difference is negative. Triangle No. 2, on the other hand, is obtuse, with the two particles, i and j, which interact via the Lennard-Jones potential on one leg of the obtuse angle. Thus the hard core of the third particle, k, tends to push j toward i [Fig. 9(b)], so that if i and j are nearest neighbors, they see more of each other's repulsive potential. The first term of E_{03V} is larger than the second, so the difference is positive. Since obtuse and acute triangles occur in every lattice, there will always be cancellation in the sum.

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Power Series of Kinetic Theory. I. Perturbation Expansion*

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In recent years intensive efforts have been made to develop, from first principles, systematic corrections to the established kinetic equations, and thereby obtain an understanding of the approach to thermal equilibrium for arbitrary macroscopic systems. These efforts, dominated by Bogoliubov's synchronization technique and "functional assumption," have met with only partial success. In fact, the method of synchronization has been shown to lead to serious difficulties when carried beyond the lowest order results, so that an H theorem is lacking for the higher order terms. To discuss the problem in full generality, we construct in this paper the direct perturbation series (and in the follow paper, Bogoliubov's synchronized series) to *all* orders in a parameter ϵ that can be identified with the potential strength. An explicit expression is obtained for the νth-order term of the s-body distribution function and a simple, systematic graphical representation of all the terms is derived. The result is obtained by the use of a matrix formalism that allows an effective decoupling of the Bogoliubov-Born-Green-Kirkwood-Yvon equations, and thereby, for a detailed analysis of the perturbation series. Bogoliubov's basic result concerning the secular behavior of perturbation theory ($F^{12}\sim t$) is deduced here as a special case of a general theorem: The νth-order term for the s-body distribution grows for large times as a polynomial in time whose leading power is $[\nu/2]$ independent of s.

I. INTRODUCTION

THE aim of nonequilibrium statistical mechanics is to determine the evolution in time of systems containing a large number of interacting particles, and thereby describe the irreversible approach to thermal equilibrium. From the basic dynamical equations one seeks an equation of the form

$$\partial f/\partial t=A[f], \tag{1.1}$$

called the kinetic equation, where A is a functional of the one particle distribution function $f(\mathbf{x},\mathbf{p},t)$, and has no explicit time dependence. Outstanding examples of such Markovian[1] equations which correspond to different gaseous regimes, are the Boltzmann equation for neutral, dilute gases, the Landau[2] equation for weakly interacting, high-temperature systems, and the kinetic equation with Debye shielding originally discovered by Bogoliubov,[3] and referred to as the Balescu-Guernsey-Lenard equation. These equations constitute the lowest order term in expansions of Liouville's equation appropriate for the regime considered.[4] In this work we will be concerned with an expansion of the Louville equation which we shall analyze to all orders.[5]

(i) The outstanding *open problem* in nonequilibrium theory is that of determining systematically the higher order corrections to these kinetic equations, if they exist. For example, the Boltzmann equation is a valid description of dilute, short-range gases, so that only binary collisions are taken into account. This restriction has the consequence that the transport coefficients are independent of the density. Furthermore, the bulk viscosity coefficient is not given by the Boltzmann equation (it vanishes identically). However, for dense gases, ($p\geq 5$ atm, $T\sim 300°$K), the transport coefficients of monatomic gases are known to be density-dependent and the bulk viscosity is nonzero. Therefore, a more general theory is required which should yield the well-established kinetic equations in lowest approximation. If such general kinetic equations could be derived from

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a fundamental point of view, one would obtain a description of higher order effects as well as a deeper understanding of the approach to thermodynamical equilibrium. The attempts in this direction have proved to be only partially successful. A most significant contribution to this problem was made by Bogoliubov who derived the Boltzmann and Landau equations by an appropriate expansion of the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy of equations. This chain of coupled linear equations for the distribution function of an s-particle cluster F^s results from integrating the Liouville equation for the system as a whole over the phase spaces of $N-s$ particles, and then taking the limit of infinite volume with fixed denity (bulk limit). Bogoliubov demonstrated that a direct power-series expansion of F^s, in terms of an appropriate parameter, resulted in "secular" terms, i.e., correction terms that grow unbounded with time. He then exploited the existence of natural time scales in the evolution of a gas to construct a "synchronized" power series without secularities, and to derive with it kinetic equations. Expecting that after a time of the order of several collision times t_c, ($t_c \sim r_0/v_{\text{th}}$ where r_0 is the range of the interaction and v_{th} the thermal speed) there should occur a simplification in the description of the system, Bogoliubov required that the s-particle functions F^s, $s>1$, depend on time only as functionals of f ("functional assumption"). The form of the functionals is completely determined in this approach by an initial condition which expresses the assumption of molecular chaos.

(ii) We give a compact account of the *synchronization method*, to establish terminology and to give an equivalence theorem essential to our discussion. We write the BBGKY equations in the form

$$(\partial/\partial t + H^s)F^s = \epsilon L^s F^{s+1}, \tag{1.2}$$

where H is a Hamiltonian operator and L a "phase-mixing" operator to be precisely defined in Sec. II. If one substitutes into Eq. (1.2) the power series

$$F^s = \sum_\nu \epsilon^\nu F^{s\nu}, \tag{1.3}$$

and attempts to equate the powers of ϵ, the correction terms $F^{s\nu}$, $\nu \geq 2$, are found to be unbounded in time (see Sec. III).

Consider, now, the "synchronized series"

$$F^s(t) = F^s[f] = \sum_\nu \epsilon^\nu F^{s\nu}[f], \tag{1.4}$$

where the time dependence of F^s is assumed to be wholly determined by that of $F^1 \equiv f$. The time dependence of F^s is therefore expressed through the kinetic equation

$$\partial f/\partial t = A[f] = \sum_\nu \epsilon^\nu A^\nu[f] \tag{1.5}$$

and determined, together with A^ν by successive approximations. Substituting Eq. (1.4) into Eq. (1.2) and comparing with Eq. (1.5) we find for a homogeneous gas

$$A^0[f] = 0, \quad A^\nu[f] = L^1 F^{2(\nu-1)}[f]. \tag{1.6}$$

We then have for F^s

$$\frac{\partial F^s[f]}{\partial t} = \int \frac{\delta F^s[f]}{\delta f}\frac{\partial f}{\partial t} d\Gamma^1$$
$$= D^0 F^{s0}[f] + \sum_{\nu=1}\sum_k \epsilon^\nu D^k F^{s(\nu-k)}[f], \tag{1.7}$$

where $d\Gamma^1$ is the single-particle phase-space volume element and for any functional χ of f

$$D^k \chi = \int \frac{\delta \chi}{\delta f} A^k d\Gamma^1.$$

We readily obtain by using the BBGKY hierarchy, Eq. (1.2)

$$\nu = 0 \quad D^0 F^{s0}[f] + H^s F^{s0} = 0,$$
$$\nu \geq 1 \quad D^0 F^{s\nu}[f] + H^s F^{s\nu}[f]$$
$$= -\sum_{k=1}^{\nu-1} D^k F^{s(\nu-k)} + L^s F^{s+1(\nu-1)}. \tag{1.8}$$

Note that t does not appear explicitly in Eqs. (1.8) and enters $F^{s\nu}$ only through the kinetic equation. The problem reduces to determining $F^{s\nu}$ and A^ν as functionals of the arbitrary function f. Bogoliubov solves, in general, the functional equation

$$D^\circ F^{s\nu} + H^s F^{s\nu} = \chi^s[f]. \tag{1.9}$$

The solution of Eq. (1.9) is determined completely by assuming the following initial condition. Let $S^k(\tau) \equiv \exp[H^k \tau]$ be the "streaming operator" for $k \geq 2$. The initial condition reads, for a homogeneous gas

$$\lim_{\tau \to -\infty} S(\tau) F^s[f(\mathbf{p}_i, t)] = \lim_{\tau \to -\infty} S(\tau) \prod_{i=1}^{s} f(\mathbf{p}_i, t). \tag{1.10}$$

This assumption implies "molecular chaos" for the initial state of the gas. This is, in effect, a definition of the direction of time. The past is that direction in which correlations vanish and the theory describes only the evolution of the system in the direction of time in which correlations grow through collisions.[6,7] In this manner, a kinetic equation can be obtained. Bogoliubov, in fact, obtained the Boltzmann equation in first order of the expansion parameter nr_0^3, the "dilution" parameter, and the Landau equation for the lowest order in ϕ_0/kT, the effective interaction strength or "coupling" parameter. He also obtained a kinetic equation for a plasma which was later made more explicit indepen-

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dently by Balescu,[8] Lenard,[9] and Guernsey.[10] Only the first-order equations were derived in Bogoliubov's paper. The triple collision correction term to the Boltzmann equation was given by Choh and Uhlenbeck who carried out the synchronized expansion to second order.[11] The meaningfulness of this term is questionable since it cannot be shown to rigorously satisfy an H theorem. Furthermore, it has been shown that the higher order terms in Bogoliubov's expansion diverge quite generally.[12] This conclusion has generated some controversy as to the convergence of the relevant integral, but recent calculations, in particular, of the transport coefficients, show that the viscosity and diffusion coefficients for two-dimensional models correspond to logarithmically divergent quantities.[13–17] For the weak-coupling regime, Su has further discussed some of these difficulties.[18]

(iii) A departure from Bogolubov's method was developed by Sandri[4] and Frieman,[19] who rederived Bogoliubov's results by a systematic extension of the time variable to a set of multiple time scales. This *method of extension* has its origin in the "time-averaging" methods used in nonlinear mechanics[20] and in the methods of "variable stretching" used in fluid dynamics.[21–23] The method makes explicit the distinction between physical time scales as introduced by Bogoliubov. In the method of extension, the slower process in the problem, the relaxation of the one-body distribution to its thermal equilibrium value, is described by an independent "slow time variable" in contrast to the "fast time variable" which describes the "relaxation" of the multibody distributions to functionals of the one-body distribution. We show here how the equations of Bogoliubov discussed above follow from this more general point of view,[24] and thus establish an equivalence theorem, Eq. (1.14), that plays a major role in our analysis. The function $F(t)$ is replaced by an extended function $\mathbf{F}(\tau_0,\tau_1\cdots\tau_n)$, that is required to coincide with $F(t)$ when

$$\tau_0=t,\quad \tau_n=\epsilon^n t. \tag{1.11}$$

The freedom in the functional dependence of the extended function is exploited to avoid the secular terms. In fact, the condition for the removal of secular terms on the fast time scale yields the kinetic equation. The extension of the time axis given by Eq. (1.11) is equivalent to the replacement

$$\partial/\partial t=\partial/\partial\tau_0+\epsilon(\partial/\partial\tau_1)+\epsilon^2(\partial/\partial\tau_2)+\cdots. \tag{1.12}$$

Combining this with the power expansion for F^s [Eq. (1.3)] we have

$$\partial\mathbf{F}^s/\partial t=\sum_{\nu=0}\sum_{k=0}^{\nu}\epsilon^\nu(\partial\mathbf{F}^{s(\nu-k)}/\partial\tau_k). \tag{1.13}$$

Note the equivalence of Eq. (1.13) to Eq. (1.7) with

$$D^k\chi[f]=\partial\chi/\partial\tau_k. \tag{1.14}$$

The Bogoliubov limit, $\chi[f]$, is obtained from the multiple time scale function χ from the formula

$$\chi[f]=\chi(\tau_0=\infty,\,\tau_n=\epsilon^n t|\,\mathbf{f}^0), \tag{1.15}$$

where $\mathbf{f}^0$ is evaluated at $\tau_0=\infty$, $\tau_n=\epsilon^n t$ and $n>0$. We have thus obtained Bogoliubov's synchronized expansion with a more general method which makes explicit the natural time scales of the problem through the τ_k. It is informative to examine these time scales for the various physical situations. For a neutral gas (such as an inert gas) nr_0^3 is usually small and ϕ_0/kT is of order one and the Boltzmann equation is appropriate. For a "hot plasma" ("Landau gas"), $nr_0^3\sim 1$ but ϕ_0/kT is small. The lowest order equation appropriate for this regime was first given by Landau. Other regimes can be analyzed by ordering nr_0^3 and ϕ_0/kT with respect to ϵ.

(iv) The major purpose of this work is to attack the *power-series solutions in their entirety*. Attempts in this direction have, so far, been only partially conclusive.[25,26] We adopt the point of view of the variation of parameters and order nr_0^3 and ϕ_0/kT for convenience according to the weak-coupling scheme. We then proceed to construct the νth-order term in the series for both finite times and in the limit of large τ_0 which corresponds to Bogoliubov's synchronized solution. Since we are interested here in the expansion to all orders, it is necessary to use a compact operator formalism. In Sec. II we develop the BBGKY hierarchy and display for it a compact operator matrix representation which provides an effective "decoupling" of the hierarchy and thus considerably simplifies the analysis. With this formalism, the functions F^s are shown to be composed of products of the operators I and L, called, respectively, the interaction and phase-mixing operators, the "propagators" ζ, and "free-particle" distributions f_0. This suggests a diagrammatic representation, and we have employed one throughout this paper. F^s may be written directly in terms of diagrams

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and operations performed on them. In Sec. III we discuss the power series expansions of the BBGKY system to all orders. We find it unnecessary to introduce the correlation functions and we work directly with the probability densities, F^s, themselves. The direct perturbation series, Eq. (1.3), is constructed by displaying explicitly the νth-order term. The secular terms are classified in detail for any given order, which is easily done by the use of our graphs. We obtain the general solution for F^s and demonstrate that despite the appearance of the secularities, the series may be summed and compared to the formal expression for F^s obtained by a Laplace transformation of the BBGKY system. In the following paper the synchronized series is constructed exploiting its connection to the multiple-time-scale method discussed above. The use of this expansion is shown to successfully eliminate all of the secular terms. This condition corresponds to the cancellation of certain disconnected graphs, those that we call disconnected homogeneous. However, the method is shown to introduce new terms that have a highly divergent behavior. These new terms, which we call supersecularities, appear in all but the lowest order of the expansion and are given explicitly to νth order. We will also exhibit the exact formal kinetic equation of the synchronized theory in closed form. It is worth emphasizing that Bogoliubov's synchronized series which is analyzed in this work corresponds to a *very special case* of the extended series. It is our belief that the analysis of Bogoliubov's series, and of its difficulties, is a necessary preliminary for a fully satisfactory theory of irreversibility. The main results obtained in this paper are summarized in Sec. IV.

II. THE BBGKY HIERARCHY

In this section we establish the notation and develop the formal tools that are to be employed in the rest of the work. We will study the solutions of the Liouville equation with the method of variation of parameters; i.e., we shall examine the expansion of solutions in power series.

For the purpose of nonequilibrium statistical mechanics, the Liouville equation is usually rewritten in the form of the BBGKY hierarchy. This hierarchy is extremely useful in that it permits the carrying out of the limit of infinite volume (with finite density). A major feature of our analysis consists in rewriting the BBGKY hierarchy in a form that closely resembles the Liouville equation itself. This is accomplished by the introduction of some simple matrices and will allow us to exploit to advantage in the next two sections many familiar results of linear operator analysis. This new formalism is substantially simpler than any we have seen in the literature. It should be kept in mind that our main interest lies in exhibiting explicitly the nth-order term of the power series and, whenever possible, the sum and properties thereof. Of very particular interest are the asymptotic limit for large times and its interchangeability with the process of summation to all orders.

We consider a classical system of volume V containing N identical particles of mass m interacting with a repulsive pair potential $U(|\mathbf{x}_i-\mathbf{x}_j|)\equiv U_{ij}$ of finite range r_0. We assume that no external fields are present and that a specularly reflecting wall potential $w(\mathbf{x}_i)$ confines the particles to V. We will consider only the "bulk limit," i.e., $N\rightarrow\infty$, $V\rightarrow\infty$ with $n\equiv N/V$ fixed and finite. The wall potential becomes inoperative in this limit and we simply omit it. The Hamiltonian for this system is given by

$$H^N=\sum_{i=1}^{N}\frac{p_i^2}{2m}+\sum_{i<j=1}^{N}U_{ij}. \qquad (2.1)$$

The canonical equations of motion obtained from Eq. (2.1) are

$$\dot{\mathbf{x}}_i=\frac{\mathbf{p}_i}{m}\quad \dot{\mathbf{p}}_i=-\sum_{i<j=1}^{N}\frac{\partial U_{ij}}{\partial \mathbf{x}_i}. \qquad (2.2)$$

We normalize the probability density in the $6N$-dimensional phase space, F^N, by

$$\int\frac{d\mathbf{x}_1}{V}d\mathbf{p}_1\cdots\frac{d\mathbf{x}_N}{V}d\mathbf{p}_N\quad F^N(\mathbf{x}_1,\mathbf{p}_1\cdots\mathbf{x}_N\mathbf{p}_N,t)=1. \qquad (2.3)$$

The Liouville theorem written in terms of the time derivative that "follows the motion" is

$$DF^N/Dt=0, \qquad (2.4)$$

or, in terms of Poisson brackets

$$\partial F^N/\partial t=\{H^N,F^N\}=\sum_{i=1}^{N}[(\partial H^N/\partial\mathbf{x}_i)\cdot(\partial F^N/\partial\mathbf{p}_i) -(\partial H^N/\partial\mathbf{p}_i)\cdot(\partial F^N/\partial\mathbf{x}_i)]. \qquad (2.5)$$

Inserting Eqs. (2.1) and (2.2) into Eqs. (2.5), we obtain

$$\partial F^N/\partial t=-\sum_{i=1}^{N}\mathbf{v}_i\cdot\partial F^N/\partial\mathbf{x}_i+1/m\sum_{\substack{1\le i\le N\\ i<j}} \times\left[(\partial U_{ij}/\partial\mathbf{x}_i)\cdot\left(\frac{\partial F^N}{\partial\mathbf{v}_i}\right)+(\partial U_{ij}/\partial\mathbf{x}_j)\cdot(\partial F^N/\partial\mathbf{v}_j)\right]. \qquad (2.6)$$

It is convenient to introduce the operators I, K, and H where I_{ij} is the two-particle interaction operator given by

$$I_{ij}=\frac{1}{m}(\nabla_i U_{ij}\cdot\nabla_{vj}+\nabla_j U_{ij}\cdot\nabla_{vj}). \qquad (2.7)$$

K_i is the one-particle kinetic energy operator given by

$$K_i=\mathbf{v}_i\cdot\nabla_i$$

and H^s is the Hamiltonian operator for s bodies

$$H^s = K^s - I^s. \tag{2.8}$$

The s-body kinetic energy and interaction generators are

$$K^s = \sum_{i=1}^{s} K_i \quad \text{and} \quad I^s = \sum_{i<j}^{s} I_{ij} \; 1 \le s \le N. \tag{2.9}$$

The Liouville equation may now be written as

$$\partial F^N/\partial t + H^N F^N = 0. \tag{2.10}$$

To derive the BBGKY hierarchy, we now introduce the s particle distribution functions F^s by

$$F^s(\mathbf{x}_1\mathbf{v}_1\cdots\mathbf{x}_s\mathbf{v}_s,t) = \int F^N(d\mathbf{x}_{s+1}/v) \times (dp_{s+1})\cdots(d\mathbf{x}_N/V)(d\mathbf{p}_N). \tag{2.11}$$

Integrating Eq. (2.10) over the phase space of all but s of the particles, and using Eq. (2.11), we obtain the hierarchy of coupled equations

$$\partial F^s/\partial t + H^s F^s = [(N-s)/Vm] \times \int d\mathbf{x}_{s+1} d\mathbf{p}_{s+1} \sum_{i=1}^{s} \nabla_i U_{i(s+1)} \cdot \nabla_{vi} F^{s+1}. \tag{2.12}$$

We introduce the "phase-mixing" operator L^s by the definitions

$$L^s = \sum_{i=1}^{s} L_{is+1} \; L_{is+1} = \frac{1}{m} \int d\mathbf{x}_{s+1} d\mathbf{v}_{s+1} \nabla_i U_{is+1} \cdot \nabla_{vi}. \tag{2.13}$$

The BBGKY hierarchy may now be written in the compact form

$$\frac{\partial F^s}{\partial t} + H^s F^s = \frac{N-s}{V} L^s F^{s+1}. \tag{2.14}$$

The left-hand side of Eq. (2.14) constitutes the Liouville equation for an s-particle subsystem. The right-hand side, however, is not zero but gives the interaction of the subsystem with the other N-s particles. It requires the distribution function F^{s+1} because the interaction potential is assumed to be a two-body force.

We now take the bulk limit to guarantee an infinite Poincaré recursion time. After the bulk limit is carried out, the BBGKY equations are still invariant under time reversal. These are now given by

$$\partial F^s/\partial t + H^s F^s = n L^s F^{s+1}. \tag{2.15}$$

A. Matrix Formulation of the BBGKY Equations

We would like to make explicit in Eq. (2.15) the parameters discussed in Sec. I. This may be accomplished by making Eq. (2.15) dimensionless with r_0 as the unit of length, $V_{\text{th}} = (kT/m)^{1/2}$ as the unit of velocity and ϕ_0 as the unit of interaction energy. Utilizing the definition of F^s [Eq. (2.11)] and the normalization [Eq. (2.3)], we readily obtain the dimensionless form of Eq. (2.15)

$$\frac{\partial F'^s}{\partial t'} + K'^s F'^s - \frac{\phi_0}{kT} I'^s F'^s = (nr_0^3)\left(\frac{\phi_0}{kT}\right) L'^s F'^{s+1}, \tag{2.16}$$

where the primes have been introduced to denote dimensionless quantities, e.g.,

$$K' = \frac{r_0}{v_{\text{th}}}\left(\mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{x}_i}\right).$$

Since we shall be dealing only with the dimensionless equation (2.16) we omit the primes below. Introducing the ordering of the parameters by $nr_0^3 \sim 1$, $\phi_0/kT \sim \epsilon$, the BBGKY equations become

$$\partial F^s/\partial t + K^s F^s = \epsilon I^s F^s + \epsilon L^s F^{s+1}. \tag{2.17}$$

We shall treat Eq. (2.17) extensively with the method of variation of parameters. For this purpose, it is convenient to make the s dependence in Eq. (2.17) implicit. Let

$$F = \begin{pmatrix} F^1 \\ F^2 \\ \vdots \\ F^s \\ \vdots \end{pmatrix} \qquad \mathbf{K} = \begin{bmatrix} K^1 & & & & \\ & K^2 & & & \\ & & \ddots & & \\ & & & K^s & \\ & & & & \ddots \end{bmatrix}$$

$$\mathbf{I} = \begin{bmatrix} I^1 & & & & \\ & I^2 & & & \\ & & \ddots & & \\ & & & I^s & \\ & & & & \ddots \end{bmatrix} \qquad \mathbf{L} = \begin{bmatrix} 0L^1 & & & & \\ & 0L^2 & & & \\ & & 0L^3 & & \\ & & & \ddots & \\ & & & & 0L^s \\ & & & & & \ddots \end{bmatrix}.$$

We then write the BBGKY hierarchy in the useful matrix form

$$\partial F/\partial t + \mathbf{K} F = \epsilon \mathbf{T} F, \tag{2.18}$$

where

$$\mathbf{T} \equiv \mathbf{I} + \mathbf{L}. \tag{2.19}$$

The form Eq. (2.18) of the BBGKY hierarchy closely resembles the Liouville equation itself, Eq. (2.10). This feature will be exploited at length in the following development.

B. Formal Solution of the BBGKY Hierarchy

The solution of Eq. (2.19) can be written as

$$F(t) = [\exp(-\mathbf{K}t + \epsilon \mathbf{T}t)] F(0) = \mathbf{U}(t) F(0). \tag{2.20}$$

It will be useful to have an alternative representation for this result. Let

$$\phi \equiv [\exp(\mathbf{K}t)] F(t).$$

Then Eq. (2.18) becomes

$$\phi=\epsilon T(t)\phi,\quad T(t)=\exp(\mathbf{K}t)\mathbf{T}\exp(-\mathbf{K}t). \tag{2.21}$$

Expanding ϕ in a power series

$$\phi=\phi_0+\epsilon\phi_1+\epsilon^2\phi_2+\cdots, \tag{2.22}$$

we find $[\phi_0=F(0)]$

$$\phi_n(t)=\int_0^t dt_1\int_0^{t_1}dt_2\cdots\int_0^{t_{n-1}}dt_n \times[T(t_1)T(t_2)\cdots T(t_n)]F(0)$$
$$=\frac{1}{n!}\int_0^t dt_1\int_0^t dt_2\cdots\int_0^t dt_n\, P \times[T(t)\cdots T(t_n)]F(0), \tag{2.23}$$

where P is the chronological operator. We can, therefore, rewrite the formal solution of the BBGKY hierarchy as

$$\phi(t)=P\left[\exp\epsilon\int_0^t T(\lambda)d\lambda\right]F(0). \tag{2.24}$$

We readily obtain for the evolution operator

$$\mathbf{U}(t)=[\exp(-\mathbf{K}t)]P \times\exp\left[\epsilon\int_0^t \exp(\mathbf{K}\lambda)\mathbf{T}\exp(-\mathbf{K}\lambda)d\lambda\right]. \tag{2.25}$$

Equation (2.25) will be useful for analyzing the power series for finite times.

C. Asymptotic Behavior of the Distribution Functions

In nonequilibrium theory, we are particularly interested in the long-time asymptotic behavior of the distribution functions. We shall now analyze this limit. Introduce the Laplace transforms

$$\mathcal{L}\tilde{F}=\int_0^\infty e^{-pt}F(t)dt, \tag{2.26}$$

$$\mathcal{L}\tilde{F}=(\mathcal{L}\mathbf{U})F(0).$$

From Eq. (2.19) we find

$$\partial\mathbf{U}/\partial t+\mathbf{K}\mathbf{U}=\epsilon\mathbf{T}\mathbf{U}, \tag{2.27}$$

or by Laplace-transforming Eq. (2.27)

$$\mathcal{L}\mathbf{U}=\frac{1}{p+\mathbf{K}}\mathbf{U}(0)+\frac{1}{p+\mathbf{K}}\epsilon\mathbf{T}\mathcal{L}\mathbf{U}. \tag{2.28}$$

We have, however,

$$\mathbf{U}(0)=1,\quad \mathbf{K}\mathbf{U}(0)=0. \tag{2.29}$$

Therefore, we can write explicitly

$$\mathcal{L}\mathbf{U}=\left[1-\frac{1}{p+\mathbf{K}}\epsilon\mathbf{T}\right]^{-1}\frac{1}{p}, \tag{2.30}$$

or, for the Laplace transformed distribution,

$$\mathcal{L}\tilde{F}=\left[1-\frac{1}{p+\mathbf{K}}\epsilon\mathbf{T}\right]^{-1}\frac{F(0)}{p}. \tag{2.31}$$

The time-asymptotic limit of the distribution function F^* is obtained as usual from

$$\lim_{p\to0}p\mathcal{L}\tilde{F}=\lim_{t\to\infty}F(t)=F^*.$$

We therefore obtain from Eq. (2.31)

$$F^*=[1-\epsilon\zeta^*\mathbf{T}]^{-1}F(0), \tag{2.32}$$

where ζ^* is an inverse of $\mathbf{K}$ defined by

$$\zeta^*\equiv\int_0^\infty\exp(-\mathbf{K}\lambda)d\lambda=\lim_{t\to\infty}\int_0^t\exp(-\mathbf{K}\lambda)d\lambda. \tag{2.33}$$

We will show in the next section that substituting a power series

$$F=\sum_\nu \epsilon^\nu F^\nu$$

into the BBGKY hierarchy, Eq. (2.18) yields asymptotically for large times

$$F^\nu\underset{t}{\sim}[\zeta^*\mathbf{T}]^\nu F(0). \tag{2.34}$$

Inserting this result into the power series, we find

$$\sum_\nu \epsilon^\nu F^{\nu *}=[1-\epsilon\zeta^*\mathbf{T}]^{-1}F(0), \tag{2.35}$$

which coincides exactly with the result of Eq. (2.32). This shows that the interchange of the limits implied in Eq. (2.35) does not, *per se*, lead to difficulties. We are now in possession of the tools needed for the analysis of a direct expansion in the parameter ϵ.

III. DIRECT PERTURBATION EXPANSION

In this section we discuss the power seires in ϵ that satisfies the BBGKY hierarchy for vanishing initial correlations. This choice of the initial conditions corresponds to assuming molecular chaos at the initial time. Since the BBGKY hierarchy is time-translation–invariant, the particular selection made below of the initial time ($t=0$) is merely a matter of convenience.

Our main purpose in this section is to establish the degree of secularity that occurs at any order in ϵ. A convenient graphical representation of the perturbation-theoretic results is constructed. It will be shown that the nth-order term can be constructed from simple rules for the s-body distribution function.

A. The Asymptotic Series for Large Times

We utilize the Taylor expansion [Eq. (1.3)] for F which is taken to satisfy Eq. (2.18). In zero order we obtain the equation

$$\partial F^0/\partial t + \mathbf{K}F^0 = 0$$

whose solution can be written as

$$F^0(t) = \exp(-\mathbf{K}t \exp(-\mathbf{K}t)F^0(0). \qquad (3.1)$$

For a spatially homogeneous gas, we have

$$K_1 f^0 = \frac{\mathbf{p}_i}{m}\cdot\frac{\partial}{\partial \mathbf{x}_i} f^0(\mathbf{v}_i) = 0$$

and therefore

$$\partial f^0/\partial t = 0. \qquad (3.2)$$

As stated above, we confine ourselves to a "simple initial value problem" by requiring that all initial correlations vanish. That is,

$$F^s(0) = F^{s0}(0) = \prod^s f^0. \qquad (3.3)$$

The f^0 are "free-particle" functions. Equations (3.1) yield

$$F^{s0}(t) = \prod^s f^0 = F^{s0}(0). \qquad (3.4)$$

The νth-order equation is (the order of the perturbation expansion is always denoted by a Greek letter)

$$\partial F^\nu/\partial t + \mathbf{K}F^\nu = \mathbf{T}F^{\nu-1}. \qquad (3.5)$$

The solution of Eq. (3.5) is for all t

$$F^\nu(t) = \int_0^t \exp(-\mathbf{K}\lambda)\mathbf{T}F^{\nu-1}(t-\lambda)d\lambda. \qquad (3.6)$$

The time-asymptotic form of this function is best obtained directly from Eq. (3.5). Since $\mathbf{T}$ and $\mathbf{K}$ describe either short-range collisions or inertial motion, the asymptotic value

$$F^\nu(t) \underset{t}{\sim} F^{\nu *}$$

is well defined (in particular, it does not contain oscillatory terms). Equation (3.5) then yields ($\partial F^{\nu *}/\partial t = 0$)

$$\mathbf{K}F^{\nu *} = \mathbf{T}F^{\nu-1 *} \qquad (3.7)$$

whose solution is

$$F^{\nu *} = \mathbf{K}^{-1}\mathbf{T}F^{\nu-1 *}. \qquad (3.8a)$$

From the initial conditions chosen above, we readily see that the appropriate inverse of $\mathbf{K}$ is the operator ζ^* defined by Eq. (2.33). We thus, can rewrite Eq. (3.7) as

$$F^{\nu *} = \zeta^* \mathbf{T} F^{\nu-1 *},$$

which, by simple induction, reduces to

$$F^{\nu *} = (\zeta^*\mathbf{T})(\zeta^*\mathbf{T})F^{\nu-2 *}$$
$$= [\zeta^*\mathbf{T}]^\nu F^0. \qquad (3.8b)$$

To prepare our general analysis of the secularities of the power series, we prove in the next few paragraphs several useful lemmas.

B. Lemmas

To raise an operator to a power and to avoid confusion with the cluster superscripts, we shall always include the operator within square brackets [cf. Eq. (3.8)].[27] We rewrite Eq. (3.8) as

$$F^{\nu *} = [\zeta^*(\mathbf{I}+\mathbf{L})]^\nu F^0. \qquad (3.9)$$

We use the case $\nu = 2$ for illustration. It will be immediately clear that the extension to arbitrary ν is straightforward. We have

$$F^{2*} = ([\zeta^*\mathbf{I}]^2 + [\zeta^*\mathbf{L}]^2 + \zeta^*\mathbf{L}\zeta^*\mathbf{I} + \zeta^*\mathbf{I}\zeta^*\mathbf{L})F^0. \qquad (3.10)$$

These general results are consequences of the spatial homogeneity assumed for the gas.

Lemma 1: $\mathbf{L}F^0 = 0$

For the two-body function F^{20} we have

$$L^1 f_1^0 f_2^0 = \int d\mathbf{x}_2 d\mathbf{v}_2 \nabla_1 U_{12}\cdot\nabla_{v1} f_1^0(\mathbf{v}_1) f_2^0(\mathbf{v}_2)$$
$$= -\int d\mathbf{x}_2 d\mathbf{v}_2 \nabla_2 U_{12}\cdot\nabla_{v1} f_1^0 f_2^0$$
$$= \int d\mathbf{x}_2 d\mathbf{v}_2 U_{12} \nabla_{v1}\cdot\nabla_2 f_1^0 f_2^0$$
$$= 0, \qquad (3.11)$$

where we have set to zero the surface terms at infinity and made use of spatial homogeneity in the integration by parts. The extension to many particles gives

$$L^s F^{(s+1)0} = 0$$

or, in terms of matrix notation

$$\mathbf{L}F^0 = 0. \qquad (3.12)$$

Lemma 2: Phase Mixing of a Free Particle Gives Zero

This result is an extension of Lemma 1 above. Note that because $\mathbf{L}$ is superdiagonal the cluster index that follows an L^s is stepped up by one. The function for F^{22}, for example, is given by

$$F^{22*} = (\zeta^* I)^2(\zeta^* I)^2 f^0 f^0 + (\zeta^* L)^2(\zeta^* I)^3 f^0 f^0 f^0.$$

We consider the second term and write it out completely in terms of particle indices. The indices on the f^0 represent the incoming particles. Phase mixing by L operators absorbs some of the indices and those remaining on the extreme left denote the outgoing particles.

[27] A superscript on a round bracket will always denote a cluster index. Subscripts are particle indices.

For $s=2$ the latter will always be chosen as 1 and 2. We have

$$\zeta_{12}^*(L_{13}+L_{23}) \times[(\zeta^*I)_{12}+(\zeta^*I)_{23}+(\zeta^*I)_{13}]f_1^0f_2^0f_3^0. \quad (3.13)$$

Consider the term

$$\begin{aligned}\zeta_{12}^*L_{13}[(\zeta^*I)_{12}f_1^0f_2^0]f_3^0 &= \zeta_{12}^*\left\{\int d\mathbf{x}_3d\mathbf{v}_3\nabla_1U_{13}\cdot\nabla_{v1}[(\zeta^*I)_{12}f_1^0f_2^0]f_3^0\right\}\\ &= \zeta_{12}^*\left\{-\int d\mathbf{x}_3d\mathbf{v}_3\nabla_3U_{13}\cdot\nabla_{v1}[(\zeta^*I)_{12}f_1^0f_2^0]f_3^0\right\}\\ &= \zeta_{12}^*\left\{\int d\mathbf{x}_3d\mathbf{v}_3U_{13}\nabla_{v1}[(\zeta^*I)_{12}f_1^0f_2^0)\cdot\nabla_3f_3^0\right\}\\ &=0,\end{aligned}$$

where we have made use of the fact that the expression in the brackets is independent of $\mathbf{x}_3$. Note that because of the subscript rule, ζ_{12}^* is simply given by

$$\zeta_{12}^*\equiv\int_0^\infty \exp[-(\mathbf{v}_1\cdot\nabla_1+\mathbf{v}_2\cdot\nabla_2)\lambda]d\lambda. \quad (3.14)$$

In the example above f_3^0 is the free particle and only particles 1 and 2 interact. This result of phase mixing on a free particle is independent of s.

Lemma 3

ζ^* acting on a "homogeneous" term (i.e., independent of position) is linearly secular. Consider, in fact, any term A in our expansion for $F^{\nu *}$ which satisfies

$$\nabla_iA=0,\quad \nabla_jA=0.$$

Then

$$\begin{aligned}\zeta_{ij}^*A&=\int_0^\infty \exp[-\mathbf{v}_i\cdot\nabla_i+\mathbf{v}_j\cdot\nabla_j)\lambda]d\lambda A\\ &=\int_0^\infty d\lambda A=\lim_{t\to\infty}\int_0^t d\lambda A\\ &=(\lim_{t\to\infty}t)A.\end{aligned}$$

C. Secularities

Homogeneous terms with the divergences discussed in Lemma 3 occur for all $F^{\nu *}$, $\nu\geq 2$ (for all terms containing an $\mathbf{L}$), and give rise to what is called a "secularity." For the one-body distribution, this secular behavior may be seen directly without the use of Lemma 3. From the BBGKY equations we have

$$\partial F^{11}/\partial t\equiv\partial f^1/\partial t=L^1f^0f^0=0$$

whence, for the simple initial-value problem

$$f^1=f^1(0)=0.$$

Therefore, the correction term to f^0 appears in second order. This is given by

$$\partial f^2/\partial t\sim L^1F^{21*}=L^1(\zeta^*I)^2f^0f^0, \quad (3.15)$$

whose integral is

$$f^2\sim f^2(0)+\int_0^t dt_1L^1(\zeta^*I)^2f^0f^0 =f^2(0)+tL^1(\zeta^*I)f^0f^0. \quad (3.16)$$

f^2 cannot be a small correction to f^0 for large times ($t\sim 1/\epsilon^2$). To see the general secular behavior, we look at $s=2$. We examine the contribution to F^{22*} given by Eq. (3.13); in particular,

$$\zeta_{12}^*[L_{13}(\zeta^*I)_{13}f_1^0f_3^0]f_2^0\equiv\zeta_{12}^*A.$$

The bracket is independent of $\mathbf{x}_2$ and also of $\mathbf{x}_3$ because of phase mixing by L_{13}. Writing out the bracket we have

$$A=\int d\mathbf{x}_3d\mathbf{v}_3\nabla_1U_{13}\cdot\nabla_{v1}\int_0^\infty \exp[-(\mathbf{v}_i\cdot\nabla_1+\mathbf{v}_3\cdot\nabla_3)\lambda]d\lambda \times(\nabla_1U_{13}\cdot\nabla_{v1}+\nabla_3U_{13}\cdot\nabla_{v3})f_1^0(\mathbf{v}_1)f_3^0(\mathbf{v}_3). \quad (3.17)$$

Consider now

$$\int_0^\infty \exp(-\mathbf{v}_{13}\cdot\nabla_{13}\lambda)d\lambda\ \nabla_{13}U_{13}(\mathbf{x}_{13}) =\int_0^\infty d\lambda\nabla_{13}U(\mathbf{x}_{13}-\mathbf{v}_{13}\lambda),$$

where $\mathbf{v}_{13}\equiv\mathbf{v}_1-\mathbf{v}_3$ and $\mathbf{x}_{13}\equiv\mathbf{x}_1-\mathbf{x}_3$.

Therefore

$$\begin{aligned}A&=\int d\mathbf{v}_{13}\nabla_{v1}\cdot(\nabla_{v1}-\nabla_{v3})f^0f^0\int_0^\infty d\lambda \times\left[\int\nabla_{13}U_{13}\cdot\nabla_{13}U(\mathbf{x}_{13}-\mathbf{v}_{13}\lambda)d\mathbf{x}_{13}\right]\\ &=\int d\mathbf{v}_{13}\nabla_{v1}\cdot(\nabla_{v1}-\nabla_{v3})f^0f^0\int_0^\infty d\lambda\ g(\mathbf{v}_{13}\lambda). \quad (3.18)\end{aligned}$$

We see that A is spatially homogeneous and ζ_{12}^*A is secular. This demonstration for $s=2$, $\nu=2$ may be seen to hold for general value s of s by simply adding free particles to the expression for A. For higher values of ν we obtain a similar result plus other terms that increase as higher powers of t. For νth order the greatest secularity is of the form $t^{[\nu/2]}$ where $[\nu/2]$ is the integer part of $\nu/2$. At a given order of the perturbation expansion all the powers lower than the maximum can occur. We shall give in the next subsection a complete classification of secularities by means of a graphical analysis. One may write expressions for $F^{s\nu}$ directly in terms of the graphs and use them exclusively if desired. One gains in convenience and insight into the behavior of the various terms, and a one to one correspondence to the algebra is maintained by appropriate rules.

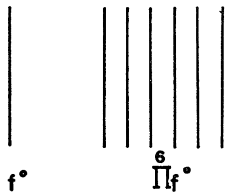


FIG. 1. Free particles.

D. Graph Theory

The components of the asymptotic limit for F^ν are f^0, I, L, and ζ^*. These are represented as follows:

(1) Vertical undirected straight lines represent f^0 and $\prod^s f^0$ (Fig. 1).

(2) The two-particle "propagation function" ζ^*_{ij} is denoted by two directed lines and the general s-particle propagator ζ^{*s} by the combination of Fig. 2.

(3) The "interactions" I_{ij} are represented by a horizontal line. For example, $\zeta^*_{ij}I_{ij}f_i^0f_j^0$ is represented in Fig. 3. Remember that we have only two-body interactions so that

$$I^s=\sum_{i<j}^{s} I_{ij}=\sum_{i<j}^{s} I_{ji}.$$

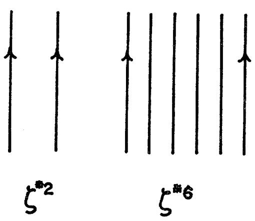


FIG. 2. Propagators.

(4) The "phase-mixing" operator

$$L^1=\int d\mathbf{x}'d\mathbf{v}'\nabla U(\mathbf{x}-\mathbf{x}')\cdot\nabla_v$$

is represented by a horizontal line with a cross indicating the phase mixed variable. Thus, $L'(\zeta^*I)^2f^0f^0$ is represented in Fig. 4. A graph such as the one in Fig. 4 is called a "skeleton." It gives the form of the term but does not tell which particle is phase mixed. A complete graph is a labeled one as shown in Fig. 5. There is a one-to-one correspondence between complete graphs and the terms of the perturbation expansion.

From our general expression for $F^{\nu*}$, i.e.,

$$F^{\nu*}=[\zeta^*(\mathbf{I}+\mathbf{L})]^\nu F^0,$$

we see that a term of order ν will have the following

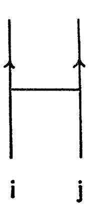


FIG. 3. Two-particle interaction.

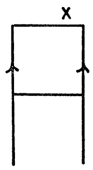


FIG. 4. Skeleton for $L\zeta^*If^0f^0$.

properties. $n(0)$ is the number of times that the operator O appears in the term considered and the symbols I, L, and ζ^* represent either matrices or their elements.

$$n(I)+n(L)=\nu. \qquad (3.19)$$

$$n(\zeta^*)=\nu. \qquad (3.20)$$

"Every interaction is followed by a single propagator."

The operator product is read from right to left. (3.21)

These simple properties facilitate the construction of terms to any order. The alternation rule, Eq. (3.21), can also be expressed by saying that horizontal lines (interactions) can touch no more than two-particle lines. This property is the defining property of "normal" graphs. Abnormal graphs that violate this property will appear in the following paper and will be shown to give rise to divergent terms that we call "supersecularities." We do not discuss here in detail time derivatives

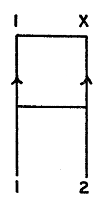


FIG. 5. $L_{12}\zeta_{12}^*I_{12}f_1^0f_2^0$.

of the distribution functions and their graphs, since these quantities play no basic role in the direct perturbation expansion. For the study of the synchronized series, however, time derivatives are crucial. We shall see in the following paper that rules similar to those of Eqs. (3.19)–(3.21) and Eqs. (3.24)–(3.25) are easily constructed for the time derivatives as well.

There are two more useful terms to define: *connected graphs* and *homogeneous graphs*. A connected graph has no free particles in it.

Figure 6(a) is a disconnected graph while 6(b) is connected. Figure 6(a) is also a particular type of disconnected graph called "disconnected homogeneous." Its connected part is just the graphical display of the A given by Eq. (3.17) and used to illustrate a secular

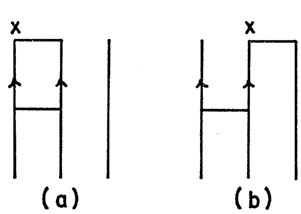


FIG. 6. Skeletons for $L^*If^0f^0f^0$.

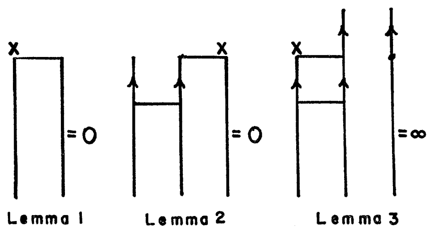
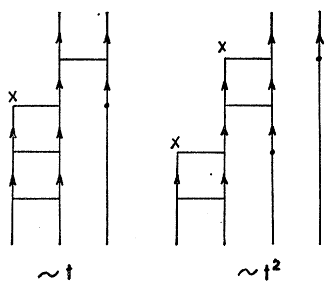


FIG. 7. Lemmas of III B.

behavior. $A=L_{13}(\zeta^*I)_{13}f_1{}^0f_3{}^0f_2{}^0$ which corresponds to Fig. 6(a) with the particles labeled 3, 1, 2, respectively. All graphs in which all lines terminate in an L (except for free particles) are spatially independent. Figure 6(b) is the inhomogeneous skeleton for $L^1(\zeta^*I)^2f^0f^0f^0$. Figure 6(b) contains two terms of this skeleton $L_{13}(\zeta^*I)_{23}\times f_1{}^0f_2{}^0f_3{}^0+L_{23}(\zeta^*I)_{13}f_1{}^0f_2{}^0f_3{}^0$ with two others being zero due to Lemma 2, and the last two corresponding to Figure 6(a). These terms are obtained from a skeleton by labeling the vertical lines in all allowable manners.

FIG. 8. Secular terms for $\nu=4$.



The lemmas of Sec. III B are now illustrated by the graphs of Fig. 7.

Higher order secularities are illustrated in Figs. 8 and 9.

The time rate of change of the one particle distribution is given for order ν by

$$\partial f^\nu/\partial t=L^1F^{2(\nu-1)}. \qquad (3.22)$$

We conclude this section with the skeletons for $\partial f^3/\partial t\sim L'F^{22*}$ which will be useful for future discus-

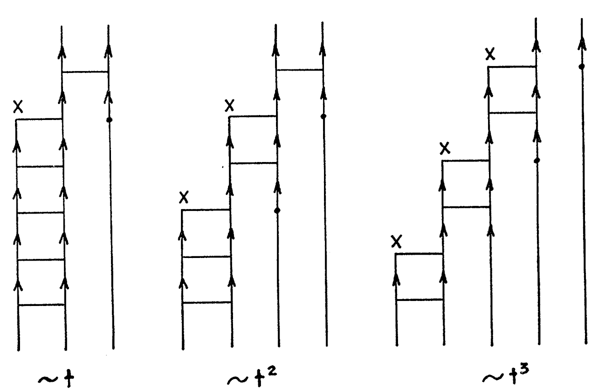
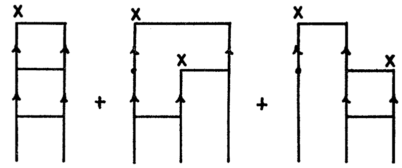


FIG. 9. Secular terms for $\nu=6$.

FIG. 10. Third-order "kinetic" equation.



sion. Since we have

$$F^{21*}=(\zeta^*I)^2f^0f^0$$

we obtain

$$\partial f^2/\partial t\sim L_{12}(\zeta^*I)_{12}f_1{}^0f_2{}^0$$

which is just the connected part of 6(a). We see again the result of Eq. (3.16), the secular behavior of f^2. Finally

$$\partial f^3/\partial t=L^1F^{22}\sim L^1(\zeta^*I\zeta^*If^0f^0+\zeta^*L\zeta^*If^0f^0f^0). \qquad (3.23)$$

This is illustrated in Fig. 10.

One should bear in mind that because of the superdiagonal nature of $\mathbf{L}$, the number of incoming and outgoing particles is not the same for any term in $F^{s\nu*}$ unless it contains only I's. In fact,

$$s=n(\text{out}), \qquad (3.24)$$

$$s+n(L)=n(\text{in}), \qquad (3.25)$$

where $n(\text{out})$ and $n(\text{in})$ denote the number of outgoing and incoming particles, respectively. By way of example, we give in Fig. 11 graphs that correspond to two-, three-, and four-body functions with four initial particles (the three graphs appear in third order).

Before examining the synchronized theory, it is of interest to note that one could develop a finite time theory rather than an asymptotic one using the evolution operator of Sec. II [Eq. (2.25)]. To see this, we expand Eq. (2.31) to second order. Our graph theory, which has been constructed from Eq. (2.32) with ζ^* as the propagator, could as well be based on Eq. (2.30) and used for finite-time expansions, with $(p+\mathbf{K})^{-1}$ as the propagator. From Eq. (2.31) we have

$$\tilde{F}=\left(1+\frac{1}{p+\mathbf{K}}\epsilon\mathbf{T}+\frac{1}{p+\mathbf{K}}\epsilon\mathbf{T}\frac{1}{p+\mathbf{K}}\epsilon\mathbf{T}+\cdots\right)\frac{F(0)}{p} \qquad (3.26)$$

$$=\int_0^\infty e^{-pt}F(t)dt.$$

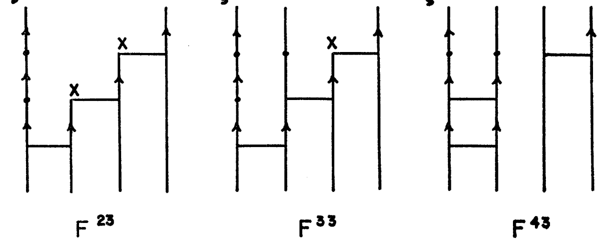


FIG. 11. Examples of F^{s3}.

Now, we insert Eq. (2.25) into the Laplace transform correct to second order

$$\tilde{F}=\int_0^\infty dt\, e^{-pt}\Big\{1+\exp(-\mathbf{K}t)\int_0^t dt_1 \exp(\mathbf{K}t_1)\epsilon\mathbf{T}\exp(-\mathbf{K}t_1)$$
$$+\exp(-\mathbf{K}t)\int_0^t dt_1 \exp(\mathbf{K}t_1)\epsilon\mathbf{T}\exp(-\mathbf{K}t_1)\int_0^{t_1} dt_2 \exp(\mathbf{K}t_2)\epsilon\mathbf{T}\exp(-\mathbf{K}t_2)\Big\}F(0)$$
$$=\Big[\frac{1}{p}+\int_0^\infty dt\, e^{-pt}\int_0^t dt_1 \exp(-\mathbf{K}t_1)\epsilon\mathbf{T}$$
$$+\int_0^\infty dt\, e^{-pt}\int_0^t dt_1 \exp(-\mathbf{K}t_1)\epsilon\mathbf{T}\int_0^{t_1} dt_2 \exp(-\mathbf{K}t_2)\epsilon\mathbf{T}\Big]F(0), \quad (3.27)$$

so that finally

$$\tilde{F}=\Big[1+\frac{1}{p+\mathbf{K}}\epsilon\mathbf{T}+\frac{1}{p+\mathbf{K}}\epsilon\mathbf{T}\frac{1}{p+\mathbf{K}}\epsilon\mathbf{T}+\cdots\Big]\frac{F(0)}{p} \quad (3.28)$$

giving the result of Eq. (3.26).

IV. SUMMARY OF RESULTS

We summarize here the main results obtained in this paper. They are based on obtaining an *explicit expression* for the νth-order term of the perturbation-series expansion for the s-particle distribution function. The result is obtained by the use of the simple matrices introduced in Sec. IIA which allow effectively for a "decoupling" of the BBGKY equations. The time asymptotic limit for the νth-order distribution F^ν can, in fact, be written in the compact form

$$F^{\nu *}=[\zeta^*\mathbf{T}]^\nu F^0. \quad (4.1)$$

The following three theorems which are based on this result, characterize the structure of perturbation theory.

(i) Explicit Construction of the νth-Order Term for the s-Body Distribution and its Graphical Representation

For given order of the perturbation theory, ν, the following rules hold and uniquely specify $F^{s\nu *}$. The function $F^{s\nu *}$ consists of a product of interaction operators (I and L) and of propagators (ζ^*), operating on

$$\prod^s f^0.$$

[The number of times that an operator 0 appears is denoted by $n(0)$.]

(a) $$n(I)+n(L)=\nu, \quad (4.2)$$

(b) $$n(\zeta^*)=\nu. \quad (4.3)$$

(c) Every interaction is followed by a single propagator, reading from right to left. (4.4)

(d) $s=n(\text{out})$ [$n(\text{out})$ is the number of outgoing particles]. (4.5)

(e) $s+n(L)=n(\text{in})$. (4.6)

The simple relations (a)-(e) completely specify the graphs that represent the distributions $F^{s\nu *}$. For finite times, the above rules apply for the Laplace transform of $F^{s\nu}$ provides ζ^* is replaced by $[p+\mathbf{K}]^{-1}$. In our formulation, in contrast with that of Priogogine and co-workers[28,29] one deals directly with the particles and their interactions.

(ii) Classification of Secularities

For fixed order ν of the perturbation expansion, there is a secular term of the form t^γ for all integral values of γ in the interval

$$1\leq\gamma\leq[\nu/2], \quad (4.7)$$

where $[\nu/2]$ is the integer part of $\nu/2$. Furthermore,

$$\gamma=n(L)=n(\text{in})-s. \quad (4.8)$$

As a consequence of Lemma 1 of Sec. III the maximum number of phase mixings (L) that can occur in νth order is $[\nu/2]$. As a corollary, the strongest secularity in νth order is $t^{(\nu/2)}$. In Figs. 8 and 9 we show the first secularities. For example, for $\nu=4$ there is a linear and a quadratic secularity. For $\nu=6$ is a linear, a quadratic, and a cubic secularity as illustrated.

(iii) The Sum of the Asymptotic Values of F^ν, $F^{\nu *}$ Yields the Correct Limit

We showed in Sec. II that

$$\sum_{\nu=0}^\infty \epsilon^\nu \lim_{t\to\infty} F^\nu=\lim_{t\to\infty}\sum_{\nu=0}^\infty \epsilon^\nu F^\nu=\lim_{t\to\infty} F. \quad (4.9)$$

It is clear that this result is predicted on the limit of large volume with fixed density taken at the very start of the development. The result may appear somewhat surprising in view of (ii), above, which implies the presence of polynomially divergent terms for $\nu\geq 2$. The

[28] I. Prigogine, *Nonequilibrium Statistical Mechanics* (Interscience Publishers, Inc., New York, 1962).

[29] R. Balescu, *Statistical Mechanics of Charged Particles* (Interscience Publishers, Inc., New York, 1963).

situation has, however, a well-known analog in the model

$$df/dt = -\epsilon f, \tag{4.10}$$

whose perturbation expansion yields a secularity of order t^ν in νth order

$$f(t)/f(0) = 1 - \epsilon t + \frac{\epsilon^2}{2!}t^2 - O(\epsilon^3 t^3). \tag{4.11}$$

Although Eq. (4.11) is a series which converges to the solution of Eq. (4.10), each term diverges for large times. In particular, the power series is not useful in giving a small correction term to each proceding one. For $t \geq 1/\epsilon$ the first few terms do not represent the series at all. The knowledge of the secular structure of the perturbation series is the essential key to the kinetic theory inagurated by Bogoliubov. In this program, in fact, the kinetic equation is the condition for the removal of the perturbation theory secularity. We have not considered in this first paper the kinetic condition which shall be analyzed in the following paper *to all orders*.

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Power Series of Kinetic Theory. II. Expansion with the Functional Ansatz*

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We discuss the synchronized expansion of the Liouville equation (i.e., the expansion with the "functional ansatz"). We utilize the multiple-time-scale method and the equivalence theorem proven in the preceding paper, which specializes this method to Bogoliubov's functional method. The technique is shown to successfully eliminate the secular behavior discussed in the preceding paper, to all orders in the series expansion for the distribution function of an arbitrary number of particles. However, new divergent terms (supersecularities) are shown to appear in the higher order terms. The distribution functions and kinetic conditions are given explicitly for νth order, and are shown to be decomposed unambiguously as the sum of two contributions: the "normal" (convergent) part and the "supersecular" (divergent) part. The normal part is proved to be given exactly by the perturbation-theory result of the previous paper with *all* secular terms removed, while the supersecular part is constituted by divergent terms which are explicitly constructed. The νth-order term can be written down without any knowledge of the lower order terms. Exploiting this result, we resum the kinetic condition to all orders. The result, if convergent, constitutes the exact kinetic equation applicable in principle to any system whose evolution can be characterized by the single-particle distribution function.

I. INTRODUCTION

THE power of the functional ansatz was demonstrated by Bogoliubov in deriving the lowest order kinetic equations by a synchronized expansion of the Liouville equation. In the preceding paper,[1] hereafter designated as GSI, we have developed the direct perturbation expansion to all orders, and discussed the secular behavior of the terms which prevent the construction of a kinetic equation. In this paper we prove that the synchronized expansion, utilizing the functional ansatz, not only eliminates the secularity in lowest order as demonstrated by Bogoliubov, but eliminates the previously discussed secular behavior to *all orders* of the expansion. The cancellation in lowest order allowed for the construction of the kinetic equation. However, in the higher order terms of the synchronized expansion, new divergent terms that we call supersecularities are shown to appear. We derive here the general expression for the νth-*order term* of the synchronized expansion and discuss its decomposition into a normal and supersecular part. The normal part is proved here to be given exactly by the perturbation theory result of GSI with *all* secular terms removed, while the supersecular part is constituted by divergent terms which are explicitly constructed.

We have shown in GSI that the direct perturbation expansion, although each order of the expansion is secular, yields upon summation the correct, finite distribution functions. In the light of this result we derive here the sum of the synchronized kinetic conditions, which corresponds to a kinetic equation which is valid,

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[1] P. Goldberg and G. Sandri, preceding paper, Phys. Rev. **154**, 188 (1967).