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]

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

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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":

$$\frac{\partial\varphi_N(t)}{\partial t}=-\lambda^2\Omega^{-N}\int\{d\mathbf{x}\}L_N'\int_0^\infty dt_1 \times\exp(-iL_Nt_1)L_N'\varphi_N(t-t_1). \quad (1)$$

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]

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}:

$$\frac{\partial\varphi_N(t)}{\partial t}=-\lambda^2\Omega^{-N}\int\{d\mathbf{x}\}L_N'\int_0^\infty dt_1 \times\exp(-iL_Nt_1)L_N'\varphi_N(t). \quad (3)$$

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

$$\int_0^\infty dt_1\exp(-iL_Nt_1)=\pi\delta(L_N)-i\mathcal{P}(L_N^{-1}). \quad (4)$$

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 $\{\mathbf{x}\}\to\{-\mathbf{x}\}$. It therefore would vanish on integration over configuration space. Only the delta function

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

contributes to the master equation:

$$\frac{\partial \varphi_N(t)}{\partial t} = -\pi\lambda^2\Omega^{-N}\int\{d\mathbf{x}\}L_N'\delta(L_N)L_N'\varphi_N(t). \quad (5)$$

It is desired to expand $\varphi_N(t)$ in eigenfunctions of the operator acting on it in Eq. (5). First, this operator is proved to be Hermitian in momentum space with positive eigenvalues:

$$\langle m|\Omega^{-N}\int\{d\mathbf{x}\}L_N'\delta(L_N)L_N'|n\rangle$$

$$=\int\{d\mathbf{p}\}\Theta_m{}^*\Omega^{-N}\int\{d\mathbf{x}\}L_N'\delta(L_N)L_N'\Theta_n.$$

The Θ's are arbitrary functions of momenta, vanishing for infinite momenta. The first L_N' may be integrated by parts in momentum space, and the result simplified by noting that $L_N'^* = -L_N'$:

$$\Omega^{-N}\int\{d\mathbf{x}\}\{d\mathbf{p}\}(L_N'\Theta_m)^*\delta(L_N)(L_N'\Theta_n).$$

The quantities $(L_N'\Theta)$ are now expanded in eigenfunctions ψ of the Hermitian operator L_N:

$$L_N'\Theta_m=\sum_i a_i\psi_i, \quad L_N'\Theta_n=\sum_j b_j\psi_j. \quad (6)$$

The matrix element becomes

$$\Omega^{-N}\int\{d\mathbf{x}\}\{d\mathbf{p}\}\sum_i a_i{}^*\psi_i{}^*\delta(L_N)\sum_j b_j\psi_j.$$

The delta function by definition picks out the eigenfunction associated with zero eigenvalue. This is true equally for the $\psi_i{}^*$ and the ψ_j. The reason is that if ψ_m is an eigenfunction of L_N with eigenvalue Λ_m, then $\psi_m{}^*$ is also an eigenfunction of L_N with eigenvalue $-\Lambda_m$, as is proved below:

$$L_N\psi_m=\Lambda_m\psi_m, \quad L_N{}^*\psi_m{}^*=\Lambda_m{}^*\psi_m{}^*.$$

Since $L_N{}^*=-L_N$, this becomes

$$L_N\psi_m{}^*=-\Lambda_m{}^*\psi_m{}^*$$
$$=-\Lambda_m\psi_m{}^*,$$

since the Λ_m are real; Q.E.D. The matrix element is thus

$$\langle m|\Omega^{-N}\int\{d\mathbf{x}\}L_N'\delta(L_N)L_N'|n\rangle$$

$$=\Omega^{-N}\int\{d\mathbf{x}\}\{d\mathbf{p}\}a_0{}^*\psi_0{}^*\delta(L_N)b_0\psi_0. \quad (7)$$

By the same process, however, its Hermitian adjoint is

$$\langle n|\Omega^{-N}\int\{d\mathbf{x}\}L_N'\delta(L_N)L_N'|m\rangle^*$$

$$=\Omega^{-N}\int\{d\mathbf{x}\}\{d\mathbf{p}\}b_0\psi_0\delta(L_N)a_0{}^*\psi_0{}^*.$$

This clearly is the same as the matrix element of Eq. (7), since $\delta(L_N)=[\delta(L_N)]^*$. The scattering operator is thus Hermitian.

Furthermore, its eigenvalue K_n is positive. To prove this,

$$\Omega^{-N}\int\{d\mathbf{x}\}L_N'\delta(L_N)L_N'\chi_n=K_n\chi_n. \quad (8)$$

Therefore

$$K_n=\langle n|\Omega^{-N}\int\{d\mathbf{x}\}L_N'\delta(L_N)L_N'|n\rangle.$$

On expanding $L_N'\chi_n$ in eigenfunctions of L_N, as in Eq. (6),

$$L_N'\chi_n=\sum_i a_{ni}\chi_i, \quad (9)$$

K_n is seen from Eq. (7) to be

$$K_n=\Omega^{-N}\int\{d\mathbf{x}\}\{d\mathbf{p}\}a_{n0}{}^*\psi_0{}^*\delta(L_N)a_{n0}\psi_0, \quad (10)$$

which is a positive form.

This proved, $\varphi_N(t)$ may now be expanded in the eigenfunctions χ_i of Eq. (8):

$$\varphi_N(t)=\sum_i c_i(t)\chi_i. \quad (11)$$

Then Eq. (5) takes the form

$$\sum_i[\partial c_i(t)/\partial t]\chi_i=-\pi\lambda^2\sum_j K_jc_j(t)\chi_j.$$

This equation may be multiplied by $\chi_m{}^*$ and integrated over momenta to give

$$\partial c_m(t)/\partial t=-\pi\lambda^2K_mc_m(t), \quad (12)$$

with solution

$$c_m(t)=A\exp(-\pi\lambda^2K_mt), \quad (13)$$

where K_m is positive and given by Eq. (10). Therefore the coefficients in the expansion, Eq. (11), are driven monotonically to zero by the master equation. The λ^2 of Eq. (13) may of course be put to unity. Its presence merely calls attention to the fact that the approach to equilibrium is only through collisions between particles, involving their intermolecular forces.

The only stationary solution of Eq. (3) or (5) would be a multiple of χ_0, i.e., as seen from Eq. (8), a solution of

$$\Omega^{-N}\int\{d\mathbf{x}\}L_N'\delta(L_N)L_N'\varphi_N{}^{\mathrm{eq}}=0. \quad (14)$$

This must hold for arbitrary $\{\mathbf{p}\}$ in $\varphi_N{}^{\mathrm{eq}}$. Examination of the proof given above from Eqs. (5) to (10) indicates that not only has the entire operator of Eq. (14) been proved positive in momentum space, but the same proof shows the operator $L_N'\delta(L_N)L_N'$ to be Hermitian and positive in phase space. Therefore, not only must Eq. (14) hold for $\varphi_N{}^{\mathrm{eq}}$, but it implies that its $\{\mathbf{x}\}$ integrand must be zero for arbitrary $\{\mathbf{x}\}$:

$$L_N'\delta(L_N)L_N'\varphi_N{}^{\mathrm{eq}}=0. \quad (15)$$

The L_N' operator on the left of the delta function may give a zero result in one of two ways. The $\partial/\partial \mathbf{p}_{rs}$ of the function on which it operates may be perpendicular to the intermolecular force between particles r and s. This could not hold for *arbitrary* $\{\mathbf{x}\}$ and $\{\mathbf{p}\}$, however. The only other way is for the function on which it operates to be independent of $\{\mathbf{p}\}$:

$$\delta(L_N)L_N'\varphi_N^{\text{eq}} = \text{independent of } \{\mathbf{p}\}. \tag{16}$$

This equation may be studied using the integral representation of the delta function:

$$\int_{-\infty}^{\infty} dt_1 \exp(-iL_N t_1)L_N'\varphi_N^{\text{eq}} = \text{independent of } \{\mathbf{p}\}. \tag{17}$$

In I, frequent use was made of $\exp(-iL_N t_1)$ as that operator which takes the particles backwards over their exact trajectories for a time t_1. Since it acts on the intermolecular force between two particles contained in the particular term of L_N', the t_1 integrand is only nonzero over a collision time, during which it has the value

$$\int_{-\infty}^{\infty} dt_1[L_N'\varphi_N^{\text{eq}}](t-t_1).$$

The $(t-t_1)$ notation means the $\{\mathbf{x}\}$ and $\{\mathbf{p}\}$ of the particles at time $(t-t_1)$ on their trajectories. There is no *explicit* t dependence of φ_N^{eq}, of course.

It is useful to note that for an arbitrary function of t and phase space,

$$id/dt = i\partial/\partial t - L_N^0 - \lambda L_N'. \tag{18}$$

In the case of Eq. (17), the function φ_N^{eq} is both time- and $\{\mathbf{x}\}$-independent; therefore

$$i\frac{d}{dt}\varphi_N^{\text{eq}} = -\lambda L_N'\varphi_N^{\text{eq}},$$

and the requirement of Eq. (17) becomes

$$\int_{-\infty}^{\infty} dt_1 \frac{d}{d(t-t_1)}\varphi_N^{\text{eq}}(t-t_1) = \varphi_N^{\text{eq}}[\{\mathbf{p}(\tau_{\text{coll}})\}] - \varphi_N^{\text{eq}}[\{\mathbf{p}(-\tau_{\text{coll}})\}] = \text{independent of } \{\mathbf{p}\}. \tag{19}$$

The difference between φ_N^{eq} for the sets of momenta before and after the collision must be independent of momenta for any $\mathbf{x}$. Yet, clearly there exist sets $\{\mathbf{x}\}$ for which some $\{\mathbf{p}\}$ result in collisions and some other $\{\mathbf{p}\}$ result in such grazing collisions they do not change the momenta. Therefore, the constant must be zero:

$$\varphi_N^{\text{eq}}[\{\mathbf{p}(\tau_{\text{coll}})\}] = \varphi_N^{\text{eq}}[\{\mathbf{p}(-\tau_{\text{coll}})\}]. \tag{20}$$

Equation (20) is therefore necessary and sufficient for an equilibrium momentum distribution. It must hold for *any* collision process.

The only functions of the momenta of, say, particles 1 and 2 which are the same before and after *any* collision between them are their kinetic energy $(2m)^{-1}(p_1^2+p_2^2)$ and their total momentum $(\mathbf{p}_1+\mathbf{p}_2)$. So the only dependence on $\mathbf{p}_1$ and $\mathbf{p}_2$ must be through these functions. The same must be true for all pairs of particles and also for all groups of more than two particles. Clearly, the only such functions are the total kinetic energy of the N particles:

$$H_N^0 = (2m)^{-1}\sum_{i=1}^{N} p_i^2, \tag{21}$$

and the total momentum of the N particles, $\sum_i \mathbf{p}_i$. This latter is zero if the box containing the system is at rest. Therefore, the momentum distribution is driven monotonically by the generalized master equation to an arbitrary function of H_N^0. The distribution then is time independent.

We now show that this arbitrary function $\varphi_N(H_N^0)$ is of the form $\alpha\exp(-\beta H_N^0)$, granted the necessary and sufficient condition that φ_N^{eq} factorizes in momentum space. Factorization implies that the momenta of different particles are not correlated when the particles are extremely long distances from each other; i.e., there are no correlations independent of positions. The only requirement which might impose such a correlation is that of given or finite total energy available to the system. If the kinetic energy of one particle was an appreciable part of the total available to the system, then one would expect the probability of such a state to be less than its value given by a canonical distribution.

The necessity of factorization is clear, since $\alpha\exp(-\beta H_N^0)$ is a product of terms $\alpha^{1/N}\exp(-\beta H_1^0)$. That it is a sufficient condition may easily be shown by an approach reminiscent of that of Maxwell.[2] Factorization requires

$$\varphi_N\Big(\sum_{i=1}^{N} p_i^2\Big) = \prod_{i=1}^{N} \varphi_1(p_i^2), \tag{22}$$

$$\ln\varphi_N\Big(\sum_{i=1}^{N} p_i^2\Big) = \sum_{i=1}^{N} \varphi_1(p_i^2). \tag{23}$$

The function $\ln\varphi_N$ may be expanded as a power series in its argument. Then Eq. (23) becomes

$$\ln\varphi_N\Big(\sum_{i=1}^{N} p_i^2\Big) = a_0 + \Big(\sum_{i=1}^{N} p_i^2\Big)a_1 + \Big(\sum_{i=1}^{N} p_i^2\Big)^2 a_2 + \cdots = \sum_{i=1}^{N} \ln\varphi_1(p_i^2).$$

Only the coefficients a_0 or a_1 may be nonzero. Squared and higher powers of the sum would introduce cross-

[2] See, e.g., A. Sommerfeld, *Thermodynamics and Statistical Mechanics* (Academic Press, Inc., New York, 1956), Sec. 23.

terms, explicitly coupling the various p_i^2. Therefore

$$\ln \varphi_N = a_0 + a_1 \sum_{i=1}^{N} p_i^2,$$
$$\varphi_N = \alpha \exp(-\beta' \sum_{i=1}^{N} p_i^2) = \alpha \exp(-\beta H_N^0). \quad (24)$$

So factorability in momentum space gives rise to the exponential form of the D.F.

This paper is incomplete without some treatment of the non-Markovian character of Eq. (1). This is not easy, nor does it seem too useful. The exact equation for $\varphi_N(t)$ of I from which Eq. (1) was derived shows from its form that for t greater than the duration of several collisions, φ_N should not vary appreciably during τ_{coll}. Furthermore, τ_{coll}, a function of the particular collision process, may be very short for some collisions. Thus, for some collisions, Eq. (3) would suffice even if φ_N was changing rapidly.

Instead of the expansion of Eq. (2), one might insert into Eq. (1) some constant time lag T characteristic of and less than an average τ_{coll}:

$$\varphi_N(t-t_1) \approx \varphi_N(t-T) \approx \varphi_N(t) - T\partial\varphi_N(t)/\partial t. \quad (25)$$

Then, instead of Eq. (12), one has

$$\partial c_m(t)/\partial t = -\pi\lambda^2 K_m c_m(t) + \pi\lambda^2 K_m T \partial c_m(t)/\partial t, \quad (26)$$

with solution

$$c_m(t) = A \exp[-\pi\lambda^2 K_m t/(1-\pi\lambda^2 K_m T)]. \quad (27)$$

This shows that, in general, the non-Markovian nature speeds up the approach to equilibrium, as one would expect. The effective nonequilibrium situation which "drives" the irreversibility is not that at time t, but that at a prior time when its nonequilibrium nature was even greater.

It was shown in I that the s-particle reduced D.F.'s, which give the spatial correlations among groups of s and fewer particles as well as their momentum dependence, are simple functionals of φ_N. Therefore, they approach equilibrium indirectly as φ_N approaches equilibrium. It has been shown[3] that the values given by the dynamical theory for these equilibrium correlations are the same as those given by classical, static equilibrium statistical mechanics.

Perhaps the *fundamental assumption* of classical equilibrium statistical mechanics is that the total energy is the only important constant of the motion; thus the equilibrium D.F. must be a function only of the energy.[4] It has here been *proved* that the mechanics of the scattering events in a fluid drive the momentum D.F. to a function of the kinetic energy. Simultaneously, reduced D.F.'s are driven to the exact values they would have if the total energy were the only constant of the motion.

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