the present theory would be required to overcome this shortcoming.

V. CONCLUSION

Low-energy photoproduction of π^+ and π^- mesons seems internally consistent and in agreement with theoretical predictions of dispersion relations, particularly if the analysis is made for constant nucleon momentum transfer, equal to that occurring at threshold. The introduction of a bi-pion interaction and a correction to the isoscalar amplitudes for the $I=\frac{1}{2}$ phase shifts gives $\Lambda/e\approx+0.50\pm0.25$. For large angles, a better knowledge of the isovector amplitudes seems neccessary before drawing detailed conclusions. Nevertheless, on the basis of the present interpretation, the constant, Λ/e, is certainly not negative and not greater than $+e$.

We are grateful to Professor H. Halban and Professor A. Blanc-Lapierre for the use of the facilities of this laboratory. In an experiment of this kind, we cannot acknowledge sufficiently the work of Professor G. R. Bishop, Dr. B. Millman, Dr. D. Isabelle, and Dr. F. Lacoste who designed and tested most of the basic facilities which we used. We thank in particular V. Round for his collaboration on the liquid target; G. Alon for assistance with the electronic circuits; H. Navelet for help during many nights of experiment; and the accelerator crew under Dr. L. Burnod for many hours of good beam. Finally, one of us (J. K. W.) would like to extend his thanks to everyone for the hospitality shown to him during his stay at the laboratory.

PHYSICAL REVIEW VOLUME 132, NUMBER 1 1 OCTOBER 1963

Cluster Formulation of the Exact Equation for the Evolution of a Classical Many-Body System

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(Received 24 April 1963)

An exact non-Markoffian equation is derived for the evolution of an infinite homogeneous system. This equation—which may be viewed as a time-dependent analog of the equilibrium virial expansion—may be readily applied when the forces between particles include infinite repulsions. The derivation of this equation from Liouville's equation is analogous to Mayer's derivation of the virial expansion from the partition function. In this way the formal development of nonequilibrium statistical mechanics is placed on a similar footing to that of equilibrium statistical mechanics, and a many-body problem is reduced to understanding the dynamics of isolated groups of particles. Fourier expansions and expansions in powers of the interaction potential are avoided by dealing with s-body Green functions (propagators) which are always convergent functions of the interaction potential. These functions correspond to multiplet collisions in ordinary configuration space between s isolated particles and are time-dependent analogs of the irreducible clusters well known in equilibrium statistical mechanics. The kernel (memory) of the equation of evolution consists of a linear sum of the time-dependent irreducible clusters. The non-Markoffian behavior of the equation of evolution is, thus, directly given by the time dependence of these clusters, and is explicitly related to incompleted collisions. The equation of evolution is solved in the asymptotic limit of long times. In this limit it is found (because the kernel rapidly vanishes) that the equation reduces to a Markoffian master equation involving a scattering operator for both completed and incompleted collisions in configuration space.

I. INTRODUCTION

EVER since Van Hove[1] derived an exact non-Markoffian equation for the irreversible evolution of a many-body system there has been an increased activity in the field of nonequilibrium statistical mechanics. This activity was inspired by Van Hove's demonstration that, with sufficient determination, it is possible to obtain exact (if formal) solutions of difficult statistical mechanical problems.

More recently, Prigogine and co-workers[2] have obtained exact equations for all the Fourier components of the distribution function and for a wide class of initial states.

The methods used by Van Hove and Prigogine are necessarily characterized by their excessive complexity and their use of topological notions whose physical content is somewhat obscure. Their results are correspondingly complicated and difficult to apply—except in certain limiting cases (weak interactions, low density).

Another characteristic of these equations is that they are not *directly* applicable to interaction potentials with infinite repulsions (hard cores). This is because the kernels of these equations are expressed as expansions in the interaction potential. Hence, in order to rigorously apply these equations to hard-core interactions one must first sum higher Born approximations (sum

[1] L. Van Hove, Physica **23**, 441 (1957).
[2] I. Prigogine and P. Balescu, Physica **27**, 629 (1961). This paper refers to earlier related work.

ladder diagrams). To perform these summations to all orders in the density is no easy task and would only serve to further complicate matters.

An important question which previous investigations have not fully answered concerns the details of the evolution of a large system for long times. For example, it is not rigorously proven, to all orders, that the equations of evolution eventually reduce to Markoffian equations as the time becomes asymptotically large. Prigogine presents a sufficient condition for this to happen—namely, that the Laplace transform of the kernel (memory) of the equation of evolution be regular (throughout the complex transform plane) except for simple poles not at the origin. This condition, however, is certainly not satisfied in general. To determine the long time behavior of the equations of evolution—including the characteristic times after which they become Markoffian and the precise manner in which this is influenced by the range of the potential—it is necessary to know the explicit behavior of the kernel, or its transform, in considerable detail.

The purpose of the article, then, is (1) to obtain a simplified derivation of an exact equation for the evolution of a large classical homogeneous system in such a form that it may be readily applied when the density is not necessarily small and when the forces between particles include infinite repulsions; and (2) to study, in detail, the behavior of this equation for long times.

The method of derivation that we shall follow is in the spirit of Prigogine and Van Hove in that we seek the solution of Liouville's equation in the form of an initial value problem. The details of this solution, however, are different and simpler. For example, we do not deal with expansions in powers of the interaction potential—which correspond to "virtual collisions" in Fourier transform space. Such expansions are avoided by dealing with Green functions (propagators) which correspond directly to collisions in ordinary configuration space, and which are always convergent functions of the interaction potential.

Our derivation of a generalized master equation from Liouville's equation is, in many respects, similar to Mayer's derivation of the virial expansion from the partition function. We shall take advantage of the analogies which exist between the equilibrium and nonequilibrium problems in order to simplify the derivation and its physical interpretation, and we shall deal with mathematical objects which are clear analogs of those already well known in equilibrium theory.[3]

In Sec. II A we write the "binary collision expansion" of the formal Green function (exponential operator, propagator) solution of Liouville's equation. This expansion is entirely analogous to the Mayer f_{ij} expansion of the partition function. Indeed, the "binary collision" operators are a time-dependent analog of the Mayer f_{ij}'s and shall be henceforth referred to as "time-dependent f_{ij}'s." In Sec. II B we define clusters of these time-dependent f_{ij}'s which are analogous to Mayer clusters, and in Sec. II C we define "irreducible clusters" of time-dependent f_{ij}'s which are time-dependent analogs of Mayer's irreducible clusters (Husimi functions), and which correspond to multiplet collisions in configuration space. In Secs. II D and II E the binary collision expansion is regrouped in terms of these time-dependent irreducible clusters, and the result is integrated over all initial configuration space to yield an exact equation (non-Markoffian master equation) for the monotonic evolution of momentum functions—in the limit of an infinite system. This equation, whose kernel is a sum of time-dependent irreducible cluster integrals, is a time-dependent analog of the equilibrium virial expansion.

In Sec. III the equation of evolution is solved for asymptotically long times. In this limit it is found (because the memory "dies off" rapidly) that the equation reduces to a Markoffian master equation involving a scattering operator for "completed" and "incompleted" collisions in configuration space. The contributions to this scattering operator which are due to binary and ternary collisions, and which are of first and second order in the density are discussed further.

II. EXACT EQUATION FOR THE EVOLUTION OF ϕ

A. Binary Collision Expansion

We wish to study the evolution in time of any function of the momenta of the particles of a classical system of N-pair interacting particles. If $\{\mathbf{P}(t)\}$ and $\{\mathbf{R}(t)\}$ denote the N-vector momenta and N-vector positions of the particles at time t then the evolution of any function $F_N(t)$ of the form

$$F_N(t)=F_N(\{\mathbf{R}(t)\},\{\mathbf{P}(t)\})$$

is determined by[4]

$$dF_N(t)/dt=iL_NF_N(t)\,, \tag{1}$$

[3] M. S. Green, Physica 24, 393 (1958). [M. S. Green and R. A. Piccerelli have since made extensive use of the analogies between equilibrium and nonequilibrium theory to derive a generalized Boltzmann equation which is valid to all orders in the density. (This work was reported at the Conference on Statistical Mechanics at Brown University, 1962).]

[4] Equation (1) is simply the equation of motion for a system with a time-independent Hamiltonian. It is not quite the same as Liouville's equation, given by

$$-\partial F_N(t)/\partial t=iLF_N(t).$$

Strictly speaking, then, $F_N(t)$ is a function of the phase $\{\mathbf{R}(t)\}$, $\{\mathbf{P}(t)\}$—not a probability density. The important point to be born in mind, however, is that the details and results of this work are valid for Liouville's equation as well as for (1) so that for all intents and purposes $F_N(t)$ may be regarded as a probability density as well as a phase function. The reason we have chosen to deal with Eq. (1) instead of with Liouville's equation is that the propagators associated with Eq. (1) project phase points *forward* in time and are less confusing than the propagators associated with Liouville's equation. The latter propagators project phase points *backward* in time.

where the Liouville operator L_N is defined by

$$L_N \equiv -i\sum_{k=1}^{N} m^{-1}\mathbf{P}_k\cdot\partial/\partial\mathbf{R}_k - i\sum_{1\leqslant k\leqslant s\leqslant N}\mathbf{F}_{ks}\cdot[\partial/\partial\mathbf{P}_k-\partial/\partial\mathbf{P}_s] \equiv L_N{}^0+\sum_{1\leqslant k\leqslant s\leqslant N} L_{ks}\,. \tag{2}$$

Here, $\mathbf{R}_k$ and $\mathbf{P}_k$ are the initial vector position and momentum of particle k, $\mathbf{F}_{ks}=\mathbf{F}(\mathbf{R}_k-\mathbf{R}_s)=-[\partial/\partial(\mathbf{R}_k-\mathbf{R}_s)]V(\mathbf{R}_k-\mathbf{R}_s)$ is the initial force between particles k and s, and $V(\mathbf{R}_k-\mathbf{R}_s)$ is the interaction potential between particles k and s. We note that $V(\mathbf{R}_k-\mathbf{R}_s)$ need not be centrally symmetric, nor have any symmetry whatsoever in all that follows.

Equation (1) has the formal solution

$$F_N(t)=e^{itL_N}F_N(0)\equiv G_N(t)F_N(0)\,,$$

where $G_N(t)$ is the N-particle propagator (Green's function) which has the property of displacing a phase point along its path in phase space from its position at time zero to its position at time t.

We shall obtain an exact equation for the evolution of the momentum function $\phi(t)$ defined (providing it converges) by

$$\phi(t)\equiv V^{-N}\int d\{\mathbf{R}\}F_N(t)=V^{-N}\int d\{\mathbf{R}\}e^{itL_N}F_N(0) =\phi(\{\mathbf{P}\},t)=\phi(\{\mathbf{P}(t)\})\,, \tag{3}$$

where $F_N(0)=F_N(\{\mathbf{P}\})$, V is the total volume of the system, and $\int d\{\mathbf{R}\}$ denotes the integral over the initial configurations of all the particles.

The equation for $\phi(t)$ shall be obtained by evaluating the integral in (3) in a manner resembling the evaluation of the analogous configuration integral of the classical partition function (p. f.). The exponential operator e^{itL_N} has a formal resemblence to the classical equilibrium distribution function and, indeed, the operator e^{itL_N} may be expanded in terms of time-dependent f_{ij}'s in analogy with the expansion of the classical p. f. in terms of Mayer f_{ij}'s.

This expansion of e^{itL_N}, which is called the binary collision expansion,[5] involves propagators of the form

$$G_n(t)\equiv\exp[it(L_N{}^0+\sum_{1\leqslant k\leqslant s\leqslant n} L_{ks})]\,. \tag{4a}$$

The propagator $G_n(t)$ is the formal solution of Liouville's equation for a system of N particles in which the subset of n particles 1, 2, $\cdots$, n are interacting with each other whereas the remaining $(N-n)$ particles have no interactions and, hence, move freely. The propagator $G_n(t)$ thus involves the solution of an n-body problem. [The momentum of each of the $(N-n)$ free particles is, of course, constant.]

The binary collision expansion involves two special cases of $G_n(t)$ given by

$$G_0(t)\equiv e^{itL_N{}^0}\,,\qquad G_{(ij)}(t)\equiv e^{it(L_N{}^0+L_{ij})}\,. \tag{4b}$$

The "free-particle" propagator $G_0(t)$ is the (trivial) solution of Liouville's equation for a system of N noninteracting particles (free particles). The binary collision propagator $G_{(ij)}(t)$ is the solution of Liouville's equation for a system of N particles in which there is an interaction between the two particles i and j, while the remaining $(N-2)$ particles are noninteracting and move freely. The binary collision propagator $G_{ij}(t)$ merely involves the solution of a two-body problem.

In terms of these propagators the binary collision expansion of e^{itL_N} is given exactly (for any pair interaction) by[5]

$$G_N(t)\equiv e^{itL_N}=G_0(t)+\sum_{n=1}^{\infty}\sum_{\{\alpha\}}^{N}\int_0^t dt_1\int_{t_1}^t dt_2\cdots \times\int_{t_{n-1}}^t dt_n\, G_{\alpha_1}(t_1)iL_{\alpha_1}G_{\alpha_2}(t_2-t_1)\cdots \times G_{\alpha_n}(t_n-t_{n-1})iL_{\alpha_n}G_0(t-t_n)\,, \tag{5}$$

where the single "binary" index α_k denotes the pair of particles indices i_kj_k, with $i_k<j_k$, and the summation,

$$\sum_{\{\alpha\}}^{N}\equiv\sum_{\alpha_1}^{N}\sum_{\alpha_2}^{N}\cdots\sum_{\alpha_n(\alpha_k\neq\alpha_{k+1})}^{N}$$

denotes the sum of each of the binary indices α_1, α_2, $\cdots\alpha_n$ over all the $\frac{1}{2}N(N-1)$ possible pairs of particle indices with the restriction that

$$\alpha_k\neq\alpha_{k+1}\,,\quad (1\leqslant k\leqslant n-1)\,,$$

i.e., that no *adjacent* pair of α's have the same two-particle indices. (This sum does include terms in which adjacent α's have at most one-particle index in common, and terms in which nonadjacent α's have both particle indices in common.)

The time-dependent notation in Eq. (5) is rather cumbersome. For this reason we shall simply denote the time-dependent integral operators which appear in (5) by $f_{\alpha k}$ as follows:

$$f_{\alpha k}\equiv f_{\alpha k}(t-t_{k-1})\equiv\int_{t_{k-1}}^t dt_k G_{\alpha k}(t_k-t_{k-1})iL_{\alpha k}\,, \tag{6}$$

which is a time-dependent analog of the Mayer f_{ij}, so that the binary collision expansion of e^{itL_N}, Eq. (5), may be written in the convenient and suggestive form

$$G_N(t)\equiv e^{itL_N}=G_0+\sum_{n=1}^{\infty}\sum_{\{\alpha\}}^{N} f_{\alpha_1}\cdots f_{\alpha_n}G_0\,, \tag{7}$$

[5] A. J. F. Siegert and Ei Teramoto, Phys. Rev. **110**, 1232 (1958); T. D. Lee and C. N. Yang, *ibid.* **113**, 1165 (1959); J. Weinstock, *ibid.* **126**, 341 (1962). [The analogy between the time-dependent f_{ij} and the Mayer f_{ij}, as well as the analogy between the binary collision expansion and the Mayer f_{ij} expansion, is discussed here. We shall not make use of these results however, since they are only exact for the special case of rigid sphere interactions.]

where now in this new notation

$$f_{\alpha_1}\cdots f_{\alpha_n}G_0\equiv\int_0^t dt_1 G_{\alpha_1}(t_1)iL_{\alpha_1}\cdots \times\int_{t_{n-1}}^t dt_n G_{\alpha_n}(t_n-t_{n-1})iL_{\alpha_n}G_0(t-t_n).$$

Upon substitution of (7) into (3) we obtain

$$\phi(t)\equiv V^{-N}\int d\{\mathbf{R}\}[G_0+\sum_{n=1}^{\infty}\sum_{\{\alpha\}}^{N} f_{\alpha_1}\cdots f_{\alpha_n}G_0]F_N(0)$$

$$=V^{-N}\int d\{\mathbf{R}\}G_N(t)F_N(0), \qquad (8)$$

which bears a formal resemblance to the Mayer expansion of the classical p. f.[5] The analogies which exist between (8) and the Mayer expansion are more than formal, and we shall make use of these analogies in order to derive an equation for the evolution of $\phi(t)$ involving time-dependent irreducible cluster integrals.

The derivation of this equation of evolution from (8) is based upon the fact, as we shall see, that the right side of (8) becomes a linear function of ϕ in the limit of an infinite system. Hence, we shall regroup the terms (f products) in (8) in such a way that the linear relation between ϕ and the right side of (8) is transparent, and then we shall let the system become infinite.[6]

This regrouping is obtained by expressing the terms in (8) as a linear sum of time-dependent irreducible clusters which are a simple analog of Mayer's clusters. To obtain these clusters we must first introduce the Mayer notion of "connectedness" to the products of time-dependent f_{ij}'s in (8). The irreducible clusters may then be defined by a recursion relation involving connected products of f's.

B. Time-Dependent Clusters

As the first step in the derivation of a closed equation for ϕ from (8), we shall define clusters of f's by introducing a notion of connectedness related to that in Mayer's equilibrium theory. Accordingly, for any product of f's,

$$f_{\alpha_1}f_{\alpha_2}\cdots f_{\alpha_n},$$

which appears in (8) we imagine drawing a point in space for each particle index which appears in this product so that if there are k different particle indices there will be k points in space just as in Mayer's theory. We then imagine drawing n distinct line segments through each of the n pairs of particle indices α_1, α_2, $\cdots\alpha_n$ so that to each f_{α_k} in this product there corresponds a distinct line segment connecting the pair of particles α_k.

It may then happen that a group of line segments connect a group of particles together, directly or indirectly, so that through each pair of particles in this group there passes a continuous line. The f's which correspond to such a connected group of line segments are said to form a "connected product" or "cluster" of f's, and the particles which are so connected by this group of line segments are said to be connected to each other in a cluster—just as in Mayer's theory.[7]

In this way we see that all the particles which appear in a given product of f's may be grouped into disjoint clusters (two clusters are said to be disjoint if they have no particles in common). This, too, is completely analogous to equilibrium theory.

As examples, we see that in the f product

$$f_{12}$$

particles 1 and 2 are connected to each other in a cluster, and in both f products

$$f_{12}f_{45}f_{13} \quad\text{and}\quad f_{12}f_{45}f_{13}f_{12}$$

the particles 1, 2, and 3 are connected to each other in one cluster while the particles 4 and 5 are connected to each other in another cluster—the two clusters being disjoint.

We may now define the propagator

$$[G_N(\neq i_1 i_2\cdots i_{s+1})-G_0]G_0^{-1}$$

to be the *sum of all permissible f products that can be formed from N-particle indices such that, in these f products, no pair of particle indices from among $i_1, i_2, \cdots, i_{s+1}$ are connected to each other in a cluster.* [We wish to emphasize that the indices $i_1, i_2\cdots i_{s+1}$ will appear in some f products of $G_N(\neq i_1 i_2\cdots i_{s+1})$ but that these indices must not be connected to each other in a cluster.] The propagator $G_N(\neq i_1\cdots i_{s+1})$ is very similar to G_N itself. The binary collision expansions of these two propagators differ only in that $G_N(\neq i_1\cdots i_{s+1})$ does not have the particles $i_1, i_2, \cdots, i_{s+1}$ connected to

[6] This method departs somewhat from the analogous standard derivation of the equilibrium virial expansion. One can, however, derive the equation of evolution in complete analogy with the derivation of the virial expansion as follows. One first defines "irreducible" clusters of time-dependent f_{ij}'s. The binary collision expansion may then be expressed as a sum of "at most singly connected" ordered products of these irreducible clusters (sums of products of star trees). This can then be integrated over all initial configuration space to obtain a sum of products of irreducible cluster *integrals* (the configuration integral of a product of time-dependent clusters is equal to the product of the integrals of the clusters—just as in equilibrium theory). Finally, the products of time-dependent irreducible cluster integrals are summed in the limit of an infinite system to obtain an exact equation of evolution which is a time-dependent analog of the virial expansion. Instead of following this standard method, however, we shall take a short cut which avoids complicated cluster summations.

[7] This definition of a connected product, or cluster, of f's makes no reference to the order in which the f's appear. Hence, any permutation of the f's in a given connected product of f's is also a connected product of f's. It is also to be noted that the connected product of f's defined here may contain the same f more than once—such as f_{12} in the connected product $f_{12}f_{13}f_{12}$. Products of f's which contain the same f more than once appear in the binary collision expansion given by Eq. (7) but do not appear in the Mayer f_{ij} expansion. This is one of two formal differences between the two expansions. The other difference is that the time-dependent f_{ij}'s do not commute, whereas the Mayer f_{ij}'s do commute.

each other in any of its f products. [The operator G_0^{-1}, above, is defined by the identity $G_0(-y)G_0(y)\equiv 1$, $G_0(y)^{-1}\equiv G_0(-y)$.]

It will prove useful to define $G_N(\neq i_1\cdots i_{s+1})$ in a way that emphasizes its relationship to G_N. Thus, if we define $\mathbf{C}_N(i_1\cdots i_{s+1})$ by $\mathbf{C}_N(i_1\cdots i_{s+1})G_0^{-1}\equiv$the sum of all permissible f products (from N-particle indices) in which two or more of the particles $i_1, i_2, \cdots, i_{s+1}$ are connected to each other in a cluster, then, since $(G_N-G_0)G_0^{-1}$ is the sum of *all* permissible f products [Eq. (7)],

$$G_N(\neq i_1\cdots i_{s+1})\equiv G_N-\mathbf{C}_N(i_1\cdots i_{s+1}).$$

A property of $G_N(\neq i_1\cdots i_{s+1})$ that will be useful later on is given by

$$G_N(\neq i_1\cdots i_N)-G_0=0. \tag{9}$$

This follows from the fact that $[G_N(\neq 1,2,\cdots,N)-G_0]$ is the sum of all f products in which there are no particles connected to each other. Equation (9) simply states that there are no such f products.

C. Time-Dependent "Irreducible" Clusters—(Husimi Functions)

We shall next define "irreducible clusters" by means of a recursion relation involving the propagator $G_N(\neq i_1\cdots i_{s+1})$. [These irreducible clusters, which we denote by $V_S(i_1\cdots i_{s+1})$, play a central role in this work, and in all that follows we shall find it unnecessary to define any other quantities.] This defining relation is given, for all $n>1$, by

$$G_n(t)\equiv G_0+\sum_{s=1}^{n-1}\sum_{1\leqslant i_1<\cdots<i_{s+1}\leqslant n} V_s(i_1\cdots i_{s+1}) \times G_0^{-1}G_n(\neq i_1\cdots i_{s+1}), \tag{10}$$

where the irreducible cluster $V_s(i_1\cdots i_{s+1})$ is to be determined so as to satisfy (10) for all integral values of n greater than 1. Equation (10) (for all n) is, thus, to be viewed as a definition of the function $V_s(i_1\cdots i_{s+1})$. [Equation (10) actually plays a dual role in this work since, for $n=N$, Eq. (10) provides an expression for $G_N(t)$ which, as we shall see, can be readily integrated over configuration space to yield an integral equation for ϕ.]

To determine $V_n(i_1\cdots i_{n+1})$ from (10) we substitute (9) into (10) so that (10) may be written as follows: for all n:

$$V_{n-1}(1,2\cdots n) \equiv G_n(t)-G_0-\sum_{s=1}^{n-2}\sum_{1\leqslant i_1<\cdots<i_{s+1}\leqslant n} V_s(i_1\cdots i_{s+1}) \times G_0^{-1}G_n(\neq i_1\cdots i_{s+1}). \tag{11}$$

Equation (11) is a recursion relation for the V_n's. That is, we may solve (11), recursively, for all the V_n's by solving (11) for successively increasing values of n. As examples, we shall find V_1 and V_2 from (11) by setting n equal to 2 and then 3, respectively. Thus, we set n equal to 2 in (11) and obtain

$$V_1(1,2)\equiv G_2(t)-G_0\equiv e^{it(L_N{}^0+L_{12})}-e^{itL_N{}^0} \equiv G_{(12)}(t)-G_0(t)\equiv V_1(1,2;t), \tag{12}$$

which only involves the solution of a two body problem. The integral of $V_1(1,2;t)$ over $(\mathbf{R}_1-\mathbf{R}_2)$, for large t, yields the well-known binary collision scattering operator which is related to the Boltzmann collision integral.

To obtain $V_1(12)$ in terms of f's we refer back to (5) and (6) and note that

$$G_{(12)}(t)-G_0(t)=\int_0^t dt_1\, G_{(12)}(t_1)iL_{12}G_0(t-t_1)\equiv f_{12}G_0,$$

so that (12) may be written in terms of f's by

$$V_1(12)\equiv G_{(12)}(t)-G_0(t)=f_{12}G_0. \tag{13}$$

To obtain $V_2(1,2,3)$ we set n equal to 3 in (11) and obtain

$$V_2(123)\equiv G_3(t)-G_0 - \sum_{1\leqslant i_1<i_2\leqslant 3} V_1(i_1i_2)G_0^{-1}G_3(\neq i_1,i_2). \tag{14}$$

From the definition of $[G_N(\neq i_1\cdots i_{s+1})-G_0]$ we see that $[G_3(\neq 1,2)-G_0]$ is the sum of all the f products that can be formed from the indices 1, 2, and 3 such that 1 and 2 are not connected. We thus have, since 1 and 2 are connected in $f_{12}G_0$, $f_{13}f_{23}G_0$, etc.,

$$G_3(\neq 12)-G_0\equiv f_{13}G_0+f_{23}G_0,$$

so that (14) becomes, after using (13),

$$\begin{aligned} V_2(123)\equiv{}& G_3(t)-G_0-V_1(12)G_0^{-1}(G_0+f_{13}G_0+f_{23}G_0) \\ &-V_1(13)G_0^{-1}(G_0+f_{12}G_0+f_{23}G_0) \\ &-V_1(23)G_0^{-1}(G_0+f_{12}G_0+f_{13}G_0) \\ \equiv{}& G_3(t)-G_0-(f_{12}+f_{13}+f_{23})G_0 \\ &-(f_{12}f_{13}+f_{12}f_{23}+f_{13}f_{12}+f_{13}f_{23} \\ &+f_{23}f_{12}+f_{23}f_{13})G_0. \end{aligned} \tag{15}$$

The explicit time dependence of the f's in (15) may be determined by referring back to (4a) and (6). We then find, with (13),

$$\begin{aligned} V_2(123)\equiv{}& G_3(t)+2G_0(t)-G_{(12)}(t)-G_{(13)}(t)-G_{(23)}(t) \\ &-\sum_{\alpha_1\neq\alpha_2}^{123}\int_0^t dt_1\int_{t_1}^t dt_2\, G_{\alpha_1}(t_1)iL_{\alpha_1}G_{\alpha_2}(t_2-t_1) \\ &\times iL_{\alpha_2}G_0(t-t_2) \\ \equiv{}& V_2(123;t), \end{aligned} \tag{16}$$

where the sum means that α_1 and α_2 each take on the

indices (12), (13), and (23) providing that $\alpha_1 \neq \alpha_2$. We see from (16) that $V_2(123)$ involves the solution of a three-body problem. [An integral of (16) over a region of phase space occurs as the "triple collision" term in the Boltzmann equation derived by Green.[8] This triple collision term constitutes the second-order (density) correction to the ordinary Boltzmann equation—for a spatially homogeneous system.]

By repeating the preceding calculation with n taken equal to 4, 5, 6, etc., we see that the recursion relation (11) may be solved, uniquely, for all n. This would give V_{n-1} as a function of $G_n(t)$, $G_{n-1}(t)$, $\cdots$ and $G_0(t)$ so that V_{n-1} involves the solution of an n-body problem.

The functions V_n are a time-dependent analog of the equilibrium Husimi functions[8] (equilibrium irreducible cluster sums). In fact, the binary collision expansion of V_n back into f's yields "irreducible clusters" of time-dependent f's analogous to equilibrium irreducible clusters of f's. [Physically, V_n corresponds to a collision between $(n+1)$ particles. That is, V_n is nonzero for only those regions of initial configuration space for which $(n+1)$ particles are aimed to collide at some time between time zero and time t. This is indeed analogous to the equilibrium irreducible clusters of $(n+1)$ particle which, one may say, is nonzero for only those regions of configuration space for which the $(n+1)$ particles are "initially" in contact.]

Equation (11) serves to generate all the V_n's, and in all that follows we shall consider V_n to be a known function. It is evident, from (11), that $V_n(1,2,\cdots,n+1)$ involves the solution of no more than an $(n+1)$ body problem, and that $V_n(1,2,\cdots,n+1)$ contains pair interactions (L_{ij}'s) between particles 1, 2, $\cdots$, $(n+1)$ and no other particles.

D. An Exact Equation for ϕ

In this section we shall integrate $G_N(t)$ over initial configuration space to obtain a closed equation for $\phi(t)$ in terms of the irreducible clusters of the previous section. For this purpose we shall use Eq. (10) which expresses $G_N(t)$ in a form that can be readily integrated. We thus substitute (10), with $n=N$, into (8) and obtain $\phi(t)$ in the convenient form

$$\phi(t)=V^{-N}\int d\{\mathbf{R}\}\Big[G_0+\sum_{s=1}^{N-1}\sum_{i_1<\cdots<i_{s+1}} V_s(i_1\cdots i_{s+1}) \times G_0^{-1}G_N(\neq i_1\cdots i_{s+1})\Big]F_N(0). \quad (17)$$

The integration of (17) may be divided into two steps, and these steps may be stated in the form of two equations as follows:

If $F_N(0)$ is independent of positions then as the volume V of the system approaches infinity we must have

Step (1):

$$V^{-N}\int d\{\mathbf{R}\}V_s(i_1\cdots i_{s+1})G_0^{-1}G_N(\neq i_1\cdots i_{s+1})F_N(0) = V^{-s}\int d\mathbf{R}_{i_1i_2}\cdots d\mathbf{R}_{i_1i_{s+1}}V_s(i_1\cdots i_{s+1})G_0^{-1} \times V^{-N}\int d\{\mathbf{R}\}G_N(\neq i_1\cdots i_{s+1})F_N(0), \quad (18)$$

and

Step (2):

$$V^{-N}\int d\{\mathbf{R}\}G_N(\neq i_1\cdots i_{s+1})F_N(0) = V^{-N}\int d\{\mathbf{R}\}G_NF_N(0)+sO(V^{-1}) = \phi+sO(V^{-1}), \quad (0<s<N), \quad (19)$$

where

$$\mathbf{R}_{ij}\equiv\mathbf{R}_i-\mathbf{R}_j.$$

The proofs of these two equations are formal and somewhat lengthy. These proofs will be found in Appendixes A and B.

Strictly speaking, step (1) does not require an infinite volume. It is step (2) that necessitates the following restrictions in this work:

(1) that the volume of the system be infinite, and
(2) that the total scattering cross sections be finite.

To obtain a closed equation for ϕ we merely substitute step (2) into step (1), and then substitute step (1) into (17). We then have

$$\phi(t)=\phi(0)+\sum_{s=1}^{N-1}\sum_{i_1<\cdots<i_{s+1}} V^{-s}\int d\mathbf{R}_{i_1i_2}\cdots d\mathbf{R}_{i_1i_{s+1}} \times V_s(i_1\cdots i_{s+1})G_0^{-1}[\phi+sO(V^{-1})], \quad (20)$$

where we have used the fact that $F_N(0)$ is independent of positions to obtain

$$V^{-N}\int d\{\mathbf{R}\}G_0F_N(0)=V^{-N}\int d\{\mathbf{R}\}F_N(0)=\phi(0).$$

Since the configuration integral of the irreducible cluster V_s is a time-dependent analog of the irreducible cluster integrals of the equilibrium virial expansion, we shall make use of equilibrium notation and denote the time-dependent integrals by β_s according to the definition

$$\beta_s(N,V)\equiv\sum_{1\leqslant i_1<\cdots<i_{s+1}\leqslant N}\beta_s(i_1\cdots i_{s+1}) \equiv\sum_{i_1<\cdots<i_{s+1}} V^{-s}\int d\mathbf{R}_{i_1i_2}\cdots d\mathbf{R}_{i_1i_{s+1}} \times V_s(i_1\cdots i_{s+1}), \quad (21)$$

[8] K. Husimi, J. Chem. Phys. 18, 682 (1950).

so that (20) becomes

$$\phi(t)=\phi(0)+\sum_{s=1}^{N-1}\beta_s(N,V)G_0^{-1}\phi + [\sum_{s=1}^{N-1}s\beta_s(N,V)G_0^{-1}]O(V^{-1}). \quad (22)$$

It can be shown that in the limit of an infinite system (N, $V\to\infty$, $N/V=$ finite constant) the cluster integrals all converge to a function of (N/V). We may, thus, define

$$\beta_s\equiv\beta_s(N/V)\equiv\lim_{N,V\to\infty}\beta_s(N,V). \quad (23)$$

Hence, within the radius of convergence of the expansion

$$\sum_{s=1}^{\infty}s\beta_s,$$

Eq. (22) for ϕ becomes, as the size of the system approaches infinity,

$$\phi(t)=\phi(0)+\sum_{s=1}^{\infty}\beta_sG_0^{-1}\phi. \quad (24)$$

Equation (24) is a closed equation for ϕ, and it is to be understood that it is exact only in the limit of an infinite system.

[In the limit of an infinite system the dynamical recurrence time is also infinite and, hence, there will be no such recurrence. This means that the solution of (24) for $\phi(t)$ will not exhibit Poincaré cycles. It will, instead, approach a state of equilibrium for all time t. (The "source" of the dynamical recurrence, although we have not explicitly included it in the Hamiltonian, is provided by the walls of the system. In going to the limit of an infinite system we have "removed" the walls by placing them at infinity.)]

Equation (24) is not yet complete because we have not explicitly stated the time dependence of $\beta_sG_0^{-1}\phi$. We shall do this in the next section.

E. Explicit Time Dependence—The Exact Non-Markoffian Equation for $\phi(t)$

The reader will recall that, for convenience of notation, we have suppressed explicit time dependences in the preceding derivation. This was done by introducing the symbol f_α in (6) so that (5) could be written in the form of (7).

To regain this time dependence in (24) we must, essentially, expand (24) back into f products and then refer back to (5) where we shall find the explicit time dependence of these f products are given. This is done in Appendix C where it is found that the time-dependent function of which $\beta_sG_0^{-1}\phi$ is a symbol is exactly given by

$$\beta_sG_0^{-1}\phi\equiv\int_0^t dy\left(\frac{\partial\beta_s(y)}{\partial y}\right)\phi(t-y), \quad (25)$$

where

$$\beta_s(y)\equiv\lim_{N,V\to\infty}\sum_{i_1<\cdots<i_{s+1}}V^{-s}\int d\mathbf{R}_{i_1i_2}\cdots d\mathbf{R}_{i_1i_{s+1}} \times V_s(i_1\cdots i_{s+1};y) \equiv\lim\sum_{i_1<\cdots i_{s+1}}\beta_s(i_1\cdots i_{s+1};y) \quad (26)$$

and $V_s(i_1\cdots i_{s+1};y)$ is defined by the recursion relation in (11).

Substituting (25) into (24) then yields an equation for the evolution of the momentum function $\phi(t)$:

$$\phi(t)=\phi(0)+\int_0^t dy\{\sum_{s=1}^{\infty}\frac{\partial\beta_s(y)}{\partial y}\}\phi(t-y). \quad (27)$$

This equation for $\phi(t)$ is exact in the limit of an infinite system. [It is interesting to note that this equation takes the form of an integral equation, and, hence, has the initial conditions built into it. Consequently, (27) may be seen to satisfy the initial value of $\phi(t)$. This, of course, is to be expected since (27) is exact for all time t.]

To cast (27) into the usual form of an integro-differential equation (generalized master equation) we simply change the variable of integration in (27) from y to $(t-y)$ and then differentiate (27) with respect to t. We then obtain, with primes denoting derivatives with respect to arguments:

$$\frac{\partial\phi(t)}{\partial t}=\int_0^t dy\{\sum_{s=1}^{\infty}\beta_s''(t-y)\}\phi(y) +\{\sum_{s=1}^{\infty}\beta_s'(0)\}\phi(t). \quad (28)$$

But it is proven in Appendix D that $[\sum\beta_s'(0)]$ is equal to zero so that the above equation becomes

$$\frac{\partial\phi(t)}{\partial t}=\int_0^t dy\{\sum_{s=1}^{\infty}\beta_s''(t-y)\}\phi(y). \quad (29)$$

Equation (29) is an exact, non-Markoffian master equation for the evolution of the momentum function $\phi(t)$. It is an exact equation for all time t and for all interaction potentials (whether or not they have any symmetry) providing (1) the system is infinite, (2) the scattering cross sections are finite, and (3) there are no initial spatial correlations.

The time-dependent cluster integral $\beta_s(t-y)$ which appears in the kernel of this equation, involves the solution of a well-defined $(s+1)$ body problem in ordinary configuration space, and is a time-dependent generalization of the equilibrium irreducible cluster integral (virial coefficient). We thus see that the non-Markoffian equation for the spatially homogeneous case may be viewed as a formal time-dependent analog of the equilibrium virial expansion. The time-dependent

irreducible cluster $\beta_s(t)$, unlike the equilibrium irreducible clusters, involve the solution of a dynamical $(s+1)$-body problem and cannot be readily calculated in great detail. One can, however, set up a systematic approximation scheme for the calculation of $\beta_s(t)$, by means of the binary collision expansion, which is directly applicable to interaction potentials with hard cores. One can also determine the time dependence of $\beta_s(t)$ with little difficulty. This will be discussed in the following article.[9]

A distinctive feature of the generalized master equation in (29) is that it is directly applicable to interaction potentials with infinite repulsions (hard cores) since $\beta_s''(t)$ is a convergent function of such potentials.

Another feature of Eq. (29) is that its kernel (memory) is explicitly expressed in terms of Green functions which correspond to collisions in configuration space—not to virtual collisions in Fourier transform space. The relationship between the memory and the finite duration of a collision is thus direct and meaningful.

Equation (29) is equivalent to the Prigogine and Resibois[2] non-Markoffian equation when there are no initial spatial correlations. The kernel of the latter equation is expressed in terms of diagrams and corresponds to an expansion in powers of the interaction potential, whereas the kernel of the former is expressed in terms of the dynamics of isolated groups of particles $\beta_s(t)$ and corresponds to an expansion in powers of the density.

It is rather easy to understand the significance of the diagrams in the theory of Prigogine and Resibois in terms of the irreducible clusters $\beta_s''(t)$. The relationship between these diagrams and $\beta_s''(t)$ is as follows: The expansion of the Laplace transform of $\beta_s''(t)$ in powers of the interaction potential is equal to the sum of all irreducible diagonal fragments which can be formed from groups of $(s+1)$ particles.

III. SOLUTION OF THE NON-MARKOFFIAN EQUATION FOR LARGE TIMES—MARKOFFIAN MASTER EQUATION

A. Solution for Large t

We wish to show that for large enough times t the non-Markoffian terms in (29) "die off," resulting in a Markoffian master equation. To accomplish this, we will solve (29) for $\phi(t)$ by Laplace transforms in the asymptotic limit of large t.

Thus, if we define $\beta(t)$ by

$$\beta(t)\equiv\sum_{s=1}^{\infty}\beta_s(t)\,, \tag{30}$$

and if we define $\Lambda(E)$ to be the Laplace transform of $\beta''(t)$:

$$\Lambda(E)\equiv\int_0^\infty dt\, e^{-Et}\beta''(t)\,, \tag{31}$$

then the solution of (29), obtained by the Laplace transform method, is

$$\phi(t)=(2\pi i)^{-1}\int_{a-i\infty}^{a+i\infty}dE[E-\Lambda(E)]^{-1}e^{Et}\phi(0)\,, \tag{32}$$

where a may be any real number which (in the complex E plane) lies to the right of all singular points of the integrand in (32).

To determine the behavior of $\phi(t)$ at large t from (32) we must investigate the singularities of $[E-\Lambda(E)]^{-1}$; and this means that we must know the time dependence of $\beta(t)$.[10] The time dependence of $\beta(t)$ can be determined when t is large and, indeed, it can be shown that if t is large compared to τ_c (the duration of a binary collision), then

$$\beta''(t)\phi(0)\sim ct^{-2}e^{-(1+A)\Lambda(E^*)}\phi(0)\,, \tag{33}$$

where A is a positive number the precise value of which is not of present interest, and E^* is negative and is defined as that solution of the equation

$$[E-\Lambda(E)]\phi(0)=0 \tag{34}$$

which, in the complex E plane, lies furthest to the right of any other solution of this equation [E^*, in general, will be a function of $\phi(0)$ so that (33) need not imply that $\phi(0)$ is an eigenfunction of $\Lambda(E)$].

The proof (33) is lengthy and shall not be presented here. A procedure for calculating the time dependence of $\beta_s(t)$ is presented in the following article.[9] There we calculate $\beta_1''(t)$ and $\beta_2''(t)$ for $t>\tau_c$. [Although $\beta_1''(t)$ and $\beta_2''(t)$ converge in the limit of infinite t, it so happens that $\beta_s''(t)$ does not so converge when s is a large number. Nevertheless, it turns out that the infinite sum $\sum_{s=1}^{\infty}\beta_s''(t)\equiv\beta''(t)$ does converge as is indicated by (33).]

We may use (33) and (34) to establish three important properties of $\Lambda(E)$ and $[E-\Lambda(E)]^{-1}$. These properties provide sufficient information to determine $\phi(t)$ at large t and are stated as follows:

[9] J. Weinstock, following paper, Phys. Rev. **132**, 470 (1963).

[10] While it is true that the detailed nature of $\beta(t)$ will depend upon the details of the pair potential $V(\mathbf{R}_{ij})$, it can be shown that for time scales greater than the duration of a binary collision the essential dependence of $\beta(t)$ upon t can be determined independent of the form of $V(\mathbf{R}_{ij})$—providing it is repulsive. This is fortunate since it so happens that one need only know the behavior of $\beta(t)$ at large t in order to determine the behavior of $\phi(t)$ at large t. The time dependence of $\beta_s(t)$ is more complicated when the pair interactions include attractive parts and, hence, when bound states will occur. In such a case, $V_s(t)$ will oscillate with t, and the frequency of oscillation will depend upon the initial conditions; i.e., the frequency of oscillation will depend upon [$\mathbf{R}$]. This is not necessarily fatal, however, since [in $\beta_s(t)$] $V_s(t)$ is integrated over [$\mathbf{R}$] and, hence, the oscillating part of $V_s(t)$ will be integrated over the "frequency of oscillation." Consequently, one may well expect that the oscillatory part of $\beta_s(t)$ will be damped and relatively small when t is large.

(1). $\Lambda(E)\phi(0)$ is analytic in that part of the complex E plane which lies to the right of $(1+A)E^*$ [the singularity of $\Lambda(E)\phi(0)$ at E equal to $(1+A)E^*$ will be a logarithmic branch point].

(2). $[E-\Lambda(E)]^{-1}\phi(0)$ is analytic to the right of $(1+A)E^*$ except for isolated poles at the zeros of $[E-\Lambda(E)]\phi$.

(3). The singularity of $[E-\Lambda(E)]^{-1}\phi(0)$ which lies *furthest to the right* of the complex E plane is an *isolated pole* at $E=E^*$.

Property (1) is a consequence of the fact that the Laplace transform which defines $\Lambda(E)$ in (31) converges to a continuous function of E when the real part of E is greater than $(1+A)E^*$. The convergence of this Laplace transform follows from (33) and (34).

Property (2) is an immediate consequence of property (1).

As for property (3) we note that the singularity of $[E-\Lambda(E)]^{-1}\phi(0)$ at $E=E^*$ lies to the right of $(1+A)E^*$ [E^* is negative and A is positive; hence $E^*>(1+A)E^*$] and, hence, this singularity must be an isolated pole [a consequence of property (2)]. That this singularity of $[E-\Lambda(E)]^{-1}\phi(0)$ is the one which lies furthest to the right of the complex E plane then follows from the definition of E^*.

Property (3) states that $[E-\Lambda(E)]^{-1}\phi(0)$ is analytic when the real part of E is equal to or greater than E^* except for an isolated pole at $E=E^*$. Hence, in this particular case the asymptotic behavior of the inverse Laplace transform of $[E-\Lambda(E)]^{-1}\phi(0)$ is entirely determined by the residue of $[E-\Lambda(E)^{-1}]e^{Et}\phi(0)$ at $E=E^*$. Evaluating this residue we, thus, find that (32) becomes, for asymptotically large t,

$$\phi(t)=\{\sum_{r=0}^{n-1} t^r C_r(E^*)\}e^{\Lambda(E^*)t}\phi(0)\,, \tag{35}$$

where n is the order of the pole of $[E-\Lambda(E)]^{-1}\phi(0)$ at $E=E^*$, and $C_r(E^*)$ is equal to

$$\frac{(n-1)!}{r!(n-1-r)!}\lim_{E\to E^*}\frac{d^{n-1-r}}{dE^{n-1-r}}\left[\frac{(E-E^*)^n}{E-\Lambda(E)}\right]. \tag{36}$$

Equation (35) is the asymptotic solution of the non-Markoffian equation for $\phi(t)$ in the limit of large t. By solving for $\phi(t)$ asymptotically in time the past history has been partially forgotten. In fact, (35) does not satisfy the initial condition whereas the non-Markoffian equation, (29), does. That is, Eq. (35) would have the initial value of $\phi(t)$ equal to $[1-\Lambda'(E^*)]^{-1}\phi(0)$ rather than equal to the correct initial value $\phi(0)$.

B. Markoffian Master Equation to all Orders in Density

Equation (35) is the formal solution of a Markoffian master equation. That is, the derivative of (35) with respect to t (the derivative of this asymptotic form can be justified) yields the master equation

$$\begin{aligned}&\partial\phi(t)/\partial t=\Lambda(E^*)\phi(t)+\phi(t)O(t^{-1})\,,\\&\partial\phi(t)/\partial t=\Lambda(E^*)\phi(t)\,,\quad(\text{large } t)\,.\end{aligned} \tag{37}$$

Equation (37) is a Markoffian master equation, and the exact non-Markoffian equation approaches (37) as t approaches infinity. As we have seen, the exact equation becomes Markoffian at large t because the non-Markoffian memory $\beta''(t)$ dies off at a rapid rate—a rate more rapid than the characteristic decay rate of $\phi(t)$ itself.

The non-Markoffian memory may be understood in terms of "completed" and "incompleted" collisions.[11] That is, it is shown in the following paper that $V_s(i_1\cdots i_{s+1};t)$ is nonzero only for that region of initial configuration space which leads to a collision between all the particles $i_1,\cdots,i_{s+1}$ within the time t. Some of these collisions may still be in process at time t and are, hence, referred to as "incompleted" collision, whereas other collisions will be completed corresponding to scattering processes referred to as "completed" collisions.

The cluster integral $\beta_s(t)$, which is simply the configuration integral of $\sum_{i_1<i_2}\cdots V_s(i_1\cdots i_{s+1})$, may, thus, be divided into a completed collision part and an incompleted part. It then turns out that $\beta'(\infty)$ is entirely due to completed collisions and $[\beta'(t)-\beta'(\infty)]$ is due to incompleted collisions. The reader may verify that the exact non-Markoffian equation (29) may be written in terms of completed and incompleted collisions as follows:

$$\phi'(t)=\beta'(\infty)\phi(t)+\left(\frac{\partial}{\partial t}\right)\int_0^t dy[\beta'(t-y)-\beta'(\infty)]\phi(y)\,. \tag{38}$$

It is evident from (38) that the non-Markoffian memory is entirely due to incompleted collisions. If these incompleted collisions were to vanish we would then have a simple Markoffian equation $[\phi'(t)=\beta'(\infty)\phi(t)]$ involving only completed collisions for all t. The memory does not vanish but, instead, it approaches zero so rapidly with time that the exact equation eventually does become Markoffian.

The scattering operator $\Lambda(E^*)$ which appears in the Markoffian equation (37) involves both completed and incompleted collisions. This can be seen by noting, from (31), that

$$\Lambda(0)=\beta'(\infty)\,, \tag{39}$$

so that $\Lambda(E^*)$ may be written as

$$\Lambda(E^*)=\Lambda(0)+[\Lambda(E^*)-\Lambda(0)]\,, \tag{40}$$

[11] The author is indebeted to Dr. M. S. Green and Dr. R. A. Piccirelli for pointing out the relevance of the notions of completed and incompleted collisions to the detailed understanding of the evolution of a large system at large times (private communication).

where $\Lambda(0)=\beta'(\infty)$ is the scattering operator for completed collisions, and $[\Lambda(E^*)-\Lambda(0)]$ is the "memory" correction to the Markoffian equation due to incompleted collisions. [We wish to emphasize that completed collisions are not to be confused with "instantaneous collisions." Physically, there are no instantaneous collisions except for the special case of two-body hard-sphere collisions (the volume of configuration space which leads to *instantaneous* three-body hard-sphere collisions has measure zero, and it is shown in the following paper that those three-body hard-sphere "collisions" which contribute to $\beta_2(t)$ have a nonzero duration). It is completed collisions of a nonzero duration, rather than instantaneous collisions, which are relevant to the behavior of $\phi(t)$ for large t.]

The correction to the Markoffian equation due to incompleted collisions cannot, in general, be ignored. The Markoffian equation in Ref. 2 includes this correction—although in a different form—and is equivalent to (37). The Markoffian equations in Ref. 12, however, do not include this correction. That is, the scattering operators in the latter equations correspond to the completed collision operator $\Lambda(0)$. These equations, then, are only correct when the full scattering operator $\Lambda(E^*)$ can be approximated by $\Lambda(0)$. Such an approximation, however, is only valid to the first order in the density since, as is shown in Sec. III C, the correction $[\Lambda(E^*)-\Lambda(0)]$ is of second order in the density.

The Markoffian scattering operator $\Lambda(E^*)$ can be expressed as a power series in the density, and we shall derive the first two terms of this series in the next section.

C. Master Equation for Binary and Ternary Collisions to Second Order in the Density

It would be useful to obtain a density expansion for the kernel of the Markoffian master equation, $\Lambda(E^*)$. This would be particularly useful for gases at not too high a density since then one need only retain the first few terms of a density expansion.

To obtain the first two terms in the density expansion of $\Lambda(E^*)$ we expand $\Lambda(E^*)$ about $E^*=0$. Thus,

$$E^*=\Lambda(E^*)=\sum_{n=0}^{\infty}(n!)^{-1}\Lambda^n(0)E^{*n}. \tag{41}$$

But $\beta_1(t)=O(N/V)$ so that $\Lambda(E)$, E^*, $\Lambda(0)=O(N/V)$ and to second order in the density we need only retain the first two terms in the sum in (41). Hence, to second order in the density, we have

$$\begin{aligned}\Lambda(E^*)&=\Lambda(0)+\Lambda'(0)E^*,\\ &=\Lambda(0)+\Lambda'(0)\Lambda(E^*),\end{aligned} \tag{42}$$

so that

$$\begin{aligned}\Lambda(E^*)&=[1-\Lambda'(0)]^{-1}\Lambda(0)=\sum_{n=0}^{\infty}[\Lambda'(0)]^n\Lambda(0)\\ &=\Lambda(0)+\Lambda'(0)\Lambda(0)+O[(N/V)^3].\end{aligned} \tag{43}$$

But $\beta_1(t)$ and $\beta_2(t)$ are first and second order in the density, respectively, so that to second order in the density we have, from (43), (31), and (30),[13]

$$\Lambda(E^*)=\beta_1'(\infty)+\beta_2'(\infty)-\left[\int_0^{\infty}dtt\beta_1''(t)\right]\beta_1'(\infty)+O\left[\left(\frac{N}{V}\right)^3\right], \tag{44}$$

where $\beta_1'(\infty)$ corresponds to completed binary collisions, $\beta_2'(\infty)$ corresponds to completed ternary collisions, and $\int dtt\beta_1''(t)$ corresponds to incompleted binary collisions.

Substituting (44) into (37) we obtain

$$\frac{\partial\phi(t)}{\partial(t)}=\left\{\beta_1'(\infty)+\beta_2'(\infty)-\int_0^{\infty}dtt\beta_1''(t)\beta_1'(\infty)\right\}\phi(t). \tag{45}$$

Equation (45) gives the master equation for binary and ternary collisions to second order in the density, and involves the solution of a well-defined three-body problem.

The cluster integrals $\beta_1'(\infty)$ and $\beta_2'(\infty)$ are scattering operators in momentum space, and are referred to as "collision integrals" or "collision operators."

The operator $\beta_1'(\infty)$ is exactly the binary collision operator which appears in the well-known low-density limit of the master equation.

The ternary collision integral $\beta_2'(\infty)$ is not so well known, and is discussed in great detail in the following paper. This operator is well worth understanding since its eigenvalues are directly related to the first-order density correction of the usual density-independent transport coefficients. An operator which is entirely equivalent to $\beta_2'(\infty)$ will be found in the generalized

[12] F. Henin, P. Resibois, and F. Andrews, J. Math. Phys. **2**, 68 (1961); F. Andrews, Phys. Rev. **125**, 1461 (1962).

[13] There will also be a contribution to second order in the density from the four-particle cluster $\beta_3(t)$. That is, in addition to a "genuine" quadruple collision part which is third order in the density, $\beta_3(t)$ also contains the term

$$\sum_{i_1<i_2<i_3<i_4}V^{-3}\int d\mathbf{R}_{i_1i_2}d\mathbf{R}_{i_3i_4}dR_{i_1i_3}\{\exp[it(L_N{}^0+L_{i_1i_2}+L_{i_3i_4})]\times\exp[-itL_N{}^0]-1-f_{i_1i_2}-f_{i_3i_4}-f_{i_1i_2}f_{i_3i_4}-f_{i_3i_4}f_{i_1i_2}\}G_0,$$

which is of second order in the density (because the integrand is independent of $\mathbf{R}_{i_1i_3}$) and which corresponds to a collision between i_1 and i_2 occurring independently and simultaneously with a collision between i_3 and i_4. This term is significant for the master equation but will not appear in the Boltzmann equation because it vanishes when integrated over all momenta but one. It also vanishes when it operates upon a "dynamical flux" and, hence, will not contribute to transport coefficients. Finally, it vanishes for hard-sphere interactions but not for soft-sphere interactions.

Boltzmann equation derived by Green.[3] The connection between this operator and transport coefficients has been given by Choh and Uhlenbeck.[14]

ACKNOWLEDGMENTS

We thank Dr. M. S. Green and Dr. R. A. Piccirelli for interesting and helpful discussions.

APPENDIX A

To prove step (1) [Eq. (18)] we must use the relation

$$\int_V d\{\mathbf{R}\}G_0(t)g(\{\mathbf{R}\},\{\mathbf{P}\},t) = G_0(t)\int_V d\{\mathbf{R}\}g(\{\mathbf{R}\},\{\mathbf{P}\},t) = \int_V d\{\mathbf{R}\}g(\{\mathbf{R}\},\{\mathbf{P}\},t), \quad \text{(A1)}$$

where $g(\{\mathbf{R}\},\{\mathbf{P}\},t)$ is a function of the phase of the system.

Equation (A1) holds for any g—providing the system is infinite. To prove this, we note that

$$\int_V d\{\mathbf{R}\}G_0(t)g(\{\mathbf{R}\},\{\mathbf{P}\},t) = \int_V d\{\mathbf{R}\}g(\{\mathbf{R}+m^{-1}\mathbf{P}t\},\{\mathbf{P}\},t). \quad \text{(A2)}$$

We next change the variable of integration on the right side of (A2) from $\mathbf{R}$ to $\mathbf{R}'\equiv\mathbf{R}+m^{-1}\mathbf{P}t$, so that (A2) becomes

$$\int_V d\{\mathbf{R}\}G_0(t)g(\{\mathbf{R}\},\{\mathbf{P}\},t) = \int_{V'} d\{\mathbf{R}'\}g(\{\mathbf{R}'\},\{\mathbf{P}\},t), \quad \text{(A3)}$$

where V' is the region of integration over $\mathbf{R}'$ space.

In the limit of an infinite system, however, we have

$$V=V'=\infty,$$

so that (A3) becomes, after dropping primes,

$$\int_\infty d\{\mathbf{R}\}G_0(t)g(\{\mathbf{R}\},\{\mathbf{P}\},t) = \int_\infty d\{\mathbf{R}\}g(\{\mathbf{R}\},\{\mathbf{P}\},t), \quad \text{(A4)}$$

which is just (A1) with $V=\infty$.

[If V is finite then (A1) holds when g obeys periodic boundary or when g is independent of $\mathbf{R}$—as can be easily verified.]

[14] S. T. Choh and G. E. Uhlenbeck, Navy Theoretical Physics, Contract No. Nonr 1224(15), University of Michigan, 1958 (unpublished).

A result analogous to (A1) may be obtained for integrals of the clusters. The cluster $V_n(1, 2, \cdots, n+1)G_0^{-1}$ is a function of the free-particle operator L_N^0,

$$L_N^0\equiv\sum_{i=1}^{n+1}\mathbf{P}_i\cdot\frac{\partial}{\partial\mathbf{R}_i}+\sum_{i=n+2}^{N}\mathbf{P}_i\cdot\frac{\partial}{\partial\mathbf{R}_i},$$

as well as the $\frac{1}{2}n(n+1)$ interaction terms (L_{ij}'s),

$$L_{ij}\equiv\mathbf{F}_{ij}(\mathbf{R}_i-\mathbf{R}_j)\cdot(\partial/\partial\mathbf{P}_i-\partial/\partial\mathbf{P}_j), \quad (1\leq i<j\leq n+1)$$

for all i and j satisfying $1\leq i<j\leq n+1$. [This can be seen from (11) and (4a).] We thus see that $V_n(1, 2, \cdots, n+1)G_0^{-1}$ depends upon the positions of particles $1, 2, \cdots, n+1$ through the pair forces, $\mathbf{F}_{ij}$'s, as well as through the gradients $\sum_{i=1}^{n+1}\mathbf{P}_i\cdot\partial/\partial\mathbf{R}_i$. We also see that $V_n(1, 2, \cdots, n+1)G_0^{-1}$ depends upon the positions of the remaining $(N-n-1)$ particles $n+2, n+3, \cdots, N$ in the form of gradients

$$\left(\sum_{i=n+2}^{N}\mathbf{P}_i\cdot\partial/\partial\mathbf{R}_i\right)$$

only. It then follows from (A1) that the integral of $V_n(1, 2, \cdots, n+1)G_0^{-1}$ over the positions, $\mathbf{R}_{n+2}$, $\mathbf{R}_{n+3}$, $\cdots$, $\mathbf{R}_N$, of these $(N-n-1)$ particles commutes with $V_n(1, 2, \cdots, n+1)$—just as they commute with G_0 in (A1). Hence, for an infinite system, or if g obeys periodic boundary conditions, or if g is independent of R_{n+2}, $\cdots\mathbf{R}_N$ we must have

$$V^{-N}\int d\{\mathbf{R}\}V_n(1, 2\cdots n+1)G_0^{-1}g = V^{-(n+1)}\int d\mathbf{R}_1 d\mathbf{R}_2\cdots d\mathbf{R}_{n+1}V_n(1, 2\cdots n+1)G_0^{-1} \times\left\{V^{-N+n+1}\int d\mathbf{R}_{n+2}\cdots d\mathbf{R}_N g\right\}. \quad \text{(A5)}$$

This can obviously be generalized to

$$V^{-N}\int d\{\mathbf{R}\}V_s(i_1,\cdots i_{s+1})G_0^{-1}g = V^{-(s+1)}\int d\mathbf{R}_{i_1}\cdots d\mathbf{R}_{i_{s+1}}V_s(i_1\cdots i_{s+1})G_0^{-1} \times\left\{V^{-N+s+1}\int d\{\mathbf{R}\neq\mathbf{R}_{i_1}\cdots R_{i_{s+1}}\}g\right\}, \quad \text{(A6)}$$

since the specific particle indices involved is not relevant. (Here $\{\mathbf{R}\neq\mathbf{R}i_1\cdots\mathbf{R}i_{s+1}\}$ denotes the fact that we do not integrate over the positions $\mathbf{R}i_1$, $\mathbf{R}i_2$, $\cdots$, $\mathbf{R}i_{s+1}$.)

Since only s of the $\frac{1}{2}s(s+1)$ relative coordinates among particles $i_1, \cdots, i_{s+1}$ are independent of each other we may, in (A6), change the $(s+1)$-independent variables $\mathbf{R}i_1$, $\mathbf{R}i_2$, $\cdots$, $\mathbf{R}i_{s+1}$ to any s-independent relative coordinates—say, $\mathbf{R}i_1i_2$, $\mathbf{R}i_1i_3$, $\cdots$, $\mathbf{R}i_1i_{s+1}$—plus the center-of-mass coordinate $(s+1)^{-1}(\mathbf{R}i_1+\mathbf{R}i_2$

$+\cdots+\mathbf{R}i_{s+1})$. The center-of-mass coordinate appears only as a gradient in $V_s(i_1\cdots i_{s+1})$ and, hence, the integral of $V_s(i_1\cdots i_{s+1})$ over the center-of-mass coordinate will commute with $V_s(i_1\cdots i_{s+1})$ so that (A6) becomes

$$V^{-N}\int d\{\mathbf{R}\}V_s(i_1\cdots i_{s+1})G_0^{-1}g$$
$$=V^{-s}\int d\mathbf{R}_{i_1i_2}\cdots d\mathbf{R}_{i_1i_{s+1}}V_s(i_1\cdots i_{s+1})G_0^{-1}$$
$$\times\Big[V^{-N+s}\int d(\mathbf{R}_{i_1}+\cdots+\mathbf{R}_{i_{s+1}})(s+1)^{-1}$$
$$\times\int d\{\mathbf{R}\neq\mathbf{R}_{i_1}\cdots\mathbf{R}_{i_{s+1}}\}g\Big]. \quad \text{(A7)}$$

We may use (A7) to establish (18), step (1), by setting $g=G_N(\neq i_1\cdots i_{s+1})F_N(0)$. First, we must show that, aside from gradients, $G_N(\neq i_1\cdots i_{s+1})$ is independent of the relative positions between particles $i_1, i_2, \cdots, i_{s+1}$. To understand why this is so, we shall first briefly consider the way in which a product of f's depends upon the relative coordinates of the particles. Thus, we note, from (6), (4b), and (2), that the explicit dependence of f_{ij} upon the particle coordinates may be stated as follows:

$$f_{ij}=f(L_N{}^0, \mathbf{R}_i-\mathbf{R}_j),$$

so that, aside from gradients, the dependence of f_{ij} upon the coordinates of the particles is given by

$$f_{ij}=f(\mathbf{R}_i-\mathbf{R}_j)$$

just as in equilibrium. It then follows that, aside from gradients, a product of f's will depend upon the relative position between two given particles if, and only if, these two particles are connected to each other in a cluster. This is strictly analogous to Mayer's theory.

Since the expansion of $G_N(\neq i_1\cdots i_{s+1})$ excludes, by definition, all f products in which two or more of the particles $i_1, i_2, \cdots, i_{s+1}$ are connected to each other in a cluster, it follows that, aside from gradients $G_N(\neq i_1\cdots i_{s+1})$ is independent of the relative positions between particles $i_1, i_2, \cdots, i_{s+1}$.

The integral of $G_N(\neq i_1\cdots i_{s+1})$ over the relative positions between particles $i_1, i_2, \cdots, i_{s+1}$ will, thus, commute with $G_N(\neq i_1\cdots i_{s+1})$ so that, if $F_N(0)$ is independent of particle positions,

$$V^{-s}\int d\mathbf{R}_{i_1i_2}\cdots d\mathbf{R}_{i_1i_{s+1}}G_N(\neq i_1\cdots i_{s+1})F_N(0)$$
$$=G_N(\neq i_1\cdots i_{s+1})V^{-s}\int d\mathbf{R}_{i_1i_2}\cdots d\mathbf{R}_{i_1i_{s+1}}F_N(0)$$
$$=G_N(\neq i_1\cdots i_{s+1})F_N(0). \quad \text{(A8)}$$

We may now set

$$g=G_N(\neq i_1\cdots i_{s+1})F_N(0)$$

in (A7), and make use of (A8), and the relation

$$V^{-N}\int d\{\mathbf{R}\}\equiv V^{-s}\int d\mathbf{R}_{i_1i_2}\cdots d\mathbf{R}_{i_1i_{s+1}}V^{-N+s}$$
$$\times\int d(\mathbf{R}_{i_1}+\cdots+\mathbf{R}_{i_{s+1}})(s+1)^{-1}$$
$$\times\int d\{\mathbf{R}\neq\mathbf{R}_{i_1}\cdots\mathbf{R}_{i_{s+1}}\}$$

to obtain finally

$$V^{-N}\int d\{\mathbf{R}\}V_s(i_1\cdots i_{s+1})G_0^{-1}G_N(\neq i_1\cdots i_{s+1})F_N(0)$$
$$=V^{-s}\int d\mathbf{R}_{i_1i_2}\cdots d\mathbf{R}_{i_1i_{s+1}}V_s(i_1\cdots i_{s+1})G_0^{-1}$$
$$\times V^{-N}\int d\{\mathbf{R}\}G_N(\neq i_1\cdots i_{s+1})F_N(0), \quad \text{(A9)}$$

which is just (18), step (1), as we set out to prove.

APPENDIX B

To prove step (2), Eq. (19), we write $G_N(\neq i_1\cdots i_{s+1})$ in the form

$$G_N(\neq i_1\cdots i_{s+1})=G_N-\mathbf{C}_N(i_1\cdots i_{s+1}), \quad \text{(B1)}$$

where $\mathbf{C}_N(i_1\cdots i_{s+1})$ is defined in Sec. IIB, and then we consider the region of $\{\mathbf{R}\}$ for which $\mathbf{C}_N(i_1\cdots i_{s+1})$ vanishes. First, we note that if $\mathbf{F}_{ks}=\mathbf{F}(\mathbf{R}_{ks})$ is a short-range force then $f_{ks}(t)$,

$$f_{ks}(t)\equiv\int_0^t dt_1G_{ks}(t_1)\mathbf{F}_{ks}\cdot\left(\frac{\partial}{\partial\mathbf{P}_k}-\frac{\partial}{\partial\mathbf{P}_s}\right), \quad \text{(B2)}$$

is zero unless $\mathbf{R}_{ks}$ lies within some bounded region of finite extent. The volume of this region will depend upon the time t as well as the range of force, because the propagator $G_{ks}(t_1)$ operates on $\mathbf{F}_{ks}$ and makes the argument of $\mathbf{F}_{ks}$ a function of t_1. In fact, the only region of $\mathbf{R}_{ks}$ space for which $f_{ks}(t)$ does not vanish is just the "collision cylinder" whose length is $m^{-1}t|\mathbf{P}_k-\mathbf{P}_s|$ and whose cross section is that total scattering cross section which corresponds to the force $\mathbf{F}_{ks}$. We, thus, see that the time-dependent f, like the equilibrium Mayer f, is zero unless the separation, $\mathbf{R}_{ks}$, between k and s is less than some finite distance. This finite distance will depend upon the time as well as the range of force. The important point to bear in mind here is that this finite distance is *independent of the total volume* V of the system.

It then follows that a cluster of f's (a connected product of f's) is zero whenever the separation between any two particles in this cluster is greater than some

finite distance. This is strictly analogous to the vanishing of equilibrium clusters (Ursell functions).

Now, by definition, every f product in $\mathbf{C}_N(i_1,i_2)$ contains particles i_1 and i_2 connected to each other in a cluster and, hence, every f product in $\mathbf{C}_N(i_1,i_2)$ will vanish when the relative separation between particles i_1 and i_2 is greater than some finite distance. Consequently, there must exist a bounded region of finite extent such that $\mathbf{C}_N(i_1,i_2)$ vanishes when $\mathbf{R}i_1i_2$ lies outside of this region. If we denote this region by $V^*(i_1i_2)$, and if we also denote the region of V which is outside of $V^*(i_1i_2)$ by $[V-V^*(i_1i_2)]$, then we must have

$$\mathbf{C}_N(i_1,i_2)=0, \quad [\mathbf{R}i_1i_2 \text{ in } V-V^*(i_1i_2)] \tag{B3}$$

and hence,

$$G_N(\neq i_1,i_2)=G_N, \quad [\mathbf{R}i_1i_2 \text{ in } V-V^*(i_1i_2)]. \tag{B4}$$

{We thus see that the propagator $G_N(\neq i_1i_2)$ is closely related to the propagator G_N. Indeed, Eq. (B4) states that $G_N(\neq i_1i_2)$ is equal to G_N for that region $[V-V^*(i_1i_2)]$ of $\mathbf{R}i_1i_2$ space which does not lead to interactions (collisions, correlations) between i_1 and i_2 within a given time. This means, since $|V^*(i_1i_2)|$ is a finite volume independent of V, that when V is large, $G_N(\neq i_1i_2)$ is equal to G_N for most of $\mathbf{R}i_1i_2$ space. From (B4) and the definition of $G_N(i_1i_2)$, we may thus view $G_N(\neq i_1i_2)$ as the propagator of a system of N-interacting particles in which there are no correlations between i_1 and i_2, and which is equal to G_N for that region of $\mathbf{R}i_1i_2$ space which does not lead to correlations between i_1 and i_2.}

To establish step (2) for $s=1$ we write

$$\begin{aligned} V^{-1}\int_V d\mathbf{R}_{i_1i_2}[G_N-G_N(\neq i_1i_2)]F_N(0) \\ = V^{-1}\int_{V^*(i_1i_2)} d\mathbf{R}_{i_1i_2}[G_N-G_N(\neq i_1i_2)]F_N(0) \\ +V^{-1}\int_{[V-V^*(i_1i_2)]} d\mathbf{R}_{i_1i_2}[G_N-G_N(\neq i_1i_2)]F_N(0), \end{aligned} \tag{B5}$$

and substitute (B4) into (B5) to obtain

$$\begin{aligned} V^{-1}\int_V d\mathbf{R}_{i_1i_2}[G_N-G_N(\neq i_1i_2)]F_N(0) \\ = V^{-1}\int_{V^*(i_1i_2)} d\mathbf{R}_{i_1i_2}[G_N-G_N(\neq i_1i_2)]F_N(0) \\ = |V^*(i_1i_2)|\,V^{-1}[\langle G_NF_N(0)\rangle_{V^*(i_1i_2)} \\ -\langle G_N(\neq i_1i_2)F_N(0)\rangle_{V^*(i_1i_2)}], \end{aligned} \tag{B6}$$

where

$$\langle A\rangle_{V^*(i_1i_2)}$$

denotes the average of phase function A over the region $V^*(i_1i_2)$, and $|V^*(i_1i_2)|$ denotes the volume of region $V^*(i_1i_2)$.

Since $|V^*(i_1i_2)|$ is a finite volume independent of V, and since the average of a phase function over a finite region inside the system is also independent of the total volume V of the system,[15] we find that as V becomes infinite (B6) becomes

$$\begin{aligned} V^{-1}\int_V d\mathbf{R}_{i_1i_2}G_N(\neq i_1i_2)F_N(0) \\ = V^{-1}\int_V d\mathbf{R}_{i_1i_2}G_NF_N(0)+O(V^{-1}). \end{aligned} \tag{B7}$$

The average of (B7) over all initial configuration space thus yields

$$\begin{aligned} V^{-1}\int d\{\mathbf{R}\}G_N(\neq i_1i_2)F_N(0) \\ = V^{-N}\int d\{\mathbf{R}\}G_NF_N(0)+O(V^{-1}) \\ =\phi+O(V^{-1}), \end{aligned} \tag{B8}$$

where we have used

$$V^{-N}\int d\{\mathbf{R}\}\,V^{-1}\int d\mathbf{R}_{i_1i_2}=V^{-N}\int d\{\mathbf{R}\}.$$

Equation (B8) establishes step (2) for s equal to one.

We may establish step (2) for all s in much the same way as for s equal to one. Thus, we recall that $\mathbf{C}_N(i_1\cdots i_{s+1})$ has been defined as the sum of all f products which contain two or more of the particles $i_1, i_2, \cdots, i_{s+1}$ connected to each other in a cluster.

Hence, $\mathbf{C}_N(i_1\cdots i_{s+1})$ will be zero when all $(s+1)$ particles $i_1, \cdots, i_{s+1}$ are simultaneously separated from each other by more than some finite distance. Since only s of the $\frac{1}{2}s(s-1)$ relative coordinates between these particles are independent, we can make $\mathbf{C}_N(i_1\cdots i_{s+1})$ vanish by requiring s-independent relative coordinates to lie within those s corresponding finite regions for which all $(s+1)$ particles are sufficiently separated from each other. Thus, there exists finite regions,

$$V'(i_1i_2),\ V'(i_1i_3),\ \cdots,\ V'(i_1i_{s+1}),$$

such that

$$\mathbf{C}_N(i_1\cdots i_{s+1})=0$$

and, hence,

$$G_N(\neq i_1\cdots i_{s+1})=G_N, \tag{B9}$$

when $\mathbf{R}i_1i_2$ lies within $[V-V'(i_1i_2)]$, $\mathbf{R}i_1i_3$ lies within $[V-V'(i_1i_3)]$, etc. [We note that $V'(i_1i_2)$ is not necessarily the same as $V^*(i_1i_2)$.]

[15] There will, in general, be surface effects. Such effects, however, become vanishingly small as the volume becomes infinite. There are no such surface effects when periodic boundary conditions are assumed.

Equation (B9) thus states that

$$V^{-s}\int_{[V-V'(i_1i_2)]} d\mathbf{R}_{i_1i_2}\int_{[V-V'(i_1i_3)]} d\mathbf{R}_{i_1i_3}\cdots\int_{[V-V'(i_1i_{s+1})]} d\mathbf{R}_{i_1i_{s+1}}[G_N-G_N(\neq i_1\cdots i_{s+1})]F_N(0)=0. \tag{B10}$$

But

$$\int_{[V-V'(ks)]} d\mathbf{R}_{ks}=\int_V d\mathbf{R}_{ks}-\int_{V'(ks)} d\mathbf{R}_{ks},$$

so (B10) becomes

$$\begin{aligned}
&V^{-s}\int_V d\mathbf{R}_{i_1i_2}\int_V dR_{i_1i_3}\cdots\int_V d\mathbf{R}_{i_1i_{s+1}}[G_N-G_N(\neq i_1\cdots i_{s+1})]F_N(0)\\
&=\sum_{n_1=2}^{s+1} V^{-s}\int_V d\mathbf{R}_{i_1i_2}\cdots\int_{V'(i_1i_{n_1})} d\mathbf{R}_{i_1i_{n_1}}\cdots\int_V d\mathbf{R}_{i_1i_{s+1}}[G_N-G_N(\neq i_1\cdots i_{s+1})]F_N(0)-\sum_{1\leqslant n_1<n_2\leqslant s+1} V^{-s}\\
&\quad\times\int_V d\mathbf{R}_{i_1i_2}\cdots\int_{V'(i_1i_{n_1})} d\mathbf{R}_{i_1i_{n_1}}\cdots\int_{V'(i_1i_{n_2})} d\mathbf{R}_{i_1i_{n_2}}\cdots\int_V d\mathbf{R}_{i_1i_{s+1}}\\
&\qquad\times[G_N-G_N(\neq i_1\cdots i_{s+1})]F_N(0)+\sum_{1\leqslant n_1<n_2<n_3\leqslant s+1}\cdots\\
&=\sum_{n_1=2}^{s+1} O(V^{-1}|V'(i_1i_{n_1})|)+\sum_{1\leqslant n_1<n_2\leqslant s+1} O(V^{-2}|V'(i_1i_{n_1})||V'(i_1i_{n_2})|)+O(V^{-3})+\cdots\\
&=sO(V^{-1})+s(s-1)O(V^{-2})+O(V^{-3}).
\end{aligned} \tag{B11}$$

Integrating (B11) over all initial configuration space then yields the desired result:

$$V^{-N}\int d\{\mathbf{R}\}[G_N-G_N(\neq i_1\cdots i_{s+1})]F_N(0)=sO(V^{-1}),$$

and hence,

$$\begin{aligned}
V^{-N}\int d\{\mathbf{R}\}G_N(\neq i_1\cdots i_{s+1})F_N(0)&=V^{-N}\int d\{\mathbf{R}\}G_NF_N(0)+sO(V^{-1})\\
&=\phi+sO(V^{-1}),
\end{aligned} \tag{B12}$$

which establishes step (2) for all s.

APPENDIX C

To prove (32) we must expand β_s and ϕ into sums of f products, and then refer back to (5) and (6) to obtain the time dependence of these f products.

By definition, β_s is given in (21) as an integral over the cluster $V_s(i_1\cdots i_{s+1})$, and $V_s(i_1\cdots i_{s+1})$ may be expanded into a sum of f products involving particles $i_1, \cdots, i_{s+1}$. [See, for example, (13) and (15).]

That is,

$$\begin{aligned}
V_s(i_1\cdots i_{s+1})&\equiv\sum^{i_1\cdots i_{s+1}} f_{b_1}f_{b_2}\cdots f_{b_k}G_0\\
&\equiv\sum_k\sum_{\{b_1\cdots b_k\}}^{i_1\cdots i_{s+1}} f_{b_1}f_{b_2}\cdots f_{b_k}G_0,
\end{aligned} \tag{C1}$$

where b_i denotes some pair index from among $i_1, \cdots, i_{s+1}$, and where the restrictions upon the summations have not been explicitly stated.

Substituting (C1), (21), (23), and (8) into $\beta_sG_0^{-1}\phi$ yields

$$\begin{aligned}
\beta_sG_0^{-1}\phi=\lim_{N,V\to\infty}\sum_{i_1<\cdots<i_{s+1}\leqslant N} V^{-s}\int d\mathbf{R}_{i_1i_2}\cdots d\mathbf{R}_{i_1i_{s+1}}\sum^{i_1\cdots i_{s+1}} f_{b_1}\cdots f_{b_2}\\
\times\left\{V^{-N}\int d\{\mathbf{R}\}[G_0+\sum_{n=1}^{\infty}\sum_{\{\alpha\}}^{N} f_{\alpha_1}\cdots f_{\alpha_n}G_0]\right\}.
\end{aligned} \tag{C2}$$

To obtain the time dependence of the f product in (C2), we refer back to (6) and (5), and find

$$f_{b_1}\cdots f_{b_k}\left\{V^{-N}\int d\{\mathbf{R}\}[G_0+\sum_{n=1}^{\infty}\sum_{\{\alpha\}}^{N} f_{\alpha_1}\cdots f_{\alpha_n}G_0]F_N(0)\right\}$$

$$=\int_0^t dt_1\cdots\int_{t_{k-1}}^t dt_k G_{b_1}(t_1)\cdots G_{b_k}(t_k-t_{k-1})iL_{b_k}\left\{V^{-N}\int d\{\mathbf{R}\}[G_0(t-t_k)+\sum_{n=1}^{\infty}\sum_{\{\alpha\}}^{N}\int_{t_k}^t dt_{k+1}\int_{t_{k+1}}^t dt_{k+2}\cdots\right.$$

$$\left.\times\int_{t_{k+n-1}}^t dt_{k+n}G_{\alpha_1}(t_{k+1}-t_k)\cdots G_{\alpha_n}(t_{k+n}-t_{k+n-1})iL_{\alpha_n}G_0(t-t_{k+n})]F_N(0)\right\}. \quad \text{(C3)}$$

If we change the dummy variables of integration from t_{k+s} to

$$t_s'\equiv t_{k+s}-t_k$$

for $s=1, 2, \cdots, n$ we find that the bracketed term on the right side of (C3) becomes

$$\{\quad\}=\left\{V^{-N}\int d\{\mathbf{R}\}\left[G_0(t-t_k)+\sum_{n=1}^{\infty}\sum_{\{\alpha\}}^{N}\int_0^{t-t_k}dt_1'\int_{t_1'}^{t-t_k}dt_2'\cdots\int_{t_{n-1}'}^{t-t_k}dt_n'\right.\right.$$

$$\left.\left.\times G_{\alpha_1}(t_1')\cdots G_0(t-t_n')\right]F_N(0)\right\}\equiv\phi(t-t_k). \quad \text{(C4)}$$

Substituting (C4) into (C3), and then substituting (C3) into (C2) we obtain

$$\beta_s G_0^{-1}\phi=\lim_{N,V\to\infty}\sum_{i_1<\cdots<i_{s+1}} V^{-s}\int d\mathbf{R}_{i_1i_2}\cdots d\mathbf{R}_{i_1i_{s+1}}\sum^{i_1\cdots i_{s+1}}\int_0^t dt_1\cdots\int_{t_{k-1}}^t dt_k G_{b_1}(t_1)\cdots G_{b_k}(t_k-t_{k-1})iL_{b_k}\phi(t-t_k). \quad \text{(C5)}$$

We now (1) reverse the order of integration in (C5), (2) bring the t_k integration in front of the summations, and (3) set t_k equal to y. Equation (C5) then becomes

$$\beta_s G_0^{-1}\phi=\lim\int_0^t dy\left[\sum_{i_1<\cdots<i_{s+1}} V^{-s}\int d\mathbf{R}_{i_1i_2}\cdots d\mathbf{R}_{i_1i_{s+1}}\sum^{i_1\cdots i_{s+1}}\int_0^y dt_{k-1}\cdots\int_0^{t_2}dt_1\right.$$

$$\left.\times G_{b_1}(t_1)\cdots G_{b_k}(y-t_{k-1})iL_{b_k}\right]\phi(t-y). \quad \text{(C6)}$$

But

$$\frac{\partial}{\partial y}\int_0^y dt_k\int_0^{t_k}dt_{k-1}\cdots\int_0^{t_2}dt_1 G_{b_1}(t_1)\cdots G_{b_k}(t_k-t_{k-1})iL_{b_k}G_0(y-t_k)$$

$$=\int_0^y dt_{k-1}\cdots\int_0^{t_2}dt_1 G_{b_1}(t_1)\cdots G_{b_k}(y-t_{k-1})iL_{b_k}+\int_0^y dt_k\cdots\int_0^{t_2}dt_1 G_{b_1}(t_1)\cdots G_0(y-t_k)iL_0. \quad \text{(C7)}$$

Substituting (C7) into (C6) and making use of the fact that

$$L_0\phi(t-y)=0$$

we finally obtain the desired result, Eq. (32).

$$\beta_s G_0^{-1}\phi=\int_0^t dy\left[\frac{\partial\beta_s(y)}{\partial y}\right]\phi(t-y), \quad \text{(C8)}$$

where, with (C1),

$$\beta_s(y)=\lim_{N,V\to\infty}\sum_{i_1<\cdots<i_{s+1}} V^{-s}\int d\mathbf{R}_{i_1i_2}\cdots d\mathbf{R}_{i_1i_2}\sum^{i_1\cdots i_{s+1}}\int_0^y dt_k\int_0^{t_k}dt_{k-1}\cdots\int_0^{t_2}dt_1 G_{b_1}(t_1)\cdots G_{b_k}(t_k-t_{k-1})iL_{b_k}G_0(y-t_k)$$

$$\equiv\lim_{N,V\to\infty}\sum_{i_1<\cdots<i_{s+1}} V^{-s}\int d\mathbf{R}_{i_1i_2}\cdots d\mathbf{R}_{i_1i_{s+1}}V_s(i_1\cdots i_{s+1};y). \quad \text{(C9)}$$

It is assumed in (C8) that differentiation with respect to y commutes with integration over configurations.

APPENDIX D

To prove that

$$\beta'(0)=\sum_{s=1}^{\infty}\beta_s'(0)=0,$$

we combine (C7) and (C9) to obtain the expanded form of $\beta_s'(t)$,

$$\beta_s'(t)=\lim_{N,V\to\infty}\sum_{i_1<\cdots<i_{s+1}}V^{-s}\int d\mathbf{R}_{i_1i_2}\cdots d\mathbf{R}_{i_1i_{s+1}}\sum^{i_1\cdots i_{s+1}}\left[\int_0^t dt_{k-1}\cdots\int_0^{t_2}dt_1G_{b_1}(t_1)\cdots iL_{b_k}\right.$$
$$\left.+\int_0^t dt_k\cdots\int_0^{t_2}dt_1G_{b_1}(t_1)\cdots G_0(t-t_k)iL_0\right]. \quad \text{(D1)}$$

But the propagator $G_b(\tau)$ is an exponential function of τ so that, for small enough t, (D1) becomes

$$\beta_s'(t)=\sum_{i_1<\cdots<i_{s+1}}V^{-s}\int d\mathbf{R}_{i_1i_2}\cdots d\mathbf{R}_{i_1i_{s+1}}\sum^{i_1\cdots i_{s+1}}O(t^{k-1}). \quad \text{(D2)}$$

From the binary collision expansion of $V_s(i_1\cdots i_{s+1})$ it can be seen that for $s\geqslant 2$ we must have $k>1$ so that (assuming the limit can be taken) (D2) becomes, in the limit $t\to 0$,

$$\beta_s'(0)=0, \quad (s\geqslant 2). \quad \text{(D3)}$$

For s equal to 1, k is also equal to 1, and we proceed as follows, to prove $\beta_1'(0)=0$.

$$\beta_1'(0)=\lim_{t\to 0}\left(\frac{\partial}{\partial t}\right)\sum_{i_1<i_2}V^{-1}\int d\mathbf{R}_{i_1i_2}\int_0^t dt_1G_{i_1i_2}(t_1)iL_{i_1i_2}G_0(t-t_1),$$

$$=\lim_{t\to 0}\left(\frac{\partial}{\partial t}\right)\sum V^{-1}\int d\mathbf{R}_{i_1i_2}[G_{i_1i_2}(t)-G_0(t)],$$

$$=\lim_{t\to 0}\sum V^{-1}\int d\mathbf{R}_{i_1i_2}[i(L_{i_1i_2}+L_0)G_{i_1i_2}(t)-iL_0G_0(t)],$$

$$=i\sum V^{-1}\int d\mathbf{R}_{i_1i_2}L_{i_1i_2},$$

$$=-i\sum V^{-1}\int d\mathbf{R}_{i_1i_2}\frac{\partial V(\mathbf{R}_{i_1i_2})}{\partial\mathbf{R}_{i_1i_2}}\cdot\left[\frac{\partial}{\partial\mathbf{P}_{i_1}}-\frac{\partial}{\partial\mathbf{P}_{i_2}}\right],$$

$$=0, \quad \text{(D4)}$$

since the volume integral of the gradient of $V(\mathbf{R}i_1i_2)$ will produce a vanishing surface integral of $V(\mathbf{R}i_1i_2)$. [It is assumed, in (D4), that the limit and the derivative can be taken inside the integral.] Combining (D4) and (D3) we have the desired result,

$$\beta'(0)=\sum_{s=1}^{\infty}\beta_s'(0)=0.$$