Evolution of Reduced Distribution Functions for Inhomogeneous Dense Classical Fluids

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The evolution of reduced distribution functions is studied for an inhomogeneous dense classical fluid by methods previously used to study homogeneous fluids. So long as only short-range order is present in the fluid and the variation in properties caused by the inhomogeneity is negligible over distances of the order of the region of a collision, then the evolution equations for the one-particle and s-particle distribution functions are obtained. They take a simple Markovian form if the one-particle distribution changes negligibly in times of the order of the duration of a collision. The operators involved in the evolution equations are studied. Their physical meaning and relationship to the classical Boltzmann equation are considered.

RECENTLY, methods were presented by the author for studying exactly the mechanical evolution of reduced distribution functions (D.F.'s) describing a homogeneous dense classical fluid.[1] In order to understand transport properties, inhomogeneous systems must be treated. This problem has been previously attacked by the Brussels group.[2] In this paper, the methods of I are used to simplify and generalize some of the work.

In an inhomogeneous system, ensemble averages of quantities dependent on individual particles are averages over the one-particle reduced D.F., defined thus:

$$f_1(\mathbf{x}_1,\mathbf{p}_1)=N\int\{d\mathbf{x}\}_{\neq 1}\{d\mathbf{p}\}_{\neq 1}f_N. \tag{1}$$

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

$$\begin{aligned}&f_1(\mathbf{x}_1,\mathbf{p}_1,t)\\&=\frac{N}{2\pi i}\int_c dz\,\exp(-izt)\int\{d\mathbf{x}\}_{\neq 1}\{d\mathbf{p}\}_{\neq 1}(L_N{}^0-z)^{-1}f_N(0)\\&\quad-\frac{N\lambda}{2\pi i}\int_c dz\,\exp(-izt)\int\{d\mathbf{x}\}_{\neq 1}\{d\mathbf{p}\}_{\neq 1}(L_N{}^0-z)^{-1}\\&\qquad\times L_N'(L_N-z)^{-1}f_N(0),\end{aligned} \tag{2}$$

which is to be compared with Eq. (I.11). The same argument that gave Eq. (I.13) now gives

$$\begin{aligned}&f_1(\mathbf{x}_1,\mathbf{p}_1,t)\\&=\frac{1}{2\pi i}\int_c dz\,\exp(-izt)(L_1{}^0-z)^{-1}f_1(\mathbf{x}_1,\mathbf{p}_1,0)\\&\quad-\frac{N\lambda}{2\pi i}\int_c dz\,\exp(-izt)(L_1{}^0-z)^{-1}\\&\qquad\times\int\{d\mathbf{x}\}_{\neq 1}\{d\mathbf{p}\}_{\neq 1}L_N'(L_N-z)^{-1}f_N(0).\end{aligned} \tag{3}$$

Equation (I.15) may be used to treat the first term in Eq. (3), yielding

$$\begin{aligned}&\frac{i}{2\pi i}\int_0^\infty dt_1\int_c dz\,\exp[-iz(t-t_1)]\exp(-iL_1{}^0t_1)f_1(\mathbf{x}_1,\mathbf{p}_1,0)\\&\quad=\int_0^\infty dt_1\,\delta(t-t_1)\exp(-iL_1{}^0t_1)f_1(\mathbf{x}_1,\mathbf{p}_1,0)\\&\quad=H(t)\exp(-iL_1{}^0t)f_1(\mathbf{x}_1,\mathbf{p}_1,0).\end{aligned} \tag{4}$$

Because there were no discontinuities on the real axis, the contour c could be lowered to it. The z integral then gave the delta function. The interpretation of Eq. (4) using Eq. (I.6) gives what one would expect of a non-interacting system: $f_1(0)$ evaluated at the position the particle had at time zero, such that a straight-line trajectory would bring it to $\mathbf{x}_1$ at time t.

The second term of Eq. (3) may be treated similarly:

$$\begin{aligned}&-\frac{N\lambda}{2\pi}\int_0^\infty dt_1\int_0^\infty dt_2\int_c dz\,\exp[-iz(t-t_1-t_2)]\exp(-iL_1{}^0t_1)\\&\qquad\times\int\{d\mathbf{x}\}_{\neq 1}\{d\mathbf{p}\}_{\neq 1}L_N'i\exp(-iL_Nt_2)f_N(0)\\&=-N\lambda\int_0^\infty dt_1\int_0^\infty dt_2\,\delta(t-t_1-t_2)\exp(-iL_1{}^0t_1)\\&\qquad\times\int\{d\mathbf{x}\}_{\neq 1}\{d\mathbf{p}\}_{\neq 1}L_N'i\exp(-iL_Nt_2)f_N(0)\\&=-N\lambda\int_0^\infty dt_2\,H(t-t_2)\exp[-iL_1{}^0(t-t_2)]\\&\qquad\times\int\{d\mathbf{x}\}_{\neq 1}\{d\mathbf{p}\}_{\neq 1}L_N'i\exp(-iL_Nt_2)f_N(0).\end{aligned} \tag{5}$$

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

[2] I. Prigogine and R. Balescu, Physica **26**, 145 (1960). F. C. Andrews, J. Math. Phys. **2**, 91 (1961).

The physical interpretation of the t_2 integral is the same as that of the t_1 integral of Eq. (I.16). Once again, Eq. (5) would be exact, thus impossibly difficult, if one did not take advantage of the presence of only short-range order. After no more than ν particles have interacted ($\nu \ll N$), the group of colliding particles may be traced back along their trajectories until after some τ_{corr} they are outside the range of initial correlation and no longer interacting. Only the free-particle motion carries them.

As in I, the contribution from Eq. (5) may be cut off at $t_2=\tau_{\text{corr}}$, since its subsequent contribution is shown below to be correctly given by the first term involving scattering. Also as in I, the final operator in Eq. (5) is now given one explicit intermediate stage of noncorrelation. The analog of Eq. (I.18) is then

$$\frac{-N\lambda}{2\pi i}\int_c dz\,\exp(-izt)(L_1^0-z)^{-1}\int\{d\mathbf{x}\}_{\neq 1}\{d\mathbf{p}\}_{\neq 1}L_N' \times(L_N-z)^{-1\star}\sum_{n=0}^{\infty}(-\lambda)^n[L_N'(L_N^0-z)^{-1}]^n f_N(0). \quad (6)$$

By the star notation is meant that at that point all spatial *correlation* from the right is removed. The only $\{\mathbf{x}\}$ dependence remaining is that of the external gradient. In I, one could just insert the integration, $\Omega^{-N}\int\{d\mathbf{x}\}$, but here there still is the $\{\mathbf{x}\}$ dependence from the gradient; thus the star notation is convenient.

In Eq. (6), a particular set of dummy particles, $\{\nu\}_{\neq 1}$, may be picked by introducing the factor $N^{(\nu-1)}/(\nu-1)!$, which for $N\gg\nu$ is the number of ways of choosing $(\nu-1)$ bodies from N. The $n=0$ term of Eq. (6) may then be written, using Eq. (1),

$$\frac{-\lambda}{2\pi i(\nu-1)!}\int_c dz\,\exp(-izt)(L_1^0-z)^{-1} \times\int\{d\mathbf{x}\}_{\neq 1}\{d\mathbf{p}\}_{\neq 1}L_N'(L_N-z)^{-1}\prod\{f_1(\nu,0)\}.$$

The number of f_1's in the product is the number of different particles involved in the $(L_N-z)^{-1}$ operator. They are factorized because the separate particles are uncorrelated. This clearly is just what the second term of Eq. (3) gives for $t>\tau_{\text{corr}}$, as discussed following Eq. (5). On using Eq. (I.9) and separating the $n=0$ term, this becomes

$$\frac{-\lambda}{2\pi i(\nu-1)!}\int_c dz\,\exp(-izt)(L_1^0-z)^{-1} \times\int\{d\mathbf{x}_\nu\}_{\neq 1}\{d\mathbf{p}_\nu\}_{\neq 1}L_\nu'(L_\nu^0-z)^{-1}\prod\{f_1(\nu,0)\} +\frac{\lambda^2}{2\pi i(\nu-1)!}\int_c dz\,\exp(-izt)(L_1^0-z)^{-1} \times\int\{d\mathbf{x}_\nu\}_{\neq 1}\{d\mathbf{p}_\nu\}_{\neq 1}L_\nu'(L_\nu-z)^{-1}L_\nu'(L_\nu^0-z)^{-1} \times\prod\{f_1(\nu,0)\}. \quad (7)$$

In I, the counterpart to the first term of Eq. (7) was zero by the argument of Eq. (I.21). Here, this argument is not quite valid, since the configuration integral is of the form

$$\int\{d\mathbf{x}_\nu\}_{\neq 1}L_\nu'\prod\{f_1[\mathbf{x}_\nu(-\tau),0]\},$$

where $\mathbf{x}_\nu(-\tau)$ is the position particle ν had on its straight-line trajectory at time $(t-\tau)$. The sign of L' is changed on the interchange $\{\mathbf{x}_{\nu 1}\}\rightarrow\{-\mathbf{x}_{\nu 1}\}$. All this interchange does to $\{f_1[\mathbf{x}_\nu(-\tau),0]\}$ is to move the position of the pair of particles involved by a distance of at most the range of the forces. Assuming the gradient in f_1 to be small enough that its change is negligible over distances of the order of the range of the forces, the first term of Eq. (7) may again be dropped. Of course, in cases of a more severe gradient (e.g., shock waves in a dense fluid), such terms would have to be studied.

The general approach of this paper is now illustrated. The first term of Eq. (7) is dropped, and Eq. (I.5) is used in the second term:

$$\frac{\lambda^2}{2\pi(\nu-1)!}\int_0^\infty dt_1\int_0^\infty dt_2\int_0^\infty dt_3 \times\int_c dz\,\exp[-iz(t-t_1-t_2-t_3)]\exp(-iL_1^0t_1) \times\int\{d\mathbf{x}_\nu\}_{\neq 1}\{d\mathbf{p}_\nu\}_{\neq 1}L_\nu'i\exp(-iL_\nu t_2)L_\nu'i \times\exp(-iL_\nu^0t_3)\prod\{f_1(\nu,0)\} =\frac{\lambda^2}{(\nu-1)!}\int_0^\infty dt_2\int_0^\infty dt_3\,H(t-t_2-t_3) \times\exp[-iL_1^0(t-t_2-t_3)]\int\{d\mathbf{x}_\nu\}_{\neq 1} \times\int\{d\mathbf{p}_\nu\}_{\neq 1}L_\nu'i\exp(-iL_\nu t_2)L_\nu'i\exp(-iL_\nu^0t_3) \times\prod\{f_1(\nu,0)\}. \quad (8)$$

As in deriving Eq. (5), the z integral yielded a delta function, which was used to perform the t_1 integral. Because the exponential operator in t_2 acts on L_N' its integral is nonzero only for times $t<\tau_{\text{coll}}$, as noted often in I. Equation (8) is to be compared with the first term of Eq. (I.23). The place of the $(t-t_1)$ in the latter is here taken by the t_3 integral over the slowly varying argument. The place of $\varphi_N(0)$ is here taken by the last exponential operator acting on the set of f_1's. This shows, perhaps more vividly than in *I*, the meaning of the time factors arising in the integrands in I. They represent times of free flight between collisions.

It would now be possible to study the terms in Eq. (6) for $n>0$ to get something analogous to the second term of Eq. (I.23). There would be one additional

dummy time variable, its integral being to τ_{corr}. Then more and more periods of uncorrelated motion could be introduced, as in I, to give an exact equation for f_1. This will not be done here in interest of brevity. The notational problems leading to the star in Eq. (6) would be magnified as more particles became involved in the further scatterings.

The knowledge gained in I enables our directly taking the partial derivative of Eq. (3) with respect to t. The general form of the right-hand side is illustrated by the contributions of Eqs. (4), (5), and (8). 'Differentiating partially with respect to t yields $-iL_1{}^0f_1$ plus in every case a contribution from the delta function which arises on differentiating the Heaviside function. This latter contribution from Eq. (4) is zero for $t>0$. This contribution from Eq. (5) may be simplified, since the t_2 integral may be performed over the delta function:

$$-i\lambda NH(\tau_{\text{corr}}-t)\times\int\{d\mathbf{x}\}_{\neq 1}\{d\mathbf{p}\}_{\neq 1}L_N'\exp(-iL_Nt)f_N(0). \quad (9)$$

This is analogous to the last term of either Eq. (I.26) or (I.27). Similar treatment of Eq. (8) yields

$$\frac{i\lambda^2}{(\nu-1)!}\int\{d\mathbf{x}_\nu\}_{\neq 1}\{d\mathbf{p}_\nu\}_{\neq 1}L_\nu' i\times\int_0^\infty dt_2\exp(-iL_\nu t_2)L_\nu' H(t-t_2)\exp[-iL_\nu{}^0(t-t_2)]\times\prod\{f_1(\nu,0)\}. \quad (10)$$

Comparison of this with Eq. (4) shows that the last exponential operator acting on the product of f_1's is the contribution of the form of Eq. (4) to $\prod\{f_1(\nu,t-t_2)\}$. This is in complete analogy to what was found in I. As further terms are included, one gets the equation analogous to Eq. (I.27):

$$\frac{\partial f_1(1)}{\partial t}+iL_1{}^0f_1(1)=\frac{i\lambda^2}{(\nu-1)!}\int\{d\mathbf{x}_\nu\}_{\neq 1}\{d\mathbf{p}_\nu\}_{\neq 1}L_\nu' i\int_0^\infty dt_2\exp(-iL_\nu t_2)L_\nu'\times\prod\{f_1(\nu,t-t_2)\}H(t-t_2)-i\lambda NH(\tau_{\text{corr}}-t)\times\int\{d\mathbf{x}\}_{\neq 1}\{d\mathbf{p}\}_{\neq 1}L_N'\exp(-iL_Nt)f_N(0). \quad (11)$$

This final evolution equation is valid in general for inhomogeneous systems possessing only short-range order in which the gradients in properties are negligible over distances of the order of the region of a ν-body collision. For $t>\tau_{\text{corr}}$ it simplifies to give a form analogous to Eq. (I.28):

$$\frac{\partial f_1(1)}{\partial t}+\mathbf{v}_1\cdot\frac{\partial f_1(1)}{\partial\mathbf{x}_1}=-\frac{\lambda^2}{(\nu-1)!}\int\{d\mathbf{x}_\nu\}_{\neq 1}\{d\mathbf{p}_\nu\}_{\neq 1}L_\nu'\times\int_0^\infty dt_2\exp(-iL_\nu t_2)L_\nu'\prod\{f_1(\nu,t-t_2)\}. \quad (12)$$

The equation is non-Markovian in the sense found in I. The spatial dependence of $\{f_1(\nu)\}$ is, as derived, that for the particles at the moment they enter their collision. But, Eq. (11) or (12) is valid only if the gradients in f_1 are negligible over molecular distances. Thus, the $\{\mathbf{x}_\nu\}$ dependence of the f_1's may be taken to be all at the same spot, say $\mathbf{x}_1$.

Comparison of Eq. (12) with Eq. (I.28) shows that the only real difference between the homogeneous and the inhomogeneous cases, for small gradients, is that a product of one-particle momentum D.F.'s in the homogeneous case is replaced by a product of $c^{-1}f_1$'s in the inhomogeneous case. The spatial dependence of each f_1 is the same, that of the location of the collision.

The approach to equilibrium demanded by the right-hand side of Eq. (12) has been studied.[3] It leads quickly to a Markovian form, as the $\{f_1\}$ become slowly varying:

$$\frac{\partial f_1(1)}{\partial t}+\mathbf{v}_1\cdot\frac{\partial f_1(1)}{\partial\mathbf{x}_1}=\frac{i\lambda^2}{(\nu-1)!}\int\{d\mathbf{x}_\nu\}_{\neq 1}\{d\mathbf{p}_\nu\}_{\neq 1}L_\nu'(L_\nu-i\epsilon)^{-1}\times L_\nu'\prod\{f_1(\nu,t)\}. \quad (13)$$

The concentration dependence of Eq. (13) is not obvious, but concentration dependence of similar operators has been studied elsewhere.[4]

Equation (13) represents a generalized Boltzmann equation, valid to order c^ν. That Eq. (13) indeed is a Boltzmann-type equation is easily seen. Since $L_\nu=L_\nu{}^0+\lambda L_\nu'$, the right-hand side of Eq. (13) becomes

$$\begin{aligned}&\frac{i\lambda}{(\nu-1)!}\int\{d\mathbf{x}_\nu\}_{\neq 1}\{d\mathbf{p}_\nu\}_{\neq 1}(L_\nu-L_\nu{}^0)(L_\nu-i\epsilon)^{-1}\times L_\nu'\prod\{f_1(\nu,t)\}\\&=\frac{i\lambda}{(\nu-1)!}\int\{d\mathbf{x}_\nu\}_{\neq 1}\{d\mathbf{p}_\nu\}_{\neq 1}[1-L_\nu{}^0(L_\nu-i\epsilon)^{-1}]\times L_\nu'\prod\{f_1(\nu,t)\}\\&=\frac{-i\lambda}{(\nu-1)!}\int\{d\mathbf{x}_\nu\}_{\neq 1}\{d\mathbf{p}_\nu\}_{\neq 1}L_\nu{}^0(L_\nu-i\epsilon)^{-1}\times L_\nu'\prod\{f_1(\nu,t)\}. \quad (14)\end{aligned}$$

[3] F. C. Andrews, Phys. Rev. **125**, 1469 (1962).
[4] F. C. Andrews, Physica **27**, 1054 (1961).

The first term in the bracket was zero for a reason similar to that discussed in the paragraph following Eq. (7). By using Eq. (I.15), this may be written

$$\frac{\lambda}{(\nu-1)!}\int\{d\mathbf{x}_\nu\}_{\neq 1}\{d\mathbf{p}_\nu\}_{\neq 1}L_\nu^0 \times\int_0^\infty dt_1\exp(-iL_\nu t_1)L_\nu'\prod\{f_1(\nu,t)\}$$
$$=\frac{\lambda}{(\nu-1)!}\int\{d\mathbf{x}_\nu\}_{\neq 1}\{d\mathbf{p}_\nu\}_{\neq 1}L_\nu^0 \int_0^\infty dt_1[L_\nu'\prod\{f_1(\nu,t)\}][\{\mathbf{x}(t-t_1)\},\{\mathbf{p}(t-t_1)\}]. \quad (15)$$

The final bracket means that the first bracketed quantity has the positions and momenta which the particles would have had at time $(t-t_1)$. Since the f_1's are slowly varying, their explicit t dependence is neglected.

For an arbitrary function of phase space and time,

$$id/dt=i\partial/\partial t-L_\nu^0-\lambda L_\nu'. \quad (16)$$

Over a collision time, $\partial f_1/\partial t$ is zero, and over a region of a collision, $L_\nu^0 f_1$ is zero. Thus, one may use the equation

$$id/dt=-\lambda L_\nu', \quad (17)$$

to simplify Eq. (15):

$$\frac{-i}{(\nu-1)!}\int\{d\mathbf{x}_\nu\}_{\neq 1}\{d\mathbf{p}_\nu\}_{\neq 1}L_\nu^0 \times\int_0^\infty dt_1\frac{d}{d(t-t_1)}\prod\{f_1(\nu,t-t_1)\}$$
$$=\frac{1}{(\nu-1)!}\int\{d\mathbf{x}_{\nu 1}\}_{\neq 1}\{d\mathbf{p}_{\nu 1}\}_{\neq 1} \times\sum_{j=1}^{\nu}\mathbf{v}_j\cdot\frac{\partial}{\partial\mathbf{x}_j}[\prod\{f_1(\nu,t-\tau_{\text{coll}})\} -\prod\{f_1(\nu,t)\}]. \quad (18)$$

This equation has been much discussed elsewhere,[5] where it was formulated from the Liouville equation by more direct but less instructive methods. Here, we shall simply consider the case for $\nu=2$. The f_1's, viewed as functions of $\mathbf{x}_{12}=\mathbf{x}_1-\mathbf{x}_2$ and $\mathbf{r}_{12}=\mathbf{x}_1+\mathbf{x}_2$, over the collision region are functions only of $\mathbf{x}_{12}$, not of $\mathbf{r}_{12}$. Therefore

$$\mathbf{v}_1\cdot\partial/\partial\mathbf{x}_1+\mathbf{v}_2\cdot\partial/\partial\mathbf{x}_2=\mathbf{v}_{21}\cdot\partial/\partial\mathbf{x}_{21},$$

where $\partial/\partial\mathbf{x}_{21}=\partial/\partial\mathbf{x}_2-\partial/\partial\mathbf{x}_1$. Then Eq. (18) becomes

$$\int d\mathbf{x}_{21}d\mathbf{p}_{21}\mathbf{v}_{21}\cdot\frac{\partial}{\partial\mathbf{x}_{21}}[f_1(1')f_1(2')-f_1(1)f_1(2)]$$
$$=\int d\mathbf{p}_{21}d\mathbf{S}_{21}\cdot\mathbf{v}_{21}[f_1(1')f_1(2')-f_1(1)f_1(2)]. \quad (19)$$

The notation is obvious, and Eq. (18) is the collision integral of the classical two-particle Boltzmann equation.[6] As surface of integration, one may choose a cylinder about particle 1 with axis parallel to $\mathbf{v}_{21}$. The base of the cylinder for which $\mathbf{dS}_{21}\cdot\mathbf{v}_{21}<0$ gives no contribution, because there $f_1'=f_1$. The base of the cylinder for which $\mathbf{dS}_{21}\cdot\mathbf{v}_{21}>0$ gives the customary collision integral.

The simple interpretation above of the operators involved in I indicates that the terms in the equations of I which seemed proportional to t (i.e., to the time of free propagation) actually were proportional to tv/l, where v is the intermolecular velocity and l the mean-free-path.

The way now is clear to write down the functional equation for f_s by analogy with Eq. (I.39). For inhomogeneous systems, f_1 replaces $c\varphi_1$. As in I, the equation is written without explicitly noting ν, but it is implied. Realizing that the equation actually is non-Markovian, like Eq. (I.39), we skip on to consider its Markovian form, analogous to Eq. (I.42):

$$f_s(\{s\},t)=c^{s-N}\Omega^{s-N}\int\{d\mathbf{x}\}_{\neq\{s\}}\{d\mathbf{p}\}_{\neq\{s\}}\sum_{n=0}^{\infty}(-\lambda)^n \times[(L_N^0-i\epsilon)^{-1}L_N']^n\prod_{j=1}^{N}f_1(j,t). \quad (20)$$

This equation is valid under the same conditions as Eq. (13). It has been previously formulated from the Prigogine diagram technique by the author.[2] It could have been formulated from the Liouville equation by less instructive methods.[5] Its existence was postulated by Bogoliubov in 1946,[7] and his suggestion was subsequently utilized by Choh and Uhlenbeck.[8]

The meaning of Eq. (20) is easily seen. On separating the $n=0$ term and using Eqs. (I.9) and (I.15), Eq.

[5] F. C. Andrews, J. Chem. Phys. **35**, 922 (1961).

[6] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *The Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), Chap. 7.

[7] N. N. Bogoliubov, J. Phys. (U.S.S.R.) **10**, 265 (1946).

[8] S. T. Choh and G. E. Uhlenbeck, *The Kinetic Theory of Phenomena in Dense Gases* (Navy Theoretical Physics, Contract No. Nonr 1224(15), University of Michigan, 1958).

(20) becomes

$$f_s(\{s\},t)=\prod_{j=1}^{s} f_1(j,t)-N^{s-N}\int\{d\mathbf{x}\}_{\neq\{s\}}\{d\mathbf{p}\}_{\neq\{s\}}$$

$$\times i\int_0^\infty dt_1\exp(-iL_Nt_1)\lambda L_N'\prod_{j=1}^{N} f_1(j,t). \quad (21)$$

Equation (21) may be treated like Eq. (15), using Eq. (17):

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

$$\times\prod_{j=1}^{N} f_1[\mathbf{x}_j(t-\tau_{\text{coll}}),\mathbf{p}_j(t-\tau_{\text{coll}}),t]. \quad (22)$$

The lower limit of the t_1 integral cancelled the first term on the right-hand side of Eq. (21). The result, Eq. (22), is extremely simple. As expected, under the requirements imposed to derive Eq. (22), it merely states that the reduced s-particle D.F. is a constant of the motion during a ν-body collision. This interpretation of the Brussels operator has been presented previously by less convincing means.[9]

[9] F. C. Andrews, Bull. classe sci. Acad. roy. Belg. **46**, 475 (1960).

The author feels that with the other papers of this series,[1,3,4] this clarifies somewhat the philosophical problem of the mechanical approach to equilibrium in classical fluids. One takes certain information about a system known not to be "in equilibrium" and builds this information into an ensemble. One studies, then, the mechanical evolution of the ensemble, using its distribution function to calculate predictions of values of observables for the system. As time goes on, most of the information built initially into the nonequilibrium ensemble becomes completely meaningless, as it is diffused into "correlations" involving huge numbers of particles. Finally, the simple mechanical motion of the ensemble destroys enough information that the value of any observable predicted for the system from the ensemble is essentially time independent, the same as that which would be predicted if one knew virtually nothing about the initial state of the system and used "equilibrium statistical mechanics" from the start. Wall effects play no important role in the significant aspects of the approach to equilibrium in such a mechanical system.

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