Exact Evolution of Reduced Distribution Functions in a Homogeneous Dense Classical Fluid

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The exact evolution of reduced distribution functions is studied for a homogeneous dense classical fluid by methods which are equivalent to the diagram technique of Prigogine and co-workers. No diagrams or Fourier expansions are used in this work, however. So long as only short-range order is present in the fluid, exact equations for the evolution of the momentum distribution function and for reduced s-particle distribution functions are obtained. They are seen to be non-Markovian in a sense explicitly related to the finite duration of a collision. Simple Markovian equations—a generalized master equation for momenta and a functional equation for correlations—result only when the momentum distribution changes negligibly in times of the order of the duration of a collision.

I. PRELIMINARIES

FOR the past five years, the group at Brussels under the leadership of Prigogine has been developing a means of studying mechanical systems obeying the Liouville equation.[1] The technique involves extensive use of modern perturbation theory, e.g., summations over classes of diagrams, study not of the distribution function but of its Fourier coefficients, etc. The resulting difficulties to the reader have kept this work from being appreciated as much as it might otherwise have been.

It was the hope of the author in undertaking the research presented here that by approaching the problem from a somewhat different viewpoint, greater generality and more mathematical and physical insight might be obtained, at least for the problem of classical fluids. Whether the type of approach presented here will prove as versatile as that characterized by diagrams and Fourier expansions, e.g., in studies of plasmas, quantum effects, turbulence, etc., remains to be seen.

We shall study the time evolution of an ensemble of classical systems, each system containing N particles in a volume Ω. The ensemble is described completely by the N-particle distribution function (D.F.), f_N. The exact equation of motion is given by the Liouville equation[2]:

$$i\partial f_N/\partial t = L_N f_N \equiv (L_N{}^0 + \lambda L_N{}') f_N. \tag{1}$$

The λ is viewed merely as a convenient counting parameter. At no time in this work is it assumed small. For a classical fluid, the operators are given explicitly by

$$L_N{}^0 = -i \sum_{j=1}^{N} \mathbf{v}_j \cdot \frac{\partial}{\partial \mathbf{x}_j}, \tag{2}$$

$$L_N{}' = i \sum_{r<s=1}^{N} \frac{\partial V_{rs}(\mathbf{x}_{rs})}{\partial \mathbf{x}_r} \cdot \frac{\partial}{\partial \mathbf{p}_{rs}}. \tag{3}$$

In this notation, $\mathbf{p}_j$, the momentum of particle j, is just the velocity of particle j, $\mathbf{v}_j$, times the particle's mass. Other notation used is

$$\mathbf{x}_{rs} = \mathbf{x}_r - \mathbf{x}_s, \quad \mathbf{p}_{rs} = \mathbf{p}_r - \mathbf{p}_s,$$
$$\partial/\partial \mathbf{p}_{rs} = \partial/\partial \mathbf{p}_r - \partial/\partial \mathbf{p}_s.$$

The phase space is of infinite extent in the momentum part. The configuration part is limited to the interior of a box of volume Ω. The effect of wall interactions is eliminated by imposing either periodic or zero boundary condition on f_N at the walls of the box. In such a space the operator L_N is easily seen to be Hermitian[1]:

$$\langle m|L_N|n\rangle = \int \{d\mathbf{x}\}\{d\mathbf{p}\}\, \varphi_m{}^* L_N \varphi_n = i \int \{d\mathbf{x}\}\{d\mathbf{p}\}\, \varphi_m{}^* \left[- \sum_{j=1}^{N} \mathbf{v}_j \cdot \frac{\partial}{\partial \mathbf{x}_j} + \sum_{r<s=1}^{N} \frac{\partial V_{rs}}{\partial \mathbf{x}_r} \cdot \frac{\partial}{\partial \mathbf{p}_{rs}} \right] \varphi_n.$$

The functions φ are any functions of phase space obeying the boundary conditions. This expression is integrated by parts with the requirement that φ_m and φ_n be zero at infinite momentum. Since the surface integral over the walls of the box vanishes because of the boundary condition, this becomes

$$\langle m|L_N|n\rangle = -i \int \{d\mathbf{x}\}\{d\mathbf{p}\}\, \varphi_n \left[- \sum_{j=1}^{N} \mathbf{v}_j \cdot \frac{\partial}{\partial \mathbf{x}_j} + \sum_{r<s=1}^{N} \frac{\partial V_{rs}}{\partial \mathbf{x}_r} \cdot \frac{\partial}{\partial \mathbf{p}_{rs}} \right] \varphi_m{}^*;$$

therefore

$$\langle m|L_N|n\rangle = \langle n|L_N|m\rangle^*; \quad \text{Q.E.D.}$$

We now solve Eq. (1) formally. In general, throughout this paper, $\{\mathbf{x}\}$ and $\{\mathbf{p}\}$ refer to the sets of positions and momenta of the N particles at time t. For the moment, this is noted explicitly. The Liouville equation gives f_N

[1] For an exposition of these techniques and for the literature references, see I. Prigogine, *Non-Equilibrium Statistical Mechanics* (Interscience Publishers, Inc., New York, 1961).

[2] R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, New York, 1938), Chap. 3.

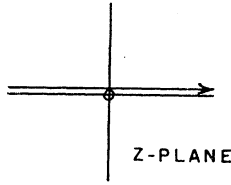FIG. 1. Contour of integration for Eq. (7).

as a constant of the motion[2]:

$$f_N[\{\mathbf{x}(t)\},\{\mathbf{p}(t)\},t] = f_N[\{\mathbf{x}(0)\},\{\mathbf{p}(0)\},0]. \qquad (4)$$

It is also clear that the solution of Eq. (1) is

$$f_N[\{\mathbf{x}(t)\},\{\mathbf{p}(t)\},t]$$
$$= \exp(-iL_N t) f_N[\{\mathbf{x}(t)\},\{\mathbf{p}(t)\},0], \qquad (5)$$

as may be seen by applying $i\partial/\partial t$ to Eq. (5) and by noting that the right-hand side correctly reduces to $f_N(0)$ for $t=0$. The exponential operator may be viewed as that operator which takes f_N *forward explicitly in time*. By combining Eqs. (4) and (5), another interpretation of the exponential operator is found,

$$\exp(-iL_N t) f_N[\{\mathbf{x}(t)\},\{\mathbf{p}(t)\},0]$$
$$= f_N[\{\mathbf{x}(0)\},\{\mathbf{p}(0)\},0], \qquad (6)$$

that of being the operator which moves the particles *backward* along their exact trajectories.

A different representation of the solution, Eq. (5), is preferred. Since L_N is Hermitian, its eigenvalues are real. On using the Cauchy integral formula,[3] Eq. (5) is seen to be identical to

$$f_N(t) = \frac{1}{2\pi i} \int_c dz \exp(-izt)(L_N - z)^{-1} f_N(0), \qquad (7)$$

where c is the contour of Fig. 1. Clearly, with t positive, the contour c, located an infinitesimal amount above the real axis, may be closed by a semicircle at infinity in the lower half-plane, thus enclosing all poles from eigenvalues of L_N. Equation (7) is the basis of this study.

It is convenient to prove here the following operator identity:

$$(A+B)^{-1} \equiv A^{-1} - A^{-1} + (A+B)^{-1}$$
$$\equiv A^{-1} - A^{-1}(A+B)(A+B)^{-1} + A^{-1}A(A+B)^{-1}$$
$$\equiv A^{-1} - A^{-1}B(A+B)^{-1}.$$

Therefore

$$(L_N - z)^{-1}$$
$$\equiv (L_N{}^0 - z)^{-1} - \lambda(L_N{}^0 - z)^{-1} L_N{}'(L_N - z)^{-1}. \qquad (8)$$

From time to time it will prove convenient to use Eq. (8) solved by iteration:

$$(L_N - z)^{-1} = \sum_{n=0}^{\infty} (-\lambda)^n (L_N{}^0 - z)^{-1} [L_N{}'(L_N{}^0 - z)^{-1}]^n, \qquad (9)$$

without proving its convergence. Summations over an infinite number of terms of Eq. (9) are always made. Physically meaningful results are consistently obtained using Eq. (9), even in the hypothetical limit of singular intermolecular potentials. It is felt that a rigorous treatment based on the mathematical theory of divergent series[4] would justify this usage.

From this point on, this paper departs radically from the methods of the Brussels group.[1,5]

II. EVOLUTION OF THE MOMENTUM D.F.

A homogeneous fluid is one with properties which do not change from point to point as a result of simple translation through the fluid. For such a system, we shall study the N-particle momentum D.F., $\varphi_N(\{\mathbf{p}\},t)$, which gives all information about momenta, but none about positions:

$$\varphi_N(\{\mathbf{p}\},t) \equiv \int \{d\mathbf{x}\} f_N(\{\mathbf{x}\},\{\mathbf{p}\},t). \qquad (10)$$

On using Eqs. (7) and (8) in (10), this becomes

$$\varphi_N(t) = \frac{1}{2\pi i} \int_c dz \exp(-izt) \int \{d\mathbf{x}\} (L_N{}^0 - z)^{-1} f_N(0)$$
$$- \frac{\lambda}{2\pi i} \int_c dz \exp(-izt) \int \{d\mathbf{x}\} (L_N{}^0 - z)^{-1}$$
$$\times L_N{}'(L_N - z)^{-1} f_N(0). \qquad (11)$$

Consider the $(L_N{}^0 - z)^{-1}$ operators of Eq. (11) as acting on the quantities to their right, expanded in eigenfunctions of the operator $L_N{}^0$. The $L_N{}^0$ is then replaced by its eigenvalue for each term of the expansion. But, since each term appears under an integral over $\{\mathbf{x}\}$, only the eigenvalue zero may arise. This is because, in $\{\mathbf{x}\}$ space, a constant is an eigenfunction of $L_N{}^0$ with eigenvalue zero:

$$L_N{}^0 \int \{d\mathbf{x}\} g(\{\mathbf{x}\}) = 0,$$

for $g(\{\mathbf{x}\})$ an arbitrary function. Therefore,

$$\int \{d\mathbf{x}\} (L_N{}^0 - z)^{-1} g(\{\mathbf{x}\}) = (-z)^{-1} \int \{d\mathbf{x}\} g(\{\mathbf{x}\}), \qquad (12)$$

and Eq. (11) becomes

$$\varphi_N(t) = \frac{1}{2\pi i} \int_c dz \exp(-izt)(-z)^{-1} \int \{d\mathbf{x}\} f_N(0)$$
$$- \frac{\lambda}{2\pi i} \int_c dz \exp(-izt)(-z)^{-1}$$
$$\times \int \{d\mathbf{x}\} L_N{}'(L_N - z)^{-1} f_N(0). \qquad (13)$$

[3] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Sec. 4.2.

[4] See, e.g., G. H. Hardy, *Divergent Series* (Oxford University Press, New York, 1949).
[5] F. Henin, P. Résibois, and F. Andrews, J. Math. Phys. **2**, 68 (1961), I. Prigogine and P. Résibois, Physica **27**, 629 (1961).

The first integral may be evaluated immediately by the residue method to yield $H(t)\varphi_N(0)$, where $H(t)$ is the Heaviside step function

$$H(t)=1, \quad t>0; \quad H(t)=0, \quad t<0.$$

It arises, because for $t<0$, the semicircle closing c must be in the upper half-plane, thereby missing the pole at $z=0$.

The second integral is of course not so easy, since it clearly represents the difference between $\varphi_N(t)$ and $\varphi_N(0)$. Indeed, if the $(L_N-z)^{-1}$ operator is replaced using Eq. (9), this second integral becomes

$$-\frac{\lambda}{2\pi i}\int_c dz \exp(-izt)(-z)^{-1}\int \{d\mathbf{x}\}L_N'$$

$$\times \sum_{n=0}^{\infty}(-\lambda)^n(L_N{}^0-z)^{-1}$$

$$\times[L_N'(L_N{}^0-z)^{-1}]^n f_N(0). \quad (14)$$

There are infinities of pole to consider. The virtue of the method here presented is its requiring the explicit treatment only of poles at the origin. The effect of other poles is given by operators which are easily handled mathematically and interpreted physically.

A pole at zero among those of Eq. (14) means that after a certain amount of interacting, a state of spatial noncorrelation is set up, as seen by Eq. (12). Then new correlation is instituted by the forces of the L_N' operators to the left of the pole at $z=0$. We seek a rigorous justification for considering only interactions separated by poles at zero (generalized *stosszahlansatz* or random phase approximation), when we know that particles do feel the effect of their past, even their distant past. Some realistic method must be adopted for breaking up the N-body interaction to throw out information about such correlations as are physically meaningless.

To do this for fluids, which have only short-range order, we only consider *correlations* involving groups of *at most* ν particles ($\nu\ll N$). Information coupling explicitly more than ν particles is thrown away as being physically meaningless. This should agree with physical reality for two reasons: (1) In a system with only short-range order, surely the only particles whose *correlation* could affect reduced D.F.'s are the particles within the region of the short-range order. (2) We know of no experiment whereby explicit correlations among larger groups of particles in a fluid may be observed. If irreversibility is defined as the presence of a way for information to be lost, then this retaining only correlations among ν or fewer particles introduces irreversibility. It does so, however, in the same way it is introduced in natural mechanical processes. We shall see below that this single restriction is enough to force the consideration of terms in Eq. (14) involving more and more poles at $z=0$.

Consider, then, the contributions to Eq. (14) in which at most the number of different particles which become involved through the operators L_N' is ν. Initial correlations among groups of more than ν particles present in $f_N(0)$ will be averaged over by a simple generalization of Eq. (12). Throughout this paper, use is made of the following identity:

$$i\int_0^{\infty}dt_1 \exp[-i(L_N-z)t_1]$$

$$\equiv \lim_{T\to\infty}i\int_0^T dt_1 \exp[-i(L_N-z)t_1]$$

$$= \lim_{T\to\infty}\frac{\exp[-i(L_N-z)T]-1}{-(L_N-z)}=(L_N-z)^{-1}. \quad (15)$$

The exponential gives zero because on the contour c, Im $z>0$. The second term of Eq. (13) becomes

$$-\frac{\lambda}{2\pi i}\int_c dz \exp(-izt)(-z)^{-1}\int \{d\mathbf{x}\}L_N'i$$

$$\times\int_0^{\infty}dt_1 \exp[-i(L_N-z)t_1]f_N(0)$$

$$=-\frac{\lambda}{2\pi}\int_0^{\infty}dt_1\int_c dz \exp[-iz(t-t_1)](-z)^{-1}$$

$$\times\int \{d\mathbf{x}\}L_N' \exp(-iL_Nt_1)f_N(0)$$

$$=-\lambda\int \{d\mathbf{x}\}L_N'i\int_0^{\infty}dt_1 H(t-t_1)$$

$$\times\exp(-iL_Nt_1)f_N(0). \quad (16)$$

This term has clear physical meaning. Changing the upper limit of the integral to t permits removing the Heaviside function. Then, on utilizing Eq. (6), this becomes

$$-i\lambda\int_0^t dt_1\int \{d\mathbf{x}\}L_N' \exp(-iL_Nt_1)f_N[\{\mathbf{x}(t)\},\{\mathbf{p}(t)\},0]$$

$$=-i\lambda\int_0^t dt_1\int \{d\mathbf{x}(t)\}L_N'(t)$$

$$\times f_N[\{\mathbf{x}(t-t_1)\},\{\mathbf{p}(t-t_1)\},0]. \quad (17)$$

The operational meaning of Eq. (17) is as follows: The distribution, $\varphi_N[\{\mathbf{p}(t)\},t]$, of $\{\mathbf{p}(t)\}$ is being calculated, so the particular $\{\mathbf{p}(t)\}$ are given. A set $\{\mathbf{x}(t)\}$ is chosen, about which the differentials $\{d\mathbf{x}(t)\}$ lie. This fixes $L_N'(t)$, and $f_N[\{\mathbf{x}(t)\},\{\mathbf{p}(t)\},0]$ may be found for this set. For a given term of L_N', the coordinates of the two particles involved in that term must be close enough together that the intermolecular force between them is

finite. During the first increment, $\Delta t_1^{(1)}$, this now-known product is the integrand of the t_1 integral. To find the integrand during the second increment, $\Delta t_1^{(2)}$, the exact equations of motion are used to calculate the positions and momenta the particles had at time $[t-\Delta t_1^{(1)}]$. Finding $f_N(\{\mathbf{x}[t-\Delta t_1^{(1)}]\}, \{\mathbf{p}[t-\Delta t_1^{(1)}]\}, 0)$ then gives the integrand for the second increment of the t_1 integral. The procedure is continued, following back in time the trajectories of the particles.

All further particles are neglected after no more than ν of them have become involved in the interaction. It is clear that if we were not able to do this, then Eq. (17) would fluctuate endlessly as a function of t. Omitting the possibility of bound states, further tracing back of the trajectories eventually finds the particles on straight-line trajectories that would have led them into their interaction. From the time these straight-line trajectories are reached, $\{\mathbf{p}(t-t_1)\}$ remains constant with further increase of t_1, and the points represented by $\{\mathbf{x}(t-t_1)\}$ get further and further separated.

Therefore, if the region in which ν or fewer bodies were initially correlated is only a small fraction of Ω, after a time τ_{corr} they are far enough away from each other that $f_N[\{\mathbf{x}(t-t_1)\}, \{\mathbf{p}(t-t_1)\}, 0]$ is independent of $\{\mathbf{x}(t-t_1)\}$. Then the D.F. contained in the t_1 integrand of Eq. (17) may be represented by $\Omega^{-N}\varphi_N[\{\mathbf{p}(t-t_1)\}, 0]$, instead of f_N. For most systems one describes by $f_N(0)$, the region of initial correlation of ν and fewer particles will indeed be very small, of the order of several times the ranges of the intermolecular forces. This is so because longer range correlations would have been difficult to establish in the fluid and hard to observe if they were there.

It will be shown below that Eq. (17), for $t>\tau_{\mathrm{corr}}$, is correctly given by terms in Eq. (14) with two poles at zero rather than one. Since Eq. (17) was formulated as if it had only one pole at zero, its contribution must be terminated at τ_{corr}. But of course, the terms in Eq. (14) which have two poles at zero must then be treated. They will lead to terms with three poles at zero, etc. Terms in Eq. (14) with more and more poles at zero must be treated in order to be consistent. Between any two poles at zero, up to ν particles may interact. This will be a consistent treatment involving all effects of up to ν-body correlations in the evolution of the reduced D.F.

For simplicity in this paper, the notation

$$\int \{d\mathbf{x}\}g(\{\mathbf{x}\}) \int \{d\mathbf{x}\}h(\{\mathbf{x}\})$$

is used without indicating that there are two sets of dummy coordinate variables. The integral on the right eliminates all spatial dependence. New spatial dependence is introduced on the left through the function g. This is then removed by the next integral.

A second pole at $z=0$ in Eq. (14) might arise at any $(L_N^0-z)^{-1}$ operator. The explicit location of this pole

may be marked by inserting the integral over $\{\mathbf{x}\}$ which gives rise to such poles:

$$-\frac{\lambda}{2\pi i}\int_c dz \exp(-izt)(-z)^{-1}$$

$$\times \int \{d\mathbf{x}\}L_N' \sum_{m=0}^{\infty} (-\lambda)^m (L_N^0-z)^{-1}$$

$$\times [L_N'(L_N^0-z)^{-1}]^m \Omega^{-N} \int \{d\mathbf{x}\}$$

$$\times \sum_{n=0}^{\infty} (-\lambda)^n [L_N'(L_N^0-z)^{-1}]^n f_N(0) \quad (18)$$

$$=-\frac{\lambda}{2\pi i}\int_c dz \exp(-izt)(-z)^{-1}$$

$$\times \int \{d\mathbf{x}\}L_N'(L_N-z)^{-1}\Big[\Omega^{-N}\varphi_N(0)$$

$$-\lambda\Omega^{-N}\int \{d\mathbf{x}\}L_N'(L_N-z)^{-1}f_N(0)\Big]. \quad (19)$$

Passage to Eq. (19) was by use of Eq. (9). The $n=0$ term has been separated from the rest of the n summation.

It now is apparent that the first term of Eq. (19) is precisely of the form of Eq. (17) for $t>\tau_{\mathrm{corr}}$. We seek correct consideration of terms in Eq. (14) involving more and more poles explicitly at zero. Thus to make Eq. (17) represent only the contribution from terms with just one pole at zero, the contribution from its t_1 integral must be cut off at τ_{corr}. Simultaneously, it now is clear in what sense the additional poles at zero have arisen. They represent states of spatial noncorrelation among groups of ν or fewer particles between interactions. If it were not for the throwing out of correlations involving more particles, a second pole at zero by itself could not rigorously arise. The contributions to $\varphi_N(t)$ in Eq. (11) from terms of Eq. (14) which contain only one pole at the origin may be written.

$$\varphi_N^{(1)}=H(t)\varphi_N(0)-\lambda\int \{d\mathbf{x}\}L_N'i$$

$$\times \int_0^{\tau_{\mathrm{corr}}} dt_1 H(t-t_1) \exp(-iL_Nt_1)f_N(0). \quad (20)$$

The contribution to φ_N from terms in Eq. (14) containing two poles at zero is given by Eq. (18) or (19). The $m=0$ term of Eq. (18) vanishes, because it is of the form

$$\int \{d\mathbf{x}\}L_N'(-z)^{-1}[\text{something independent of } \{\mathbf{x}\}]=0.$$

$$(21)$$

The $\{\mathbf{x}\}$ integral gives zero because the only $\{\mathbf{x}\}$ dependence of the integrand rests in the forces in L_N'.

For intermolecular potentials possessing inversion symmetry,

$$V_{ij}(\mathbf{x}_{ij}) = V_{ij}(-\mathbf{x}_{ij}), \qquad (22)$$

the force is an odd function of the coordinates of the pair of particles. Thus, L_N' is odd in the interchange $\{\mathbf{x}\} \to \{-\mathbf{x}\}$, and the integral of this odd function over all of configuration space vanishes.

On eliminating the $m=0$ term from Eq. (18) and using Eq. (9), Eq. (18) or (19) becomes

$$\varphi_N^{(2)} = \frac{\lambda^2}{2\pi i} \int_c dz \, \exp(-izt)(-z)^{-1} \int \{d\mathbf{x}\} L_N' \sum_{s=0}^{\infty} (-\lambda)^s (L_N^0 - z)^{-1}$$

$$\times [L_N'(L_N^0 - z)^{-1}]^s L_N'(L_N^0 - z)^{-1} \Omega^{-N} \left[\varphi_N(0) - \lambda \int \{d\mathbf{x}\} L_N'(L_N - z)^{-1} f_N(0) \right]$$

$$= \frac{\lambda^2}{2\pi i} \int_c dz \, \exp(-izt)(-z)^2 \Omega^{-N} \int \{d\mathbf{x}\} L_N'(L_N - z)^{-1} L_N' \left[\varphi_N(0) - \lambda \int \{d\mathbf{x}\} L_N'(L_N - z)^{-1} f_N(0) \right]$$

$$= \frac{\lambda^2}{2\pi i} \int_c dz \, \exp(-izt)(-z)^2 \Omega^{-N} \int \{d\mathbf{x}\} L_N' i \int_0^{\infty} dt_1 \exp[-i(L_N - z)t_1]$$

$$\times L_N' \left(\varphi_N(0) - i\lambda \int \{d\mathbf{x}\} L_N' \int_0^{\infty} dt_2 \exp[-i(L_N - z)t_2] f_N(0) \right).$$

The last step was made using Eq. (15). The two terms in the brackets are now separated and the z integrals performed by the residue method:

$$\varphi_N^{(2)} = \int_0^{\infty} dt_1 \frac{\lambda^2 i}{2\pi i} \int_c dz \, \exp[-iz(t-t_1)](-z)^2 \Omega^{-N} \int \{d\mathbf{x}\} L_N' \exp(-iL_N t_1)$$

$$\times L_N' \varphi_N(0) + \int_0^{\infty} dt_1 \int_0^{\infty} dt_2 \frac{\lambda^3}{2\pi i} \int_c dz \, \exp[-iz(t - t_1 - t_2)](-z)^2 \Omega^{-N}$$

$$\times \int \{d\mathbf{x}\} L_N' \exp(-iL_N t_1) L_N' \int \{d\mathbf{x}\} L_N' \exp(-iL_N t_2) f_N(0)$$

$$= i\lambda^2 \Omega^{-N} \int \{d\mathbf{x}\} L_N' i \int_0^{\infty} dt_1 \exp(-iL_N t_1) L_N'(1!)^{-1}(t - t_1) H(t - t_1)$$

$$\times \varphi_N(0) + i\lambda^2 \Omega^{-N} \int \{d\mathbf{x}\} L_N' i \int_0^{\infty} dt_1 \exp(-iL_N t_1) L_N'$$

$$\times \left[-\lambda \int \{d\mathbf{x}\} L_N' i \int_0^{\tau_{corr}} dt_2 \exp(-iL_N t_2)(1!)^{-1}(t - t_1 - t_2) H(t - t_1 - t_2) f_N(0) \right]. \quad (23)$$

The upper limit of the t_2 integral has been changed from ∞ to τ_{corr}. This is because, just as before, for $t_2 > \tau_{corr}$, the contribution from the second term of Eq. (23) could be made up from terms in Eq. (14) with *three* poles at zero and not two.

It is important to consider the meaning of the operator,

$$i\lambda^2 \Omega^{-N} \int \{d\mathbf{x}\} L_N' i \int_0^{\infty} dt_1 \exp(-iL_N t_1) L_N', \quad (24)$$

which acts on a function independent of $\{\mathbf{x}\}$. It takes one state of spatial noncorrelation into another by means of interaction between a group of particles. The $\exp(-iL_N t_1)$ operator acts here on L_N' as well as on

whatever is to the right of the complete operator. Therefore, the t_1 integrand can only be non-zero during the time that the two particles involved in a term of L_N' are within each others' force fields. The two particles concerned may be any of the ν interacting, so this non-zero interval may occur at any time during the complete ν-body interaction. But for times greater than the duration of the ν-body collision, τ_{coll}, the integrand is zero. The integral is written to infinity, but it only contributes to τ_{coll}. Because of the process it clearly represents, the operator of Eq. (24) may be called a *scattering operator*.

The procedure that gave Eqs. (20) and (23) is readily generalized to the case of any number, s, of poles at $z=0$. One gets a scattering operator for each

pole beyond the first. The z integral is easily performed by residues, using the formula[6]

$$\operatorname{Res}\frac{f(z)}{z^{(s+1)}}=\frac{1}{s!}\frac{\partial^{s}f(z)}{\partial z^{s}}\bigg|_{z=0}.$$

The following equation is obtained giving the exact evolution of $\varphi_{N}(t)$, subject only to the neglecting of the effects of correlations of greater than ν particles. This ν is not specifically noted in the equations of this paper, but its presence is implied in them:

$$\varphi_{N}(t)=\sum_{s=0}^{\infty}\left[i\lambda^{2}\Omega^{-N}\int\{d\mathbf{x}\}L_{N}'i\int_{0}^{\infty}dt_{j}\exp(-iL_{N}t_{j})L_{N}'\right]^{s}$$

$$\times\left[(s!)^{-1}(t-\sum_{j=1}^{s}t_{j})^{s}H(t-\sum_{j=1}^{s}t_{j})\varphi_{N}(0)\right.$$

$$-\lambda\int\{d\mathbf{x}\}L_{N}'i\int_{0}^{\tau_{\text{corr}}}dt_{s+1}(s!)^{-1}(t-\sum_{j=1}^{s+1}t_{j})^{s}$$

$$\left.\times H(t-\sum_{j=1}^{s+1}t_{j})\exp(-iL_{N}t_{s+1})f_{N}(0)\right]. \quad (25)$$

The meaning of the $s=0$ term is clarified by noting the convention used in this paper:

$$\sum_{j=0}^{0}t_{j}=0.$$

Equation (25) is now differentiated with respect to the time, t. Differentiating the Heaviside functions yields delta functions of their arguments. This gives something of the form $\tau^{s}\delta(\tau)$, so is non-zero only for the $s=0$ term. For $t>0$, the $s=0$ term is

$$-\lambda\int\{d\mathbf{x}\}L_{N}'i\int_{0}^{\tau_{\text{corr}}}dt_{1}\,\delta(t-t_{1})\exp(-iL_{N}t_{1})f_{N}(0).$$

The t_{1} integral can now be performed easily. The differentiated form of Eq. (25) is given below. The index s has been changed to $r+1$. The $s=0$ term follows the rest, and its t_{1} integral has been performed:

$$\frac{\partial\varphi_{N}(t)}{\partial t}=\sum_{r=0}^{\infty}\left[i\lambda^{2}\Omega^{-N}\int\{d\mathbf{x}\}L_{N}'i\right.$$

$$\times\int_{0}^{\infty}dt_{j}\exp(-iL_{N}t_{j})L_{N}'\bigg]^{(r+1)}$$

$$\times\left[(r!)^{-1}(t-\sum_{j=1}^{r+1}t_{j})^{r}H(t-\sum_{j=1}^{r+1}t_{j})\varphi_{N}(0)\right.$$

$$-\lambda\int\{d\mathbf{x}\}L_{N}'i\int_{0}^{\tau_{\text{corr}}}dt_{r+2}(r!)^{-1}(t-\sum_{j=1}^{r+2}t_{j})^{r}$$

$$\times H(t-\sum_{j=1}^{r+2}t_{j})\exp(-iL_{N}t_{r+2})f_{N}(0)\bigg]$$

$$-i\lambda H(\tau_{\text{corr}}-t)\int\{d\mathbf{x}\}L_{N}'$$

$$\times\exp(-iL_{N}t)f_{N}(0). \quad (26)$$

Comparison of Eq. (26) with (25) shows that Eq. (26) is identical to

$$\frac{\partial\varphi_{N}(t)}{\partial t}=i\lambda^{2}\Omega^{-N}\int\{d\mathbf{x}\}L_{N}'i$$

$$\times\int_{0}^{\infty}dt_{1}\exp(-iL_{N}t_{1})L_{N}'\varphi_{N}(t-t_{1})H(t-t_{1})$$

$$-i\lambda H(\tau_{\text{corr}}-t)\int\{d\mathbf{x}\}L_{N}'$$

$$\times\exp(-iL_{N}t)f_{N}(0). \quad (27)$$

The simplicity of Eq. (27) is striking, considering that it gives exactly the evolution of *any* ensemble representing a classical homogeneous fluid having only short-range order. The first term on the right side of Eq. (27) is of the form of Eq. (42), discussed above. The second term represents contributions in which the *only* pole explicitly at $z=0$ came as a result of the $\{x\}$ integration overall. This was discussed following Eq. (17) above.

For times greater than τ_{corr} and τ_{coll}, the entire last term and the Heaviside function of the first term vanish. Particles no longer *explicitly* feel their initial correlations, and enough time has elapsed to complete a collision. From then on, it is *only* completed scattering events which change φ_{N}:

$$\frac{\partial\varphi_{N}(t)}{\partial t}=i\lambda^{2}\Omega^{-N}\int\{d\mathbf{x}\}L_{N}'i$$

$$\times\int_{0}^{\infty}dt_{1}\exp(-iL_{N}t_{1})L_{N}'\varphi_{N}(t-t_{1}). \quad (28)$$

The equation for φ_{N} is non-Markovian, in that $\partial\varphi_{N}(t)/\partial t$ depends on knowledge of φ_{N}, not only at time t, but at all times, $(t-t_{1})$, for $t_{1}<\tau_{\text{coll}}$.

The non-Markovian Eq. (28) is exact for $t>\tau_{\text{corr}}$. It becomes of simple Markovian form only if $\varphi_{N}(t)$ is slowly enough varying that it may be treated as constant during τ_{coll}. More explicitly, if the Taylor series expansion

$$\varphi_{N}(t-t_{1})=\varphi_{N}(t)-t_{1}\partial\varphi_{N}(t)/\partial t+\cdots$$

is used in Eq. (28) and the first term is an adequate representation, then the following simple Markovian equation describes the evolution of φ_{N}:

$$\frac{\partial\varphi_{N}(t)}{\partial t}=i\lambda^{2}\Omega^{-N}\int\{d\mathbf{x}\}L_{N}'i$$

$$\times\int_{0}^{\infty}dt_{1}\exp(-iL_{N}t_{1})L_{N}'\varphi_{N}(t); \quad (29)$$

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[6] Reference 3, Sec. 4.5.

$$\frac{\partial \varphi_N(t)}{\partial t} = i\lambda^2 \Omega^{-N} \int \{d\mathbf{x}\} L_N{}'(L_N - i\epsilon)^{-1} L_N{}' \varphi_N(t). \qquad (30)$$

Equation (30) was obtained using Eq. (15). The term in epsilon (an arbitrarily small positive quantity) was inserted in order to damp explicitly the behavior at infinity. It was shown above that behavior for $t_1 > \tau_{coll}$, let alone infinity, cannot affect the result. We call either Eq. (29) or (30) the *generalized Master equation*.

In a subsequent paper,[7] Eq. (28) will be shown to give a monotonic approach to equilibrium. The non-Markovian behavior quickly leads to Markovian behavior. The Markovian equation has the unique stationary solution,

$$\varphi_N \Big(\sum_{i=1}^{N} p_i{}^2 \Big).$$

Also in a subsequent paper,[8] the operators of these equations are further studied. It is shown that Eq. (30) is of the type of the Boltzmann collision equation, generalized to consider not just two-body, but ν-body collisions in a homogeneous system. It could have been deduced directly from the reduced Liouville equation by less instructive methods given elsewhere to formulate a generalized Boltzmann equation.[9]

III. EVOLUTION OF THE REDUCED s-PARTICLE D.F.

The reduced s-particle D.F. is customarily defined thus:

$$f_s(\mathbf{x}_1 \cdots \mathbf{x}_s, \mathbf{p}_1 \cdots \mathbf{p}_s)$$

$$= \frac{N!}{(N-s)!} \int d\mathbf{x}_{s+1} \cdots d\mathbf{x}_N d\mathbf{p}_{s+1} \cdots d\mathbf{p}_N f_N; \qquad (31)$$

$$\lim_{N \gg s} f_s(\{s\}) = N^s \int \{d\mathbf{x}\}_{\neq\{s\}} \{d\mathbf{p}\}_{\neq\{s\}} f_N.$$

It is important to realize that if the intermolecular forces are all two-body, then the ensemble averages of significant macroscopic observables may be made from f_2, not f_N.[10] This is true even at liquid densities.

Inserting the representation of f_N from Eq. (7) into Eq. (31) yields

$$f_s(\{s\}) = \frac{N^s}{2\pi i} \int_c dz \exp(-izt)$$

$$\times \int \{d\mathbf{x}\}_{\neq\{s\}} \{d\mathbf{p}\}_{\neq\{s\}} (L_N - z)^{-1} f_N(0). \qquad (32)$$

[7] F. C. Andrews, Phys. Rev. **125**, 1469 (1962).
[8] F. C. Andrews, Phys. Rev. **125**, 1473 (1962).
[9] F. C. Andrews, J. Chem. Phys. **35**, 922 (1961).
[10] See, e.g., J. H. Irving and J. G. Kirkwood, J. Chem. Phys. **18**, 817 (1950).

This is the counterpart to Eq. (11). It is identical to what one would get from Eq. (31) using Eq. (5), rather than (7):

$$f_s(\{s\}) = N^s \int \{d\mathbf{x}\}_{\neq\{s\}} \{d\mathbf{p}\}_{\neq\{s\}} \exp(-iL_N t) f_N(0). \qquad (33)$$

Once again, Eq. (6) may be used to interpret the exponential operator. The $\{\mathbf{x}_s\}$ and $\{\mathbf{p}_s\}$ are given, since their distribution is being calculated. These s particles plus up to $(\nu - s)$ others, which we call *dummy particles*, are traced back over their trajectories during the period from t to 0. In all cases in which f_s is used to calculate observables, $\{\mathbf{x}_s\}$ is a set of points located very close to each other. Their distances apart will be of the order of the range of the intermolecular forces. So for times longer than that necessary for the ν particles to finish their interaction and pass outside the region of their initial correlation, Eq. (33) is constant with respect to further increases in t.

This constancy would never occur if we were not throwing out terms in the expansion of the inverse operator of Eq. (32) which involve correlations of more than ν particles. If such correlations were kept, Eq. (33) would correctly give f_s for all times. From the study of Sec. II, it is clear how this problem should be approached. We shall call the time after which Eq. (33) becomes constant the *initial time*, τ_{init}. For $t > \tau_{init}$, the contribution from Eq. (33) would be unchanged if $f_N(0)$ were replaced by $\Omega^{-N} \varphi_N(0)$. This is part of the contribution from the expanded form of Eq. (32) with one pole explicitly at $z = 0$. Once again, treatment of this expansion involving more and more poles at zero is in order.

Here, as in Eq. (18), the explicit location of the first pole at zero may be noted in the expanded form of Eq. (32):

$$f_s{}^{(1)} = \frac{N^s}{2\pi i} \int_c dz \exp(-izt) \int \{d\mathbf{x}\}_{\neq\{s\}} \{d\mathbf{p}\}_{\neq\{s\}}$$

$$\times \sum_{m=0}^{\infty} (-\lambda)^m (L_N{}^0 - z)^{-1} [L_N{}' (L_N{}^0 - z)^{-1}]^m \Omega^{-N}$$

$$\times \int \{d\mathbf{x}\} \sum_{n=0}^{\infty} (-\lambda)^n [L_N{}' (L_N{}^0 - z)^{-1}]^n f_N(0);$$

$$(34)$$

$$f_s{}^{(1)} = \frac{N^s}{2\pi i} \int_c dz \exp(-izt) \int \{d\mathbf{x}\}_{\neq\{s\}} \{d\mathbf{p}\}_{\neq\{s\}}$$

$$\times \sum_{m=0}^{\infty} (-\lambda)^m [(L_N{}^0 - z)^{-1} L_N{}']^m (-z)^{-1} \Omega^{-N}$$

$$\times \Big[\varphi_N(0) - \lambda \int \{d\mathbf{x}\} L_N{}' (L_N - z)^{-1} f_N(0) \Big].$$

Use has been made of Eq. (9). On treating the $m=0$ term separately from the rest, this becomes

$$f_s{}^{(1)} = N^s\Omega^{-s} \int \{d\mathbf{p}\}_{\neq\{s\}} \varphi_N(t) - \frac{N^s\lambda}{2\pi i} \int_c dz \exp(-izt)$$

$$\times \int \{d\mathbf{x}\}_{\neq\{s\}}\{d\mathbf{p}\}_{\neq\{s\}} (L_N-z)^{-1}L_N{}'(-z)^{-1}\Omega^{-N}$$

$$\times \left[\varphi_N(0) - \lambda \int \{d\mathbf{x}\} L_N{}'(L_N-z)^{-1}f_N(0) \right]. \quad (35)$$

The $m=0$ term was easily recognizable as giving $\varphi_N(t)$ by comparison with Eq. (13). On using Eq. (15), this becomes

$$f_s{}^{(1)} = c^s \int \{d\mathbf{p}\}_{\neq\{s\}} \varphi_N(t) - \frac{N^s\lambda}{2\pi i} \int dz \exp(-izt)(-z)^{-1}$$

$$\times \int \{d\mathbf{x}\}_{\neq\{s\}}\{d\mathbf{p}\}_{\neq\{s\}} i$$

$$\times \int_0^\infty dt_1 \exp[-i(L_N-z)t_1]L_N{}'\Omega^{-N}$$

$$\times \left[\varphi_N(0) - \lambda \int \{d\mathbf{x}\} L_N{}'(L_N-z)^{-1}f_N(0) \right]. \quad (36)$$

The second term of this is a form familiar from Sec. II, and the generalization to any number of poles at zero may immediately be written down. There will be the contribution from Eq. (33) for the case of no pole at zero. This term must be cut off at τ_{init}. Then there will be contributions from each non-zero number of different poles explicitly at zero:

$$f_s(t) = N^s H(\tau_{\text{init}}-t)$$

$$\times \int \{d\mathbf{x}\}_{\neq\{s\}}\{d\mathbf{p}\}_{\neq\{s\}} \exp(-iL_N t)f_N(0) + c^s$$

$$\times \int \{d\mathbf{p}\}_{\neq\{s\}} \varphi_N(t) - c^s\Omega^{s-N}\lambda \int \{d\mathbf{x}\}_{\neq\{s\}}\{d\mathbf{p}\}_{\neq\{s\}} i$$

$$\times \int_0^\infty dt_1 \exp(-iL_N t_1)L_N{}' \sum_{u=0}^\infty \left[i\lambda^2\Omega^{-N} \int \{d\mathbf{x}\} L_N{}' i \right.$$

$$\times \int_0^\infty dt_j \exp(-iL_N t_j)L_N{}' \Big]^u \left[(u!)^{-1}\left(t- \sum_{j=1}^{u+1} t_j\right)^u \right.$$

$$\times H\left(t- \sum_{j=1}^{u+1} t_j\right)\varphi_N(0) - \lambda \int \{d\mathbf{x}\} L_N{}' i$$

$$\times \int_0^{\tau_{\text{corr}}} dt_{u+2}(u!)^{-1}\left(t- \sum_{j=1}^{u+2} t_j\right)^u H\left(t- \sum_{j=1}^{u+2} t_j\right)$$

$$\left. \times \exp(-iL_N t_{u+2})f_N(0) \right]. \quad (37)$$

Comparison of Eq. (37) with (25) shows that Eq. (37) is identical to

$$f_s(t) = c^s \int \{d\mathbf{p}\}_{\neq\{s\}} \varphi_N(t) - c^s\Omega^{s-N} \int \{d\mathbf{x}\}_{\neq\{s\}}\{d\mathbf{p}\}_{\neq\{s\}}$$

$$\times i \int_0^\infty dt_1 \exp(-iL_N t_1)\lambda L_N{}' \varphi_N(t-t_1)H(t-t_1)$$

$$+ N^s H(\tau_{\text{init}}-t) \int \{d\mathbf{x}\}_{\neq\{s\}}\{d\mathbf{p}\}_{\neq\{s\}}$$

$$\times \exp(-iL_N t)f_N(0). \quad (38)$$

This equation is exact and is the counterpart of Eq. (27) for φ_N.

Again, for times greater than τ_{init} and τ_{coll}, the entire last term and the Heaviside function vanish. The initial correlations no longer are explicitly felt. Only collisions between previously uncorrelated particles contribute to f_s:

$$f_s(t) = c^s \int \{d\mathbf{p}\}_{\neq\{s\}} \varphi_N(t) - c^s\Omega^{s-N} \int \{d\mathbf{x}\}_{\neq\{s\}}\{d\mathbf{p}\}_{\neq\{s\}}$$

$$\times i \int_0^\infty dt_1 \exp(-iL_N t_1)\lambda L_N{}' \varphi_N(t-t_1). \quad (39)$$

The equation for f_s is non-Markovian in the same sense that Eq. (28) is non-Markovian. The non-Markovian Eq. (39) is exact for $t > \tau_{\text{init}}$.

Again, if $\varphi_N(t)$ varies slowly enough in τ_{coll} to be essentially constant, the functional equation for f_s becomes of a simple Markovian type, which is given below in three equivalent forms:

$$f_s(t) = c^s \int \{d\mathbf{p}\}_{\neq\{s\}} \varphi_N(t) - c^s\Omega^{s-N} \int \{d\mathbf{x}\}_{\neq\{s\}}\{d\mathbf{p}\}_{\neq\{s\}}$$

$$\times i \int_0^\infty dt_1 \exp(-iL_N t_1)\lambda L_N{}' \varphi_N(t); \quad (40)$$

$$f_s(t) = c^s \int \{d\mathbf{p}\}_{\neq\{s\}} \varphi_N(t) - c^s\Omega^{s-N} \int \{d\mathbf{x}\}_{\neq\{s\}}\{d\mathbf{p}\}_{\neq\{s\}}$$

$$\times (L_N-i\epsilon)^{-1}\lambda L_N{}' \varphi_N(t); \quad (41)$$

$$f_s(t) = c^s\Omega^{s-N} \int \{d\mathbf{x}\}_{\neq\{s\}}\{d\mathbf{p}\}_{\neq\{s\}}$$

$$\times \sum_{n=0}^\infty (-\lambda)^n [(L_N{}^0-i\epsilon)^{-1}L_N{}']^n \varphi_N(t). \quad (42)$$

We again emphasize that the non-Markovian behavior in the evolution of φ_N through Eq. (28) leads monotonically to Markovian behavior.[7] The Markovian behavior of φ_N, Eq. (30), leads monotonically to the equilibrium form $\varphi_N{}^{\text{eq}} = \alpha \exp(-\beta H_N{}^0)$, where $H_N{}^0$ is

the kinetic energy of the N particles. It can then be shown that this equilibrium form of φ_N inserted in Eq. (42) gives rise to the exact values of the equilibrium correlations in an ensemble, previously known from the Ursell-Mayer theory of static equilibrium statistical mechanics.[11]

The operators of Eqs. (40)–(42) are further studied in a subsequent paper[8] and shown to represent the formation of correlations among s or fewer particles

by collisions among ν and fewer bodies. The equations could have been deduced more directly by less instructive means.[9]

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[11] F. C. Andrews, Physica **27**, 1054 (1961).

Approach to Equilibrium in a Dense Classical Fluid

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The equation derived in a previous paper for the exact evolution of the momentum distribution function of a homogeneous dense classical fluid is studied. The Markovian form of this equation is found to drive the momentum distribution monotonically to an arbitrary function of the kinetic energy of the system. This function must be canonical if it factorizes in momentum space. Incorporation of the non-Markovian effects in the evolution equation through a simple approximation does not destroy the approach to equilibrium. Since reduced s-particle distribution functions previously were shown to be functionals of the momentum distribution, they also monotonically approach equilibrium.

IN a previous paper,[1] it was shown that $\varphi_N(\{\mathbf{p}\})$, the N-particle momentum distribution function (D.F.) for a homogeneous classical fluid possessing only short-range order, evolves according to the following equation for times longer than a properly defined "molecular correlation time":

$$\frac{\partial \varphi_N(t)}{\partial t} = -\lambda^2 \Omega^{-N} \int \{d\mathbf{x}\} L_N' \int_0^\infty dt_1$$

$$\times \exp(-iL_N t_1) L_N' \varphi_N(t-t_1). \quad (1)$$

All symbols and operators in Eq. (1) are defined and discussed in I.

Consider Eq. (1) with $\varphi_N(t-t_1)$ expanded in a Taylor series about $\varphi_N(t)$:

$$\varphi_N(t-t_1) = \varphi_N(t) - t_1 \frac{\partial \varphi_N(t)}{\partial t} + \frac{t_1^2}{2!} \frac{\partial^2 \varphi_N(t)}{\partial t^2} - \cdots. \quad (2)$$

The t_1 integrand of Eq. (1) may be nonzero only over the duration of a collision, τ_{coll}, involving ν or fewer particles.[1]

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[1] F. C. Andrews, Phys. Rev. **125**, 1461 (1962) (referred to as I throughout this paper).

We first study Eq. (1) with only the first term of the expansion, Eq. (2), inserted. This simple Markovian form, or generalized master equation, is valid if $\varphi_N(t)$ varies negligibly during τ_{coll}:

$$\frac{\partial \varphi_N(t)}{\partial t} = -\lambda^2 \Omega^{-N} \int \{d\mathbf{x}\} L_N' \int_0^\infty dt_1$$

$$\times \exp(-iL_N t_1) L_N' \varphi_N(t). \quad (3)$$

It is convenient to find the symmetric and antisymmetric parts of the exponential integral operator in L_N, using the identity

$$\int_0^\infty dt_1 \exp(-iL_N t_1) = \pi \delta(L_N) - i \mathcal{P}(L_N^{-1}). \quad (4)$$

The delta function is symmetric in L_N; the principal part of L_N^{-1} is antisymmetric. The antisymmetric part is not needed, since it gives zero in Eq. (3). This is because an operator antisymmetric in L_N is necessarily antisymmetric in $\{\mathbf{x}\}$. The complete $\{\mathbf{x}\}$ dependence of the integrand of Eq. (3) would then rest in the action of three operators, each one odd in the interchange $\{\mathbf{x}\} \rightarrow \{-\mathbf{x}\}$. It therefore would vanish on integration over configuration space. Only the delta function