\theta_{i\alpha}F_2^{n-1}(i,\alpha)$$

$$=\sum_{l=1}^{n-1}c^l\int dx_\alpha\sum_{i\epsilon\{S\}}\theta_{i\alpha}\Omega_2^{n-1,l-1}(i,\alpha)F_1(\alpha)F_1(i)$$

$$\times\prod_{j\neq i}F_1(j)\prod_{\beta\epsilon\{l-1\}}F_1(\beta). \tag{6.22}$$

When these operations are performed and the resulting expressions together with (6.22) are substituted into (6.17) and (6.14), we obtain the recursion relations determining the operators Ω_s^{nl}. For $l=0$,

$$\Omega_s^{n,0}=\mathcal{P}\delta K_s\Omega_s^{n-1,0}; \tag{6.23}$$

for $1\leq l\leq n-2$,

$$\Omega_s^{nl}=\mathcal{P}\Big[\delta K_s\Omega_s^{n-1,l}$$

$$+\int dx_\alpha\sum_{i\epsilon\{s\}}\theta_{i\alpha}(\Omega_{s+1}^{n-1,l-1}-\Omega_2^{n-1,l-1}(i,\alpha))\Big]$$

$$-\mathcal{P}\sum_{m'\geq1}\sum_{m''\geq1}\sum_{\nu'=0}^{m'-1}\sum_{\nu''=0}^{m''-1}\delta^{Kr}(m'+m'',n-1)\delta^{Kr}$$

$$\times(\nu'+\nu'',l-1)\Omega_s^{m'\nu'}\sum_{\substack{i\epsilon\{S\}\\ i\epsilon\{\nu'\}}}\int dx_\alpha\theta_{i\alpha}\Omega_2^{m''\nu''}(i\alpha); \tag{6.24}$$

and for $l=n-1$,

$$\Omega_s^{n,n-1}=\mathcal{P}\int dx_\alpha\sum_{i\epsilon\{S\}}\theta_{i\alpha}(\Omega_{s+1}^{n-1,l-1}-\Omega_2^{n-1,l-1}(i,\alpha)). \tag{6.25}$$

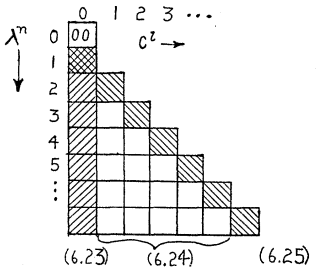
The starting equation is

$$\Omega_s^{1,0}=\mathcal{P}\delta K_s, \tag{6.26}$$

and all Ω_s^{nl} operators can be determined successively. They are essentially sums of various products of $\mathcal{P}$ and of θ_{ij}. It is instructive to consider the triangular table (Table I) resulting from allowed powers of λ and c. The outmost left column ($l=0$) corresponds to successive approximations to the evolution of s particles by themselves. More and more dummy variables, representing the scattering at given s points of the phase space with particles of the medium (hence powers of c),

[28] That is, once the boundary condition has been accepted and it has been "split" into: $\exp(-\tau K^0)F_s^0\to F_1(x,t)\cdots F_1(x_s,t)$ and $\exp(-\tau K^0)F_s^n\to0$ for each n, there is not much choice and (6.18) seems to be unique. But to say that one *derives* (6.18) is to put the cart before the horse; we take the boundary condition (B) with the "uncorrelated" F_s *as a product* and we split it as above *just because we want* the zeroth approximation to be a product, on basis of physics and experience of known kinetic equations, such as Boltzmann equation.

TABLE I. A schematic representation of Ω_s^{nl} and its recursion relations. Similarly gridded terms (boxes) are related by the indicated recursion relations.



are involved, as we move to the right of the table. The terms with maximum l for given n, i.e., $\lambda^{n+1}c^n$ are the ones retained in the Balescu–Lenard equation which described the collective motion of an electron gas. It is interesting to note that for these two opposite limiting cases separate recursions exist. Also a glance at (6.25) shows that it is indeed not very easy to generalize the Bogoliubov–Lenard[8] result, as pointed out by Guernsey,[8] by trying to include some more terms, for instance $\lambda^{n+2}c^n$. Then we see that, to take an example, the recursion for $\Omega_s^{4,2}$ involves the Ω's with superscripts (3, 2), (3, 1), (2, 1), (1, 0)—in this case all lower Ω's, and the simplicity of (6.25) is entirely lost.

Also the two separate recursions do not alter the sequence of propagators and θ operators, which is the same as in $C(z=+i0)$ or $\psi_0(z=+i0)$, i.e., $\mathcal{P}\theta\mathcal{P}\theta\mathcal{P}\theta\cdots$. The recursion (6.24) alters this sequence through the second term of it. Now if we drop this term from the recursion, the resulting recursions are very similar to the ICA recursions we derived from Prigogine theory in Sec. V. Indeed it is not difficult to show that they are exactly equivalent provided

$$\int dp^{N-s}\rho_0=\prod_{j=1}^{s}F_1(p_j,t). \tag{6.27}$$

That is, the VDF is assumed factorizable. Thus we can define H_s^n by

$$\int dp^{N-s}\hat{H}_s^n\rho_0=\sum_{l=0}^{n-1}c^l\Omega_s^{nl}\prod_{j}^{s+l}F_1(j), \tag{6.28}$$

and the left-hand side integral annihilates the superfluous F_1's of $N-s-l$ variables on which $\hat{H}_s^n$ does not act. Then we find for $\hat{H}_s^n$ exactly the earlier recursion (5.20), the starting point being

$$\hat{H}_s'=\Omega_s^{1,0}=\mathcal{P}\delta K_s, \tag{6.29}$$

and the zeroth approximation F_s^0 as before being given by (6.15) which makes the agreement complete:

$$\hat{H}_s^n=h_s^n. \tag{6.30}$$

Thus the ICA *corresponds to an approximation within the Bogoliubov theory.*[29] Therefore, now reversing the argument, the simplified recursion (6.24) together with (6.23) and (6.25), lead to kinetic equations

$$\partial_t\rho_0=i\psi_0(0)\rho_0 \tag{5.2}$$

$$\rho''(\{\mathbf{k}\},t)=C(\{\mathbf{k}\},\{0\};+i0)\rho_0(t) \tag{5.5}$$

We proceed now to show that (6.23), (6.25), and the complete recursion (6.24) lead to the complete Markovian kinetic equation for the VDF (5.1) [i.e., (4.15)] and to the full expression (5.5) for ρ'' [i.e., (5.22)–(5.24)] instead.

We note that the only difference with the ICA recursion is the presence of the second term of (6.24). The latter is composed of two terms which are similar to the second term of the recursion (5.35) derived in Sec. V. Indeed the second term, when allowed to operate on the corresponding product is F's;

$$\int dx_\alpha\theta_{i\alpha}\Omega_2^{m''\nu''}F_1(i)F_1(\alpha)\prod_{\beta\epsilon\{\nu''\}}F_1(\beta), \tag{6.31}$$

is nothing else than a term in the expansion of $\partial_t F_1(i)$ in double series $\lambda^{m''}c^{\nu''}$. It corresponds to $[X]_{m''+1}$ further expanded in a power series of c. The first part of the considered term is similarly a term in the c expansion of $\hat{O}_{M-m}$. And the rest of our recursions has been shown to correspond to ICA to which corresponds (in the abbreviated notation) the first term of the right-hand side of (5.35). Thus the structure of these recursions, (6.23)–(6.25) and (5.35) is essentially the same. The details of algebra showing their exact identity is based on the following observations. (a) The intermediate Fourier state between $\hat{O}_{M-m}$ and $[X]^m$ must be zero, by the very definitions of $\hat{O}$ and X [cf. (5.23)]. (b) Although $X\rho_0(t)$ is equal to $\partial_t\rho_0$ which contains many derivatives $\partial_t F_1(j)$, there is an implicit restriction following from integration over $N-s$ momenta in calculating any RDF F_s, namely that any term $\partial_t F(j)$ will vanish upon this integration unless the variable j is operated upon before the integration or it belongs to the final set $\{s\}$ of variables which will not be integrated upon. In the diagram language we are restricted to semiconnected diagrams. Thus, assuming again (6.27), we rewrite (5.35) as follows:

$$\hat{O}_M\backsim\mathcal{P}\delta K_N\hat{O}_{M-1}$$
$$-\mathcal{P}\sum_{m=2}^{M-1}\hat{O}_{M-m}\sum_{j\epsilon\{S\}}\partial_t F_1(j)\prod_{\substack{l\neq j\\ l\epsilon\{S\}}}F_1(l), \tag{6.32}$$

where $\{S\}$ stands for the set of variable labels appearing in $\hat{O}_{M-m}$ at least once plus the set of $\{s\}$ variables

[29] The approximation is

$$\sum_{m=1}^{n}D_mF_s^{n-m}=D_mF_s^0$$

for every n, in the right-hand side of (6.14).

whose 3-vector projections into the p space will not be integrated over. (c) The powers of c can be hidden formally by the same device we used in (6.28). Then the second term of (6.24) takes the appearance of the second term in (6.32) and the identity of (6.32) and combined (6.23)–(6.25) is apparent.

VII. DISCUSSION

To summarize the result; the set of Prigogine–Résibois Markovian equations reads

$$\partial_t \rho_0 = X\rho_0(t) \quad (X \equiv \Omega i\psi), \tag{4.15}$$

$$\rho(\{\mathbf{k}\}, t) = \rho'(\{\mathbf{k}\}, t) + \rho''(\{\mathbf{k}\}, t), \tag{4.10}$$

$$(\partial_t + i\sum \mathbf{k}_j \mathbf{v}_j)\rho'(\{k\}, t) = X_{\{k\},\{k\}}\rho'(\{k\}, t), \tag{4.16}$$

$$\rho_k'' = \int_0^t \sum_{\{k'\}} \mathfrak{C}(\{k\}, \{k'\}; \tau)\rho'(\{k'\}; t-\tau)\, d\tau. \tag{4.13}$$

When the following simplifying assumptions are introduced

$$\rho(\{k\}, t) = \rho''(\{k\}, t) \,(\rho' = 0) \quad \text{(A)}; \tag{7.1}$$

hence

$$\sum_{\{k'\}} \mathfrak{C}(\{k\}, \{k'\}, \tau) \to \mathfrak{C}(\{k\}, \{0\}; \tau); \tag{7.2}$$

and also

$$t \to \infty \quad \text{in} \quad \int_0^t d\tau \quad \text{(B)} \tag{7.3}$$

together with

$$\int dp^{N-S}\rho_0(t) = \prod_{j=1}^{s} F_1(p_j, t), \tag{6.27}$$

the following system of equations results:

$$\partial_t \rho_0 = X\rho_0 \tag{4.15}$$

$$\rho''(\{k\}, t) = \int_0^\infty d\tau \mathfrak{C}(\{k\}, \{0\}; \tau)\rho_0(t-\tau). \tag{5.4}$$

This system was shown to be strictly equivalent to the Bogoliubov theory carried on to all powers of λ in a most general way.

It is not very easy to assert the validity of the simplifying assumptions precisely because of the generality of the Prigogine–Résibois derivations and of the generality of our discussion. It seems clear to us that (B) is linked to the Markovian regime; our discussion in Sec. VI shows that (B) leads to a correct Markovian equation (4.15) and therefore it would be inconsistent to try to keep the equation for ρ'' more general while agreeing to (4.15). Thus it appears that the most serious approximation is the neglect of ρ'. These Fourier coefficients vanish as we approach the equilibrium state and they are functionals of themselves at time $t=0$. Unfortunately, no calculation of ρ' for any system has so far been made. Prigogine and Résibois discussed very briefly[3] the implications of assumption (A), (7.1). They gave arguments that, indeed, one can expect ρ' to vanish quite rapidly after times of the order of several collision times. It should be perhaps stressed that one cannot expect to reach specific conclusions which would be generally valid since the relaxation times as well as all other relevant quantities depend crucially on the intermolecular force potential. The validity of the reduction to a Markovian system of equations may depend very strongly on the particulars of the system under consideration and on the initial conditions; the latter are expressed by the destruction term D in the general equation (4.9), and it remains to be checked in each case whether really in the physical problem considered $D(t)$ is negligible. However, we have shown in full generality that *if* these assumptions can be made, then the resulting equations *are* identical whether arrived at from either the Prigogine–Résibois of the Bogoliubov theory. Conversely, our considerations show the extent of validity of the Bogoliubov theory in precise terms. The extent to which the physical conditions underlying "the Bogoliubov regime" (4.15), (5.4) are verified can be calculated or estimated in quantitative terms by making recourse to the more general Prigogine–Résibois kinetic equations, of which the Bogoliubov kinetic equations will be a particular case in any situation.