ANNALS OF PHYSICS **118**, 187–229 (1979)

Kinetic Theory of Dense Fluids.* I

BYUNG C. EU

Department of Chemistry, McGill University, Montreal, Quebec, Canada

Received May 16, 1978

A kinetic theory of dense fluids is presented in this series of papers. The theory is based on a kinetic equation for subsystems which represents a subset of equations structurally invariant to the sizes of the subsystem that includes the Boltzmann equation as an element at the low density limit. There exists a H-function for the kinetic equation and the equilibrium solution is uniquely given by the canonical distribution functions for the subsystems comprising the entire system. The cluster expansion is discussed for the N-body collision operator appearing in the kinetic equation. The kinetic parts of transport coefficients are obtained by means of a moment method and their density expansions are formally obtained. The Chapman-Enskog method is discussed in the subsequent paper.

I. INTRODUCTION

In Gibbs' statistical mechanics [1] of equilibrium systems the thermodynamic observables of a system, whether it is ideal or real, can be calculated in terms of molecular parameters, temperature and density in complete agreement with experiment. For example, the entropy of a system of N interacting particles is calculated by

$$S = -k_B \int dx^{(N)} F_0^{(N)} \log F_0^{(N)}(x^{(N)}) \tag{1.1}$$

where $x^{(N)}$ denotes collectively the phases of particles and

$$F_0^{(N)} = Ce^{-\beta H}, \qquad \beta = 1/k_B T$$

with H defined by the Hamiltonian of the system and C by an appropriate normalization constant. It is now firmly established that (1.1) gives the correct entropy for arbitrary interacting particle systems.

It is well known that equilibrium statistical mechanics and therefore thermodynamics of ideal fluids can be given the kinetic theory foundation by the celebrated Boltzmann equation [2]. If the Boltzmann equation is solved by the Chapman–Enskog method [3], the equilibrium solution gives [4] rise to the thermodynamic properties, i.e., the entropy, energy, and pressure, etc. of ideal fluids (gases). It therefore can be stated that Gibbs' equilibrium statistical mechanics and thermodynamics are within the framework of Boltzmann's kinetic theory at least for ideal fluids.

* Supported in part by grants from the National Research Council of Canada.

0003-4916/79/030187-43$05.00/0

Since Mayer [5] succeeded in 1937 in obtaining the equation of state for dense interacting gases from the equilibrium statistical mechanics viewpoint, studies have been made by Bogoliubov [6], Born and Green [7], Kirkwood [8], and Yvon [9] to develop kinetic theories for dense interacting fluids as extensions of the original Boltzmann kinetic theory. Since 1946 there has been an enormous amount of works reported [10, 11] on the subject especially along the lines initiated by Bogoliubov and Kirkwood.

In this series of papers we propose a kinetic theory of dense fluids which gives rise to an entropy formula similar to that in Gibbsian statistical mechanics and at the same time includes the Boltzmann kinetic theory of dilute gases in the low density limit. By solving the kinetic equation, we obtain transport coefficients for dense fluids. The kinetic equation will be solved in two different methods. The transport coefficients obtained can be used for investigating their density dependences in a way much similar to Mayer's density expansion for the equation of state of dense gases. Some aspects of density expansions will be discussed.

In Section II the kinetic equation is "derived" or rather rationalized. The main aim of this section is to show the basic ideas behind the proposed kinetic equation. It is entirely possible to investigate the kinetic theory of dense fluids by taking the kinetic equation presented below simply as a hypothesis or conjecture. It leads to the correct hydrodynamic equations and the transport coefficients which are formally in agree-agreement with the results by linear response theory for thermal phenomena as will be shown in the following paper.

In Section III the density expansions of collision operators are discussed. In Section IV the H-theorem is proved by means of the kinetic equation obtained. As a consequence, Gibbs' canonical ensemble distribution function is obtained as the unique equilibrium solution to the kinetic equation presented. In Section V various macroscopic equations are derived by using the kinetic equation. In Section VI the kinetic equation is solved in a moment method and the kinetic parts of transport coefficients are calculated for pure monatomic gases. An alternative and more rigorous solution method will be discussed in the following paper. The method is a generalization of the Chapman–Enskog theory for the Boltzmann equation. Section VII is for discussion.

II. Derivation of the Kinetic Equation

It is useful to examine the Boltzmann equation and some aspects of macroscopic systems in order to enable us to go beyond the theory of Boltzmann.

Since the Boltzmann equation contains only single particle distribution functions, it basically describes the temporal and spatial evolution of a single uncorrelated particle whose interaction with the rest of the system is described by a collision with another uncorrelated particle. Note also that the collision zone is translationally invariant and the distribution functions do not change over the distance of order of molecular interaction. Precisely due to this lack of spatial correlation between particles in Boltzmann's theory, the thermodynamic functions derived from the solution to the Boltzmann equation take inevitably the forms for ideal fluid systems. This defect

can be corrected to some extent by following the program put forward by Bogoliubov [6] and later elaborated by Choh and Uhlenbeck [10a]. Although the Bogoliubov–Choh–Uhlenbeck theory should in principle lead to a proper account of the Gibbsian statistical mechanics of equilibrium systems, it is not possible to demonstrate that it indeed is connected to the latter, primarily because the general expansion formula is lacking in the density development of the collision operator for dense gases, and secondly because the lack of the general expansion formula consequently makes it rather difficult to prove the H-theorem or an equivalent theorem which would make unique the equilibrium solution to the generalized Boltzmann equation in their theory. Probably, there exists such a theorem even for the Bogoliubov–Choh–Uhbenbeck theory, but it would take an enormously complex mathematical relationship between the distribution functions and the entropy so that it would be almost impossible to guess it [10b]. Therefore, it is necessary to look for an alternative theory.

In order to prepare ourselves for such an alternative, let us examine the Boltzmann equation,

$$\frac{\partial}{\partial t} F_1(\mathbf{r}, \mathbf{v}) + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}} F_1(\mathbf{r}, \mathbf{v}) = C[F_1, F_2] \tag{2.1}$$

where

$$C[F_1, F_2] = n \int d\mathbf{P}_2 \int db\, d\theta b \sin\theta\, 2\pi \mid v_{12} \mid [F_1' F_2' - F_1 F_2] \tag{2.2}$$

with the standard notations. This is the well-known Boltzmann collision integral which may be derived in some approximations from the integral

$$C_{BBGKY} = -n \int dx_2\, \mathscr{F}_{12} \cdot \frac{\partial}{\partial \mathbf{P}_1} F_{12}(x_1, x_2; t) \tag{2.3}$$

where $x_i = (r_i, P_i)$, n is the bulk density, F_{12} the two-particle distribution function, and $\mathscr{F}_{12}$ the force between 1 and 2. If $C[F_1, F_2]$ is replaced by C_{BBGKY}, (2.1) becomes the leading member of the so-called *BBGKY* hierarchy. Thus, we interpret the equation as describing the evolution of the single particle distribution function F_1 which is determined by the interaction of particle 1 with the rest of the system and this interaction is effectively described by F_{12}, the two-particle distribution function, and the force $\mathscr{F}_{12}$. Boltzmann in essence assumed that this interaction could be effectively accounted for by approximating F_{12} with the product of two single particle distribution functions, $F_1 F_2$. It has been demonstrated in numerous analyses and resarches on the Boltzmann equation that such an approximation indeed is valid in the low density limit. In Bogoliubov's theory it is proposed to calculate F_{12} in a different way, by regarding F_{12} as a functional of F_1 as far as its time evelution is concerned.

Whether one follows the Boltzmann theory or the Bogoliubov theory, there is a common basic feature. That is, the system under consideration is always divided into two distinct parts; one the observed object, i.e., one or more particles, and the other the rest of the system which perturbs the observed object and as a consequence influences the evolution of the distribution of the former. In the Boltzmann theory the

observed object is a single particle and in the Bogoliubov theory there are an infinite number of them forming a hierarchy, i.e., one particle, two particles, etc.

In the Boltzmann theory the view that the interaction between the observed object and the rest of the system can be accounted for by F_1F_2 entails a qualitative alteration in the character of the system if there exist interactions between particles, since the approximation $F_{12} \rightarrow F_1F_2$ essentially makes the system a collection of independent particles which is not the picture of the system one has had at the outset. If the interactions are weak between particles, then this approximation appears quite reasonable, but it nevertheless makes a qualitative difference to the results obtained of the macroscopic properties from the Boltzmann theory, since they turn out to be pertaining to ideal fluids.

This approximation is in effect equivalent to replacing the Hamiltonian of an interacting many-particle system with that of a free particle system. However weak the interactions may be, it is a qualitatively drastic approximation. This qualitatively drastic nature of approximation will disappear, if the particles are paired two each into correlated pairs which are assumed to be non-interacting. An important feature of this approximation is that the free particle assumption is removed. Going a step further, if we visualize correlated trimers of particles and assume that they do not interact with each other, the drastic nature of the free particle assumption is so much reduced accordingly due to the interactions retained between the particles in trimers. If this process is continued to a sufficiently large size of clusters of particles, then a stage will be eventually reached where the approximation is really good, since the interaction between two, say, l-member clusters will be sufficiently small, compared with the "internal" energy of the clusters, if l is large, mainly owing to the fact that the major contribution to the intercluster interaction energy will come from the particles on the peripheries of the clusters and this intercluster interaction energy will constitute only a small portion of the entire interaction energy of two completely separated clusters. Therefore, in this limit the energy of the entire system can be well approximated by an additive form of Hamiltonian, i.e.,

$$H = \sum_{\alpha} H_{\alpha}, \tag{2.4}$$

where H_{α} denote the Hamiltonians of the cluster of particles. The H_{α}, of course, consists of the kinetic and the potential energy. The important feature of (2.4) is in the neglect of the interactions between the clusters (subsystems) of the system. If we assume that the interaction potentials are pairwise additive, then the difference between

$$H = \sum_{i=1}^{N} H_{0i} + \frac{1}{2}\sum_{j\neq k}^{N}\sum V_{jk}\,; \qquad H_{0i} = \frac{\mathbf{P}_i^2}{2m_i}, \tag{2.5}$$

and

$$H' = \sum_{\alpha=1}^{\nu}\left(H_{0\alpha} + \frac{1}{2}\sum_{j\neq k}^{s}\sum V_{jk}\right) \tag{2.6}$$

is

$$\tfrac{1}{2}\sum_{j\neq k}^{N}\sum V_{jk} - \tfrac{1}{2}\sum_{\alpha=1}^{\nu}\sum_{j\neq k}^{s}\sum V_{jk},$$

where N is the total number of particles, s the number of particles in the subsystems, ν the number of subsystems such that

$$\nu s = N \tag{2.7}$$

and the particle indices j and k must be understood to be in the set (subsystem), whenever a sum over the subsystem index occurs. The difference above can be much reduced, if the interaction strength of V_{jk} is increased by ν-fold in each subsystem which is allowed to occupy the entire volume of the system, each time when the whole system is divided into ν subsystems. Then (2.4) takes the form

$$H = \sum_{\alpha=1}^{\nu} H_\alpha \tag{2.8}$$

where

$$H_\alpha = H_{0\alpha} + \tfrac{1}{2}\nu\sum_{j\neq k}^{s}\sum V_{jk}, \tag{2.9}$$

$H_{0\alpha}$ denoting the kinetic energy of the subsystem α. The number ν plays in (2.8) and (2.9) a role similar to a charging parameter which is increased stepwise as the system is divided into a corresponding number of subsystems occupying the whole volume. It is a kind of renormalization of potential strength and its effect is to maintain the effect of correlation at the same level as the system is thinned by division into ν subsystems. A further discussion is given below on the charging (renormalization) process. Observe also that the Hamiltonian in (2.8) is additive in the limit of large s. The idea of dividing the system into a large number of almost independent subsystems of sufficiently many particles is in line with the general view of macroscopic systems and the way they are believed to evolve toward equilibrium from a nonequilibrium state [12b].

The notion of additivity of energy is quite basic to thermodynamics and equilibrium statistical mechanics. Underlying in this important notion is the implicit assumption that the components comprising the whole system do not interact significantly with each other. In practice, this assumption can be made meaningful if the interactions between the components (subsystems) are negligibly small, compared with the energy content of the whole subsystems. This condition is in general met by macroscopic size subsystems, since the "surface energies" are comparably quite small, if the subsystems are large enough. We emphasize that however small and negligible the inter-subsystem interaction energies may be, it is through such interactions that the system eventually reaches equilibrium. We will see that such interactions are indeed appropriately taken into consideration in the present kinetic theory. We also observe that this concept of additivity of energy is essential for deriving [12] canonical ensemble

distribution functions from microcanonical ensembles in equlilibrium statistical mechanics.

Inasmuch as Boltzmann's "Stosszahlansatz" essentially amounts to neglecting the correlation between particles, i.e., interaction, the above consideration now seems to make it logical to think that if a similar assumption is made on higher order distribution functions, say, $F_{12\cdots s,s+1\cdots 2s}$ such that

$$F_{12\cdots s,s+1\cdots 2s} \cong F_{12\cdots s}F_{s+1\cdots 2s}$$

the approximation should certainly be so much less drastic than the approximation in which

$$F_{12} \cong F_1F_2\,,$$

which is tantamount to the assumption that there is no correlation between the particles, and therefore we can anticipate an improvement in theory.

The above reasoning points to the following viewpoints of dense fluids: A macroscopic system, say, a gas or liquid, consists [12b] of small subsystems which interact with each other weakly (in the relative sense), but the particles in each subsystem may strongly interact among themselves. The size of subsystems may be viewed as much larger than the intermolecular interaction range, and the number of particles sufficientoy large, but smaller than the total number of particles in the whole system. A disturbance generated by some means within a subsystem propagates through the interactions between the particles in the subsystems and then through the interactions between the subsystems, which may be made sufficiently weak by taking the subsystem sufficiently large so that the internal energy is comparatively large. Since the coupling is relatively weak between the subsystems, the extensive macroscopic variables of the total system are additive. Note, however, that from the viewpoint of irreversibility, such weak interactions between the subsystems are essential for the eventual establishment of equilibrium and must be appropriately utilized in kinetic theory. At this point the sitaution appears quite similar to that with the Boltzmann theory of ideal fluids. There the particles interact (correlate) only to the extent that they collide according to a certain force law, driving the system to equilibrium. In our picture the subsystems which are sufficiently large interact with each other only weakly in the relative sense and thus may be regarded as free to a good approximation as far as the distribution function is concerned, yet the negligible, tenuous interactions between them drive the system to equilibrium through "collisions" between them. We now see a complete paralellism between the two pictures, i.e., Boltzmann's and the present. However, the present picture is more general in the sense that it is inclusive of the Boltzmann picture, since the Boltzmann picture is simply the case when the subsystems consist of a single particle each. By now, our idea of a kinetic equation for dense fluids takes a more definite and concrete form.

It appears quite obvious to see how Boltzmann's original idea can be generalized: In fact one can simply write down the kinetic equation (2.36) below in analogy to the Boltzmann equation and take it as a hypothesis for the theory of transport

processes described in these papers. However, we shall try to rationalize it as much as possible in the following.

In order to make our discussion simple, we assume that the system is a classical monatomic fluid of N identical molecules and there is no chemical reaction.

The distribution function $F^{(N)}$ for the whole system is described by the Liouville equation,

$$i\frac{\partial}{\partial t}F^{(N)}(x^{(N)};t) = \mathscr{L}F^{(N)}(x^{(N)};t) \tag{2.10}$$

where $\mathscr{L}$ is the Liouville operator,

$$\mathscr{L} = -i\sum_{j=1}^{N}\left(\frac{\partial H}{\partial \mathbf{P}_j}\cdot\frac{\partial}{\partial \mathbf{r}_j} - \frac{\partial H}{\partial \mathbf{r}_j}\cdot\frac{\partial}{\partial \mathbf{P}_j}\right) \equiv -i[H,\ ] = -i[H_0,\ ] + i[V,\ ]$$
$$\equiv \mathscr{L}_0 + i\mathscr{L}', \tag{2.11}$$

with the definitions,

$$\mathscr{L}_0 \equiv -i[H_0,\ ] \tag{2.12}$$

$$\mathscr{L}' \equiv i[V,\ ] \tag{2.13}$$

$$V = \tfrac{1}{2}\sum_{j\neq k}^{N}\sum V_{jk}\,. \tag{2.14}$$

The H_0 is the kinetic energy of the system. The $x^{(N)}$ denotes collectively the phases $x_i = (\mathbf{r}_i, \mathbf{P}_i)$, $i = 1, 2,..., N$, for the entire system. The phases of an l particle system will be denoted, whenever convenient, by $x^{(l)}$ which means $(\mathbf{r}_1, \mathbf{r}_2,..., \mathbf{r}_l, \mathbf{P}_1,..., \mathbf{P}_l)$ collectively. The Liouville operator for an l-particle system will be denoted by $\mathscr{L}_l$ which is defined similarly to (2.11), i.e.,

$$\mathscr{L}_l = -i[H_l,\ ] \tag{2.15}$$

where

$$H_l = H_0^{(l)} + \tfrac{1}{2}\sum_{j\neq k}^{l}\sum V_{jk} \equiv H_0^{(l)} + V_l\,. \tag{2.16}$$

It is convenient to write interaction Liouville operators $\mathscr{L}_l'$ as

$$\mathscr{L}_l' = i[V_l,\ ] = i\frac{1}{2}\sum_{j\neq k}^{l}\sum\left(\frac{\partial V_{jk}}{\partial \mathbf{r}_j}\cdot\frac{\partial}{\partial \mathbf{P}_j} + \frac{\partial V_{jk}}{\partial \mathbf{r}_k}\cdot\frac{\partial}{\partial \mathbf{P}_k}\right)$$

$$= \frac{1}{2}\sum_{j\neq k}^{l}\sum \mathscr{L}_{jk}'\,. \tag{2.17}$$

In the usual theories of dense fluids or gases the Liouville equation (2.10) is integrated over $(N-1)$, $(N-2)$,..., particle phases. Then the so-called *BBGKY* hierarchy results. Since the hierarchy is open, it is truncated or closed by some means

of approximation [8] or hypothesis [6]. We do not exactly follow either of these lines of approach.

Suppose there exists a number s satisfying the relation (2.7) such that (2.8) and (2.9) together constitute a good approximation to the total Hamiltonian. Then the object of our interest would be the evolution of the subsystems of s particles. The distribution of the s particles $F^{(s)}(x^{(s)}; t)$ will obey the equation obtained by integrating (2.10) over $(N - s)$ phases:

$$i\frac{\partial}{\partial t}F^{(s)}(x^{(s)}; t) = \mathscr{L}_s F^{(s)}(x^{(s)}; t) + V^s \int d\Gamma^{(N-s)} \mathscr{L}'_{(N-s)} F^{(N)}(x^{(N)}; t) \tag{2.18}$$

where

$$F^{(s)}(x^{(s)}; t) = V^s \int d\Gamma^{(N-s)} F^{(N)}(x^{(N)}; t), \tag{2.19}$$

$$d\Gamma^{(N-s)} = dx_{s+1} \cdots dx_N$$

and

$$\mathscr{L}'_{(N-s)} = \mathscr{L}'_{12\cdots\nu} + \sum_{\beta=1}^{\nu-1} \sum_{\beta s+1 \leqslant j<k \leqslant (\beta+1)s} \mathscr{L}'_{jk} \tag{2.20}$$

where

$$\mathscr{L}'_{12\cdots\nu} = \sum_{\alpha=1}^{\nu-1} \sum_{\beta=1}^{\nu-1} \sum_{(\alpha-1)s+1 \leqslant j \leqslant \alpha s} \sum_{\beta s+1 \leqslant k \leqslant (\beta+1)s} \mathscr{L}'_{jk} \quad (j < k). \tag{2.21}$$

Here the particles are numbered consecutively for subsystems through ν. Note that $\nu s = N$, ν being the number of subsystems with s particles each. This relation always holds between ν and s, although the s must be a limiting number for which (2.8) and (2.9) constitute a good approximation to the Hamiltonian of the entire system.

The last term on the right hand of (2.20) does not contribute to the integral in (2.18), provided that $F^{(N)}$ is equal to zero at the boundary in the phase space. Thus (2.18) may be written as

$$i\frac{\partial}{\partial t}F_1^{(s)}(x^{(s)}; t) = \mathscr{L}_s^{(1)} F_1^{(s)}(x^{(s)}; t) + V^s \int d\Gamma^{(N-s)} \mathscr{L}'_{12\cdots\nu} F^{(N)}(x^{(N)}; t), \tag{2.22}$$

where we have affixed the subscript and superscript, respectively, to $F^{(s)}$ and $\mathscr{L}_s$ in order to distinguish the subsystems. If the integration is carried out over the phases $x_{s+2}, \ldots, x_N$ in (2.21), we obtain the sth member of the *BBGKY* hierarchy. The reason why we do not carry out such integrations is in the fact that we visualize the whole system consisting of ν subsystems of s particles. Note that we have not as yet "charged" the interaction by a ν-fold as in (2.9). The meaning of (2.21) is that it now represents the interaction Liouville operator between ν subsystems.

Since we assume that the system is made up by ν subsystems, it is operationally reasonable to assume that the whole system is prepared with ν independent subsystems at the initial time $t = 0$. Since we assume that the subsystems are practically of a macroscopic size, such a preparation can be given a definite meaning (For example,

one can imagine the system made up by many bubbles containing a sufficiently large number of particles in different states, which can be simultaneously broken at $t = 0$ by some means). Then the initial condition on $F^{(N)}$ may be written in the form,

$$F^{(N)}(x^{(N)}; 0) = \prod_{\alpha=1}^{\nu} [F_\alpha^{(s)}(x^{(s)}; 0)/V^s], \tag{2.23}$$

where the symmetry of particle interchanges has been ignored for conveinence without loss of generality of the result. This initial condition seems only a special case of many possible divisions of the N particle system but it is consistent with our view to the macroscopic system that it can be prepared macroscopically by assembling large *apparently identical* systems as discussed at the beginning of the present section and above.

The formal solution to (2.10) subject to (2.23) is

$$F^{(N)}(x^{(N)}; t) = e^{-i\mathscr{L}t} \prod_{\alpha=1}^{\nu} [F_\alpha^{(s)}(x^{(s)}; 0)/V^s]. \tag{2.24}$$

If we introduce a Liouville operator $\mathscr{L}^{(0)}$ such that

$$\mathscr{L}^{(0)} = \sum_{\alpha=1}^{\nu} \mathscr{L}_s^{(\alpha)}, \tag{2.25}$$

then (2.24) may be written as

$$F^{(N)}(x^{(N)}; t) = e^{-i\mathscr{L}t} e^{i\mathscr{L}^{(0)}t} \prod_{\alpha=1}^{\nu} [F_\alpha^{(s)}(x^{(s)}; t)/V^s] \tag{2.26}$$

where

$$F_\alpha^{(s)}(x^{(s)}; t) = e^{-i\mathscr{L}_s^{(\alpha)}t} F_\alpha^{(s)}(x^{(s)}; 0), \qquad (\alpha = 1,..., \nu). \tag{2.27}$$

We now substitute (2.26) into (2.22) after "charging" the interactions of subsystems by ν-fold:

$$\mathscr{L}_s^{(\alpha)}[V_{ij}] \Rightarrow \mathscr{L}_s^{(\alpha)}[\nu V_{ij}], \tag{2.28}$$

in the sense of (2.9). The rationale for this "charging" is making the subsystems, which are thinned by a factor of ν, resemble the original system of N particles in volume V as far as the interactions between the particles go. This is equivalent to renormalizing the interaction strength by a factor ν as the original system is divided into ν subsystems. The final mathematical effect of this charging (or renormalization) is that $\mathscr{L}^{(0)} = \sum_{\alpha=1}^{\nu} \mathscr{L}_s^{(\alpha)}$ becomes almost the total Liouville operator. In fact, it is interesting to observe that there are $N(N-1)/2$ binary interaction terms in "uncharged" $\mathscr{L}$, whereas there are $N(N-\nu)/2$ binary interaction terms in the charged $\mathscr{L}^{(0)}$. Therefore, the difference in the number of binary interaction terms is $N(\nu-1)/2$ which is only $O(\nu/N)$ compared with the binary interaction terms in "uncharged" $\mathscr{L}$. We note that

in the total Liouville operator $\mathscr{L}$ in (2.26) only the $\mathscr{L}^{(0)}$ part must be "charged" according to (2.28). Then finally we obtain the equation

$$i\frac{\partial}{\partial t}F_1^{(s)}(x^{(s)};t) = \mathscr{L}_s^{(1)}F_1^{(s)}(x^{(s)};t) + V^{-N+s}\int d\Gamma^{(N-s)}\mathscr{L}'_{12\ldots\nu}\Omega_{12\ldots\nu}(t) \times \prod_{\alpha=1}^{\nu}F_\alpha^{(s)}(x^{(s)};t) \tag{2.29}$$

where

$$\Omega_{12\ldots\nu}(t) = e^{-i\mathscr{L}t}e^{i\mathscr{L}^{(0)}t}. \tag{2.30}$$

In this equation we may write

$$\mathscr{L} = \sum_{\alpha=1}^{\nu}\mathscr{L}_s^{(\alpha)} + \sum_{\alpha=1}^{\nu}\sum_{\beta=1}^{\nu}\sum\sum_{j<k}\mathscr{L}'_{jk}\ (j\in\alpha,\ k\in\beta,\ \alpha<\beta)$$

$$\equiv \mathscr{L}^{(0)} + \mathscr{L}''_{12\ldots\nu}$$

and $\mathscr{L}^{(0)}$ must be understood in the sense of (2.28). Although a renormalization group theory type argument cannot be ruled out as a way to give the kinetic equation (2.29) and the "charging process" used a more definite mathematical basis, this "charging" of $\mathscr{L}^{(0)}$ and $\mathscr{L}_s^{(\alpha)}$ does not appear possible to prove by any purely mathematical means. We will further discuss the significance of Eq. (2.29) later in this section.

In order to give $\Omega_{12\ldots\nu}(t)$ a more definite mathematical meaning, we shall assume that the function $\prod_{\alpha=1}^{\nu}F_\alpha^{(s)}(x^{(s)};0)$ and thus $\prod_{\alpha=1}^{\nu}F_\alpha^{(s)}(x^{(s)};t)$ satisfies the relation,

$$e^{\pm i\mathscr{L}^{(0)}t}\prod_{\alpha=1}^{\nu}F_\alpha^{(s)}(x^{(s)};t) = e^{\pm i\lambda t}\prod_{\alpha=1}^{\nu}F_\alpha^{(s)}(x^{(s)};t), \tag{2.31a}$$

in other words, the product function is an eigenfunction of $\mathscr{L}^{(0)}$,

$$\mathscr{L}^{(0)}\prod_{\alpha=1}^{\nu}F_\alpha = \lambda\prod_{\alpha=1}^{\nu}F_\alpha, \tag{2.31b}$$

where λ is an eigenvalue of $\mathscr{L}^{(0)}$. We will call such a function λ-class.

The operator has then a proper meaning on such a set of basis:

$$\Omega_{12\ldots\nu}(t)\prod_{\alpha=1}^{\nu}F_\alpha^{(s)}(x^{(s)};t) = e^{-i\mathscr{L}t}e^{i\lambda t}\prod_{\alpha=1}^{\nu}F_\alpha^{(s)}(x^{(s)};t). \tag{2.30a}$$

Besides the requirement that $\Omega_{12\ldots\nu}(t)$ must be defined on a basis set of functions as in (2.30a), it must also have a limit as time increases. Since it is a manybody operator for a system of a macroscopic size, it is not obvious whether there exists such a limit, say, t_p.

If the range of interaction is finite, then the average time required for a binary collision is approximately the range divided by the average relative velocity. This time

t_c is usually much shorter than the mean free path time, t_{mfp}. This time is in turn much shorter than the hydrodynamic relaxation time, t_h. Now the question is, how long is t_p ? This time is difficult to establish in general. One can only estimate it to a crude approximation. For example, if the binary collision approximation is made to $\Omega_{12\ldots\nu}(t)$ then t_p should be the same order of magnitude as t_c. In general, this would be the case when lower order collision approximations are made for $\Omega_{12\ldots\nu}(t)$. Based on this and since the time scale regime of interest for $F_\alpha^{(s)}$ is in the kinetic regime [6, 10] of $t \gg t_c$, but much shorter than t_h, we shall assume that in such a time scale (kinetic) regime $\Omega_{12\ldots\nu}(t)$ may be replaced by

$$\Omega_{12\ldots\nu}(\infty) = \lim_{t\to\infty} e^{-it\mathscr{L}} e^{it\mathscr{L}^{(0)}}. \tag{2.32}$$

This assumption appears to be equivalent in effect to the time coarse-graining, which makes the wave operator and the associated collision operator time-independent in the time scale regime of interest. The justification for this must be sought a posteriori.

This limit may be replaced by another limit (Abel's limit) according to Abel's theorem,

$$\Omega_{12\ldots\nu}(\infty) = \Omega_{12\ldots\nu}(\epsilon) = \lim_{\epsilon\to+0} \epsilon \int_0^\infty dt\, e^{-\epsilon t} e^{-i\mathscr{L}t} e^{i\mathscr{L}^{(0)}t}. \tag{2.33}$$

If (2.31b) is understood, then

$$\begin{aligned} \Omega_{12\ldots\nu}(\epsilon) &= \lim_{\epsilon\to+0} \epsilon \int_0^\infty dt\, e^{-\epsilon t} e^{-i\mathscr{L}t} e^{i\lambda t} \\ &= \lim_{\epsilon\to+0} \epsilon(\epsilon - i\lambda + i\mathscr{L})^{-1} \\ &= \lim_{\epsilon\to+0} -i\epsilon(\mathscr{L} - z)^{-1}; \qquad z = \lambda + i\epsilon, \end{aligned} \tag{2.34}$$

where $(\mathscr{L} - z)^{-1}$ is the resolvent of $\mathscr{L}$. If the transition (collision) operator is defined in terms of the wave operator thus obtained,

$$T_{12\ldots\nu}(z) = \mathscr{L}'_{12\ldots\nu}\Omega_{12\ldots\nu}(z), \tag{2.35}$$

then the equation (2.29) now takes the form

$$i\frac{\partial}{\partial t} F_\alpha^{(s)}(x^{(s)}; t) - \mathscr{L}_s^{(\alpha)} F_\alpha^{(s)}(x^{(s)}; t) = V^{-N+s} \int d\Gamma^{(N-s)} T_{12\ldots\nu} \prod_{\beta=1}^{\nu} F_\beta^{(s)}(x^{(s)}; t), \tag{2.36}$$

where the limit $\epsilon \to +0$ is understood. *This is the kinetic equation we have strived for and will be the basis of the present kinetic theory.* It is closed for $F_\alpha^{(s)}$, but is highly nonlinear. It is also an equation that describes the temporal and spatial evolution of the λ-class function $\prod_{\beta=1}^{\nu} F_\beta^{(s)}(x^{(s)}; t)$. But for the collision term, i.e., the right-hand side of (2.36), it would describe the evolution of an independent subsystem α. However, the presence of the collision term removes the independence of subsystems and their "collisions" by their relatively weak interactions subtly influence the evolution of the entire system toward equilibrium.

Equation (2.36) looks quite similar to the original Boltzmann equation. In fact, it reduces to the Boltzmann equation in the limit of low density, if the system is homogeneous. This will be discussed later. An interesting and important feature of (2.36), which we would like to discuss here, is its structural invariance to divisions of the system into all possible sizes of subsystems. Whether s is 1, 2,..., 100 or 10^{10}, its structure remains invariant. That is, if we assume that $s = 1$, then $\nu = N$ and

$$\mathscr{L}_s^{(1)} = -i \frac{\mathbf{P}_1}{m_1} \cdot \frac{\partial}{\partial \mathbf{r}_1}$$

so that (2.36) becomes a generalized Boltzmann equation for singlet distribution function $F_1^{(1)}(x_1 ; t)$:

$$\frac{\partial}{\partial t} F_\alpha^{(1)}(x_\alpha ; t) + \frac{\mathbf{P}_\alpha}{m_\alpha} \cdot \frac{\partial}{\partial \mathbf{r}_\alpha} F_\alpha^{(1)}(x_\alpha ; t)$$

$$= -iV^{-N+1} \int d\Gamma^{(N-1)} T_{12\ldots N}^{(1)}(z) \prod_{\beta=1}^{N} F_\beta^{(1)}(x_\beta ; t). \tag{2.37}$$

If $T_{12\ldots N}$ is approximated by T_{12}, a two-particle collision operator, then (2.37) leads to the Boltzmann equation. In this sense (2.37) is a generalized Boltzmann equation, but is different from other known generalized Boltzmann equations. We stress that (2.37) has a well-defined N-body collision operator. An important defect of (2.37), however, is the lack of correlations between particles, which correlate with each other only in the sense of collisions. We note that (2.37) may be looked upon as a generalization of the kinetic equation obtained by Hollinger and Curtiss [13].

Now, if the number of particles in subsystems is increased by 1, then doublet distribution functions $F_\alpha^{(2)}(x^{(2)}; t)$ are the basic quantities of interest. On this level of description the equation still looks like (2.37) in its structure, yet the correlations between particles are not completely neglected, since $F_\alpha^{(2)}$ still retains the correlation between two particles in subsystem α. (In fact, since it is sufficient to have $F_\alpha^{(2)}$ for all practical purposes in theory of transport processes, one can develop a theory with $s = 2$ in (2.36)). Therefore the neglect of intersubsystem correlations looks less severe from the viewpoint of the entire system than in the first level of description. By continuing this process, we will reach a point s beyond which (2.36) describes the evolution of the macroscopic system of interest almost rigorously. Interestingly, the evolution equation for such a collection of subsystems still looks like the generalized Boltzmann equation (2.37). We shall show in the subsequent sections that Eq. (2.36) indeed has capability of describing the irreversibility as well as transport processes of dense fluids.

The present theory is not capable of giving a mathematical proof for the existence of the limit of s or its precise value in the limit. We simply assume that such a limiting value exists. The ignorance of the precise limit, however, is not a limitation on the theory, since measurable macroscopic quantities do not depend on it which drops out of the macroscopic equations valid in the thermodynamic limit. Neither is it our intention to attempt a mathematical justification of the so-called "charging" process we have used for (2.36) except for making the folloing argument: Since we are using

$F_\alpha^{(s)}$ for calculating macroscopic quantities and $F_\alpha^{(s)}$ are normalized over the entire volume (see below), such a "charging" charging appears to be quite reasonable within the context of our picture of macroscopic systems and processes. To the extent that these two aspects are not mathematically and rigorously proved, the present theory is not "proving" why irreversibility occurs, but it does show how it can be demonstrated to occur in macroscopic systems such that kinetic theory is bridged to thermodynamics. At least the kinetic equation presented can be used as a model.

It is of course possible to write down a kinetic equation or a master equation such that the entropy of the system is defined by (1.1) and its time derivative is positive definite as was formally done by Green [7d]. However, there has not been available a theory in which a systematic development of transition probabilities (operators) is possible and moreover transport processes can be systematically described. These aspects of the present theory will become clearer as we proceed to the subsequent sections and the following paper. In the next section we first consider some aspects of the collision operator $T_{12\ldots\nu}$, which will be used in our discussions on irreversibility and transport coefficients.

III. Collision Operators and Their Density Expansions

The collision operators $T_{12\ldots\nu}(z)$ and $T_{12\ldots N}(z)$ in (2.36) and (2.37) are N-particle operators supported by λ-class functions (2.31). They are defined in terms of N-particle wave operator $\Omega_{12\ldots\nu}$ or $\Omega_{12\ldots N}$ as in (2.35), but their calculation is another matter that cannot be achieved rigorously. It will require one sort of approximation or another. Our primary purpose here is to investigate some properties of the transition operators, the equations they obey, and their density expansions.

It is instructive to begin with $T_{12\ldots N}$. It is given by the form

$$T_{12\ldots N}(z) = \mathscr{L}'_{12\ldots N}\Omega_{12\ldots N}(z). \tag{3.1}$$

In this case we have $\mathscr{L}^{(0)}$ in the form

$$\mathscr{L}^{(0)} = -i\sum_{j=1}^{N}\frac{\mathbf{P}_j}{m_j}\cdot\frac{\partial}{\partial\mathbf{r}_j} \tag{3.2}$$

since

$$\mathscr{L}_1^{(\alpha)} = -i\frac{\mathbf{P}_\alpha}{m_\alpha}\cdot\frac{\partial}{\partial\mathbf{r}_\alpha}$$

due to the fact that there is only one particle in each subsystem. Therefore, we see that

$$\mathscr{L}'_{12\ldots N} = \sum_{j<k}^{N}\sum\mathscr{L}'_{jk} \tag{3.3}$$

in the present case. Since the wave operator $\Omega_{12\ldots N}$ may be written in the form

$$\Omega_{12\ldots N}(z) = 1 - \mathscr{R}_N(z)\,\mathscr{L}'_{12\ldots N} \tag{3.4}$$

where

$$\mathscr{R}_N(z) = (\mathscr{L} - z)^{-1}, \tag{3.5}$$

the N-particle resolvent operator (propagator), we obtain a classical analog of the Lippmann–Schwinger equation for $T_{12\cdots N}$,

$$\begin{aligned} T_{12\cdots N} &= \mathscr{L}'_{12\cdots N} - \mathscr{L}'_{12\cdots N}\mathscr{R}_N(z)\,\mathscr{L}'_{12\cdots N} \\ &= \mathscr{L}'_{12\cdots N} - \mathscr{L}'_{12\cdots N}\mathscr{R}_N^{(0)}(z)\,T_{12\cdots N} \end{aligned} \tag{3.6}$$

where

$$\mathscr{R}_N^{(0)}(z) = (\mathscr{L}^{(0)} - z)^{-1}, \tag{3.7}$$

the free particle resolvent operator. Eq. (3.6) may be solved by a suitable method such as perturbation theory, etc., if the coupling is weak. We also note that there exists the following relationship:

$$\mathscr{R}_N(z) = \mathscr{R}_N^{(0)}(z) - \mathscr{R}_N^{(0)}(z)\,T_{12\cdots N}(z)\,\mathscr{R}_N^{(0)}(z) \tag{3.8}$$

which is related to (3.6) and we also note the relationship,

$$\mathscr{L}'_{12\cdots N}\mathscr{R}_N(z) = T_{12\cdots N}(z)\,\mathscr{R}_N^{(0)}(z). \tag{3.9}$$

These are the standard formulas which can be easily proved in the classical scattering theory[14] in phase space. In order to discuss the density expansion of the collision operator, it is useful to consider a cluster expansion of $T_{12\cdots N}(z)$. For this purpose let us define connected collision operators as follows:

$$T_{12}^{(1)}(z) = \mathscr{L}'_{12} - \mathscr{L}'_{12}\mathscr{R}_N^{(0)}(z)\,T_{12}^{(1)}(z) \tag{3.10}$$

$$\mathscr{T}_{123}^{(1)}(z) = T_{123}^{(1)} - T_{12}^{(1)} - T_{13}^{(1)} - T_{23}^{(1)} \tag{3.11}$$

where

$$\begin{aligned} T_{123}^{(1)} &= \mathscr{L}'_{123} - \mathscr{L}'_{123}\mathscr{R}_N^{(0)}T_{123}^{(1)}, \\ \mathscr{L}'_{123} &= \mathscr{L}'_{12} + \mathscr{L}'_{23} + \mathscr{L}'_{13}. \end{aligned} \tag{3.12}$$

The meanings of T_{12} and T_{123} are as follows: $T_{12}(z)$ is the collision operator for the collision between particles 1 and 2 imbedded in $(N-2)$ free particles acting as spectators and $T_{123}^{(1)}$ the collision operator for the three-body collisions of particles 1, 2, and 3 imbedded in $(N-3)$ free particles. Since the three particles do not necessarily collide, $T_{123}^{(1)}$ can be decomposed into two-body collision and true three-body collisions of particles 1, 2, and 3 embedded in $(N-3)$ free particles. Therefore, by subtracting the two-body collision part, we are insured of a genuine three-body collision by $\mathscr{T}_{123}^{(1)}$. By continuing similarly, we define

$$\mathscr{T}_{12;34}^{(1)} = T_{12;34}^{(1)} - T_{12}^{(1)} - T_{34}^{(1)}, \tag{3.13}$$

$$\begin{aligned} \mathscr{T}_{1234}^{(1)} = {} & T_{1234}^{(1)} - T_{123}^{(1)} - T_{124}^{(1)} - T_{234}^{(1)} - T_{12;34}^{(1)} - T_{13;24}^{(1)} \\ & - T_{23;14}^{(1)} - T_{12}^{(1)} - T_{13}^{(1)} - T_{14}^{(1)} - T_{23}^{(1)} - T_{24}^{(1)} - T_{34}^{(1)} \end{aligned} \tag{3.14}$$

where

$$T^{(1)}_{12;34} = \mathscr{L}'_{12;34} - \mathscr{L}'_{12;34}\mathscr{R}^{(0)}_N T^{(1)}_{12;34} \tag{3.15}$$

$$T^{(1)}_{1234} = \mathscr{L}'_{1234} - \mathscr{L}'_{1234}\mathscr{R}^{(0)}_N T^{(1)}_{1234} \tag{3.16}$$

$$\mathscr{L}'_{12;34} = \mathscr{L}'_{12} + \mathscr{L}'_{34}$$

$$\mathscr{L}'_{1234} = \mathscr{L}'_{12} + \mathscr{L}'_{13} + \mathscr{L}'_{14} + \mathscr{L}'_{23} + \mathscr{L}'_{24} + \mathscr{L}'_{34}$$

and $T^{(1)}_{ijk}$ are defined similarly to (3.12). In general, we define connected N-body collision operators by

$$\mathscr{T}^{(1)}_{12\cdots N} = T_{12\cdots N} - \sum_{i<j}^{N} T^{(1)}_{ij} - \sum_{i<j<k} \mathscr{T}^{(1)}_{ijk} - \sum_{i<j<k<l} \mathscr{T}^{(1)}_{ij;kl} - \cdots, \tag{3.17}$$

i.e.,

$$\mathscr{T}^{(1)}_{12\cdots N} = T_{12\cdots N} - \sum^{(C)}_{\{C_m\}} \mathscr{T}^{(1)}_{C_1C_2\cdots C_m/m1}\,. \tag{3.17a}$$

where $\sum^{(C)}_{\{C_m\}}$ means the sum over all ways of dividing the system $\{1, 2,..., N\} \equiv C$ into m disjoint clusters $C_1, C_2,..., C_m = \{C_m\}$ whose union is C. For example, if the system of N particles is divided into sets, $\{C_1 = (ij), C_2 = (1),..., C_m = (1)\}$, then

$$\mathscr{T}^{(1)}_{C_1C_2\cdots C_m} = \mathscr{T}^{(1)}_{ij,1,\ldots,1} = \mathscr{T}^{(1)}_{ij} = T^{(1)}_{ij},$$

and thus $\mathscr{T}^{(1)}_{ij,1,\ldots,1}$ is simply the two-body collision operator for i and j imbedded in $(N-2)$ particles. Similarly, if $\{C_1 = (ijk), C_2 = 1,..., C_m = 1\}$, then,

$$\mathscr{T}^{(1)}_{C_1C_2\cdots C_m} = \mathscr{T}^{(1)}_{ijk,1,1,\ldots,1} = \mathscr{T}^{(1)}_{ijk}$$

which makes up the third term in (3.17). This kind of cluster expansion was used [15] before for discussions of density expansions of time-correlation functions for transport coefficients.

Therefore, when (3.17a) is substituted into the kinetic equation (2.37), it take the form,

$$\frac{\partial}{\partial t} F^{(1)}_\alpha(x_\alpha\,;t) + \frac{\mathbf{P}_\alpha}{m_\alpha}\cdot\frac{\partial}{\partial \mathbf{r}_\alpha} F^{(1)}_\alpha(x_\alpha\,;t) = -i\sum^{(C)}_{\{C_m\}} \frac{V^{-N+1}}{m!}\int d\Gamma^{(N-1)}\mathscr{T}^{(1)}_{C_1C_2\cdots C_m}$$

$$\times \prod_{\beta=1}^{N} F^{(1)}_\beta(x_\beta\,;t) \tag{3.18}$$

$$\equiv -i\sum^{(C)}_{\{C_m\}} C_{C_1C_2\cdots C_m}\left[\prod_\beta^N F^{(1)}_\beta\right].$$

Thus, the first two lower order terms in the collision integral of (3.18) are, for example,

$$C_{2,\underbrace{1,\ldots,1}_{(N-2)}} = \frac{V^{-N+1}}{(N-1)!}\int d\Gamma^{(N-1)}\mathscr{T}^{(1)}_{2\,1\cdots 1}\prod_{\beta=1}^{N}F_\beta^{(1)}(x_\beta\,;t)$$

$$= \frac{V^{-N+1}}{(N-1)!}\int d\Gamma^{(N-1)}T_{12}\prod_{\beta=1}^{N}F_\beta^{(1)}(x_\beta\,;t) \tag{3.19}$$

$$C_{3,\underbrace{1,\ldots,1}_{(N-3)}} = \frac{V^{-N+1}}{(N-2)!}\int d\Gamma^{(N-1)}\mathscr{T}^{(1)}_{3\,1\cdots 1}\prod_{\beta=1}^{N}F_\beta^{(1)}(x_\beta\,;t)$$

$$= \frac{V^{-N+1}}{(N-2)!}\int d\Gamma^{(N-1)}\mathscr{T}^{(1)}_{123}\prod_{\beta=1}^{N}F_\beta^{(1)}(x_\beta\,;t) \tag{3.20}$$

Since the permutations of the set C_1, C_2,..., C_m lead to the same transition operator for a given set, there are $(N-1)!$ of $C_{2,1,\ldots,1}$ and $(N-2)!$ of $C_{3,1,\ldots,1}$, etc. Thus we may finally write for (3.18)

$$\frac{\partial}{\partial t}F^{(1)}(x_\alpha\,;t) + \frac{\mathbf{P}_\alpha}{m_\alpha}\cdot\frac{\partial}{\partial \mathbf{r}_\alpha}F_\alpha^{(1)}(x_\alpha\,;t)$$

$$= -iV^{-N+1}\int d\Gamma^{(N-1)}\left[\sum_{j<k}^{N}T_{jk}(z) + \sum_{j<k<l}^{N}\mathscr{T}^{(1)}_{jkl}(z) + \cdots\right]\prod_{\beta=1}^{N}F_\beta^{(1)}(x_\beta\,;t). \tag{3.21}$$

The first term on the right-hand side of (3.21) represents the contribution of binary collisions. Since some of the collision integrals vanish by the identity

$$\int dx_2\cdots dx_N\,T_{ij}F(x^{(N)};t) = 0 \qquad \text{if} \quad i,j = 2,3,\ldots,N,$$

there are only $(N-1)$ equivalent nonzero contribution to the collision integral. Thus it may be written in the form,

$$-iV^{-N+1}\int d\Gamma^{(N-1)}\sum_{j<k}^{N}T_{jk}(z)\prod_{\beta=1}^{N}F_\beta^{(1)}(x_\beta\,;t)$$

$$= -in\int dx_2\,T_{12}(z)\,F_1^{(1)}(x_1\,;t)\,F_2^{(1)}(x_2\,;t) \tag{3.22}$$

where

$$n = \lim_{\substack{N\to\infty\\ V\to\infty}}\frac{N}{V}.$$

For homogeneous systems (3.22) leads to the Boltzmann collision integral as demonstrated by many authors [6, 8, 10, 15, 16]. There are $\frac{1}{2}(N-1)(N-2)$ nonzero

equivalent contributions to the three-body term, i.e., the second term on the right hand side of (3.21). The three-body contribution may be written in the form,

$$-iV^{-N+1}\int d\Gamma^{(N-1)}\sum_{j<k<l}^{N}\mathscr{T}^{(1)}_{jkl}(z)\prod_{\beta=1}^{N}F^{(1)}_{\beta}(x_\beta\,;t)$$

$$=-i\frac{n^2}{2}\int dx_2\,dx_3\,\mathscr{T}^{(1)}_{123}(z)\prod_{\beta=1}^{3}F^{(1)}_{\beta}(x_\beta\,;t). \tag{3.23}$$

Putting (3.22) and (3.23) together into (3.21), we obtain the kinetic equation in the form,

$$\frac{\partial}{\partial t}F^{(1)}_{\alpha}+\frac{\mathbf{P}_\alpha}{m_\alpha}\cdot\frac{\partial}{\partial\mathbf{r}_\alpha}F^{(1)}_{\alpha}=-i\Big[n\int dx_2\,T_{12}(z)\prod_{\beta=1}^{2}F^{(1)}_{\beta}(x;t)$$

$$+\frac{n^2}{2}\int dx_2\,dx_3\,\mathscr{T}^{(1)}_{123}(z)\prod_{\beta=1}^{3}F^{(1)}_{\beta}(x_\beta\,;t)+\cdots\Big] \tag{3.24}$$

as a generalization of the Boltzmann equation ($\alpha=1$). The dynamics of the three-body contribution is described by (3.11) and (3.12). We emphasize that $\mathscr{T}^{(1)}_{123}$ corresponds to a connected diagram for the three-body system (123), owing to the fact that the disconnected collisions (diagrams) are subtracted from $T^{(1)}_{123}$ in the definition of $\mathscr{T}^{(1)}_{123}$. Higher order density terms may be obtained from (3.18) by resorting to a similar method. It is not difficult to see that the lth term takes the form

$$\frac{n^l}{l!}\int dx_2\cdots dx_{l+1}\,\mathscr{T}^{(1)}_{12\cdots l,l+1}(z)\prod_{\beta=1}^{l+1}F^{(1)}_{\beta}(x_\beta\,;t). \tag{3.25}$$

This term corresponds to the cluster integral of $l+1$ particles in equilibrium statistical mechanics.

Now we turn to the situation where the subsystems contain s particles so that there are ν subsystems in the N-particle systems. Then the collision operator is given by

$$T_{12\cdots\nu}(z)=\mathscr{L}'_{12\cdots\nu}\Omega_{12\cdots\nu}(z). \tag{3.26}$$

Then the wave operator $\Omega_{12\cdots\nu}(z)$ may be written as

$$\Omega_{12\cdots\nu}(z)=1-\mathscr{R}_N(z)(\mathscr{L}-\mathscr{L}^{(0)})$$

$$=1-\mathscr{R}_N(z)\,\mathscr{L}'_{12\cdots\nu}, \tag{3.27}$$

in the space supported by λ-class functions. Thus we now have the classical Lippman–Schwinger equation,[1]

$$T_{12\cdots\nu}(z)=\mathscr{L}'_{12\cdots\nu}-\mathscr{L}'_{12\cdots\nu}\mathscr{R}_N(z)\,\mathscr{L}'_{12\cdots\nu} \tag{3.28a}$$

[1] Note that in (2.29) $\mathscr{L}'_{12\cdots\nu}$ may be interpreted as $\mathscr{L}'_{(N-s)}$.

which may be rewritten as

$$T_{12\cdots\nu}(z) = \mathscr{L}'_{12\cdots\nu} - \mathscr{L}'_{12\cdots\nu}\mathscr{R}_\nu^{(0)}(z)\, T_{12\cdots\nu}(z) \tag{3.28b}$$

where

$$\mathscr{R}_\nu^{(0)}(z) = (\mathscr{L}^{(0)} - z)^{-1}. \tag{3.29}$$

This is the resolvent operator for ν independent "charged" subsystems comprising the whole system. This resolvent is diagonalized by the λ-class functions. We stress that this is not a resolvent operator for N free particles (in fact, it looks like the collision operator for ν polyatomic molecules of s atoms). There are identities similar to (3.8) and (3.9) for the present collision operator $T_{12\cdots\nu}(z)$, if $\mathscr{R}_N^{(0)}$ is replaced by $\mathscr{R}_\nu^{(0)}$.

By assuming that the resolvent operator $\mathscr{R}_\nu^{(0)}(z)$ is known, the collision operator $T_{12\cdots\nu}(z)$ may be expanded in terms of connected collision operators as for $T_{12\cdots N}(z)$. The mode of expansion is quite parallel to what was done before. We devide ν subsystems instead of N particles into all possible disjoint sets. First, we define the connected collision operators similarly to (3.10), (3.11), (3.13), and (3.14), etc.:

$$\mathscr{T}_{\alpha\beta}^{(s)} = \mathscr{L}'_{\alpha\beta} - \mathscr{L}'_{\alpha\beta}\mathscr{R}_\nu^{(0)}(z)\, \mathscr{T}_{\alpha\beta}^{(s)} \tag{3.30}$$

$$\mathscr{T}_{\alpha\beta\gamma}^{(s)} = T_{\alpha\beta\gamma}^{(s)} - \mathscr{T}_{\alpha\beta}^{(s)} - \mathscr{T}_{\alpha\gamma}^{(s)} - \mathscr{T}_{\beta\gamma}^{(s)} \tag{3.31}$$

with

$$T_{\alpha\beta\gamma}^{(s)} = \mathscr{L}'_{\alpha\beta\gamma} - \mathscr{L}'_{\alpha\beta\gamma}\mathscr{R}_\nu^{(0)}(z)\, T_{\alpha\beta\gamma}^{(s)} \tag{3.32}$$

$$\mathscr{L}'_{\alpha\beta} = \sum_{\substack{j\in\alpha \\ (j<k)}}^{s}\sum_{k\in\beta} \mathscr{L}'_{jk} \tag{3.33}$$

$$\mathscr{L}'_{\alpha\beta\gamma} = \mathscr{L}'_{\alpha\beta} + \mathscr{L}'_{\beta\gamma} + \mathscr{L}'_{\alpha\gamma},$$

and $\mathscr{T}_{\alpha\beta\gamma\delta}^{(s)}$, etc. may be defined similarly as before. Then $T_{12\cdots\nu}(z)$ may be expanded in terms of $\mathscr{T}_{C_1C_2\cdots C_m}$:

$$\begin{aligned} T_{12\cdots\nu}(z) &= \sum_{\alpha<\beta}^{\nu} \mathscr{T}_{\alpha\beta}^{(s)} + \sum_{\alpha<\beta<\gamma}^{\nu} \mathscr{T}_{\alpha\beta\gamma}^{(s)} + \cdots \\ &= \sum_{\{C_m\}}^{(C)} (m!)^{-1}\, \mathscr{T}_{C_1C_2\cdots C_m}^{(s)}. \end{aligned} \tag{3.34}$$

The factor $(m!)^{-1}$ is inserted in order to compensate the overcountings due to the permutations of the indices. Here $\mathscr{T}_{\alpha\beta}^{(s)}$ are the counterpart of $T_{ij}^{(1)}$ defined by (3.10). This represents the transition due to the collision of the subsystems α and β.

Let us investigate some aspect of $\mathscr{T}_{\alpha\beta}^{(s)}$. For notational convenience we shall drop the subscripts and superscripts for the moment from the operator just mentioned. Then let us define $\mathscr{T}_{jk}$ by the equation

$$\mathscr{T}_{jk}(z) = \mathscr{L}'_{jk} - \mathscr{L}'_{jk}\mathscr{R}_\nu^{(0)}(z)\, \mathscr{T}(z). \tag{3.35}$$

Then we have

$$\mathscr{T} = \sum_{j<k}^{s} \mathscr{T}_{jk}, \qquad (j \in \alpha, k \in \beta)$$

where the sum runs over s^2 terms since there are that many interaction terms $\mathscr{L}'_{jk}$ in $\mathscr{L}'_{\alpha\beta}$. By regarding $\mathscr{T}_{jk}$ as an element of s^2 dimensional column vector, we define a column vector

$$\mathscr{T}_C \equiv \{\mathscr{T}_{12}, \ldots, \mathscr{T}_{jk}, \ldots\}$$

and also new T_{ik} operator by

$$T_{jk} = \mathscr{L}'_{jk} - \mathscr{L}'_{jk}\mathscr{R}_v^{(0)} T_{jk}. \tag{3.36}$$

Then it is possible to put the integral equation for $\mathscr{T}$ in the following form of coupled matrix integral equation,

$$\mathscr{T}_C = T_C - \mathbf{M}\mathscr{R}_v^{(0)}\mathscr{T}_C \tag{3.37}$$

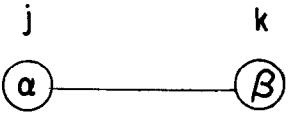
where $\mathbf{M}$ is a traceless matrix of dimension s^2 made of T_{jk},

$$\mathbf{M} = \begin{pmatrix} 0 & T_{12} & \cdots & T_{ij} & \cdots \\ T_{12} & 0 & T_{13} & \cdots & \\ \vdots & \vdots & 0 & & \\ & & & \ddots & \\ T_{ij} & & & & \ddots \\ \vdots & & & & 0 \end{pmatrix},$$

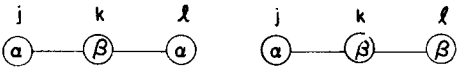
and

$$T_C = \{T_{12}, \ldots, T_{ij}, \ldots\}$$

which are an s^2-dimensional traceless matrix and column vector respectively. The operator T_{jk} defined by (3.36) describes a collision between α and β through the interaction $\mathscr{L}'_{jk}$ (or V_{jk}) of two particles $j \in \alpha$ and $k \in \beta$. Thus if we denote the collision between the subsystems by the diagram,



the second term in (3.37) corresponds to diagrams containing at least three spheres with at least two lines joining them. For example, the diagrams may look like



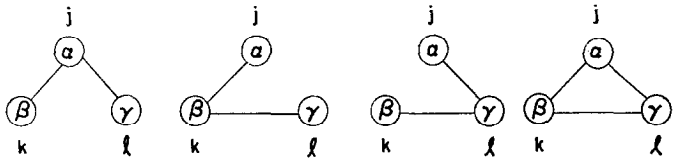
$(j \neq k \neq l)$,

which corresponds to multiple collisions between α and β. Thus we see that the approximation

$$\mathscr{T}_C \simeq T_C \tag{3.38}$$

is equivalent to a "binary collision aproximation" in the sense that there are only two particles, one each from α and β, involved during a collision between α and β. This approximation is still less severe than the one using (3.10), since the particles in each subsystem still interact.

A similar mode of discussion applies to $\mathscr{T}^{(s)}_{\alpha\beta\gamma}$. The lowest order approximation to this operator consists of three-body operators describing collisions of subsystems α, β and γ effected by 3 particles, say $j \in \alpha$, $k \in \beta$ and $l \in \gamma$. Then the diagram may be one of the following four:



Note that these diagrams do not represent simple three-body collisions, since α, β and γ are subsystems of interacting particles. We will not deal with the general theory of expansion for these collision operators here.

Therefore, if the expansion (3.34) is made use of for the collision integral in (2.36), we have

$$\begin{aligned} & i\frac{\partial}{\partial t}F_\alpha^{(s)} - \mathscr{L}_s^{(\alpha)}F_\alpha^{(s)} \\ & \quad = V^{-N+s}\int d\Gamma^{(N-s)}\left[\sum_{\alpha<\beta}^{\nu}\mathscr{T}^{(s)}_{\alpha\beta} + \sum_{\alpha<\beta<\gamma}^{\nu}\mathscr{T}^{(s)}_{\alpha\beta\gamma} + \cdots\right]\prod_{\beta=1}^{\nu}F_\beta^{(s)}(x^{(s)};t). \end{aligned} \tag{3.39}$$

The first term in the collision integral above may be written as

$$\begin{aligned} & V^{-N+s}\int d\Gamma^{(N-s)}\sum_{\beta<\gamma}^{\nu}\mathscr{T}^{(s)}_{\beta\gamma}\prod_{\beta=1}^{\nu}F_\beta^{(s)} \\ & \quad = V^{-N+s}(\nu-1)s\int d\Gamma^{(N-s)}\sum_{j=1}^{s}\mathscr{T}^{(s)}_{j,s+1}\prod_{\beta=1}^{\nu}F_\beta^{(s)} \\ & \quad = \left[\frac{N-s}{V}\right]V^{-2s+1}\int dx_{s+1}\cdots dx_{2s}\,\mathscr{T}^{(s)}_{j,s+1}F_\alpha^{(s)}F_\beta^{(s)} \end{aligned} \tag{3.40}$$

where $\mathscr{T}^{(s)}_{j,s+1}$ are defined by (3.35). The first line is due to the fact that the particle indices $s+1, s+2, \ldots, 2s$ are equivalent and so are the indices $\gamma = 1, \ldots, \nu$ and the fact that the integrals vanish if $\alpha \neq \beta$. The second line arises when integration is carried over the subsystem phases other than those of α and β. This is possible, since

the operator $\mathscr{T}_\nu^{(s)}$ contains the resolvent operator $\mathscr{R}_\nu^{(0)}(z)$ which can be expressed as a convolution of two resolvent operators, one for $\alpha + \beta$ and the other for the rest of the system:

$$\begin{aligned}\mathscr{R}_\nu^{(0)}(z) &= \mathscr{R}_{\alpha\beta}^{(0)}(z-\zeta)^* \mathscr{R}_{\nu-\alpha-\beta}^{(0)}(\zeta) \\ &= \frac{1}{2\pi i}\oint d\zeta(\mathscr{L}_\alpha + \mathscr{L}_\beta + \zeta - z)^{-1}\Big(\sum_{\gamma\neq\alpha,\beta}\mathscr{L}_\gamma - \zeta\Big)^{-1}\end{aligned}$$

where * denotes the convolution. Then, the following identity holds:

$$\begin{aligned}&\mathscr{R}_{\alpha\beta}^{(0)}(z-\zeta)^*\int d\Gamma^{(N-2s)}\mathscr{R}_{\nu-\alpha-\beta}^{(0)}(\zeta)\prod_{\gamma\neq\alpha,\beta}^{\nu}(F_\gamma^{(s)}/V^s) \\ &= \mathscr{R}_{\alpha\beta}^{(0)}(z-\zeta)^*\mathscr{R}_{\nu-\alpha-\beta}^{(0)}(-\lambda_{\nu-\alpha-\beta}+\zeta)\int d\Gamma^{(N-2s)}\prod_{\gamma\neq\alpha,\beta}^{\nu}\Big(\frac{F_\gamma^{(s)}}{V^s}\Big) \\ &= \mathscr{R}_{\alpha\beta}^{(0)}(z-\zeta)^*\mathscr{R}_{\nu-\alpha-\beta}^{(0)}(\zeta-\lambda_{\nu-\alpha-\beta}) \\ &= \mathscr{R}_{\alpha\beta}^{(0)}(z-\lambda_{\nu-\alpha-\beta})\end{aligned}$$

where $\lambda_{\nu-\alpha-\beta}$ is the eigenvalue of the operator $\sum_{\gamma\neq\alpha,\beta}\mathscr{L}_\gamma$ for the rest of the system. Consequently, the effect of the $\nu - 2$ spectator subsystems appear as a parameter $\gamma_{\nu-\alpha-\beta}$ which may be absorbed into z. This result implies that it is only necessary to replace λ in (3.35) with $\lambda - \lambda_{\nu-\alpha-\beta}$ which may be put as λ again for brevity of notation.

The collision operators $\mathscr{T}_{jk}(\lambda)$ defined by (3.35) may be approximated. For example, if the resolvent operator $\mathscr{R}_\nu^{(0)}(\lambda)$ is replaced to the lowest order approximation by the free resolvent operator $\mathscr{R}_N^{(0)}(\lambda)$, then $\mathscr{T}_{jk}(\lambda)$ simply becomes the binary collision operators and (3.40) will be, when integrated over the phases x_2 ,..., x_3 , reduced to the Boltzmann collision integral (3.22). Therefore, if such an approximation is not made on the resolvent operator, the integral (3.40) naturally leads, on integration over the phases x_2 ,..., x_s , to a collision integral, which is a generalization of the Boltzmann collision integral, since it still retains correlations within the subsystems involved. Similar arguments apply to other collision integrals in (3.39). For example, we have for three-body collision contributions

$$\begin{aligned}&V^{-N+s}\int d\Gamma^{(N-s)}\sum_{\alpha<\beta<\gamma}\mathscr{T}_{\alpha\beta\gamma}^{(s)}\prod_{\beta=1}^{\nu}F_\beta^{(s)} \\ &= \frac{\nu(\nu-1)\,s(s-1)}{2V^2}\cdot V^{-3s+2}\int dx_{s+1}\,dx_{s+2}\cdots dx_{3s}\sum_{\substack{j=1\\(j\in\alpha)}}^{s}\mathscr{T}_{j\ s+1,2s+1}\prod_{\beta=1}^{3}F_\beta^{(s)}\end{aligned} \tag{3.41}$$

where $\mathscr{T}_{j,s+1,2s+1}$ are the connected three-body collision operators with the particle indices j, $s+1$, $2s+1$ belonging respectively to subsystem α, β and γ. There is no contribution from the collision operators with two or more particle indices belonging

to a subsystem, by the definition of the collision (transition) operator $\mathscr{T}^{(s)}_{\alpha\beta\gamma}$. (Note that this is the operator connecting the three subsystems.) On substitution of (3.40) and (3.41) into (3.39), we obtain the density expansion of the collision integral of the kinetic equation (2.36). This type of density expansion will be made use of for studies of transport coefficients in the future.

When (3.40) and (3.41) are substituted into (3.39), a formal density expansion is obtained for the collision integral and the equation becomes a generalization of (3.24). It retains fully the effect of correlations between particles unlike (3.24).

IV. Some Properties of the Generalized Boltzmann Equation and the H-Theorem

Before we proceed to study transport processes, it is useful to examine some general properties of the kinetic equation proposed, (2.36).

First, we define the mass density, the total momentum, and the energy density as follows:

mass density:

$$\rho(\mathbf{r}, t) = \nu \sum_{j=1}^{s} V^{-s} \int d\Gamma^{(s)} m_j \delta(\mathbf{r}_j - \mathbf{r})\, F^{(s)}(x^{(s)}; t), \tag{4.1}$$

total momentum density:

$$\rho(\mathbf{r}, t)\, \mathbf{u}(\mathbf{r}, t) = \nu \sum_{j=1}^{s} V^{-s} \int d\Gamma^{(s)} \delta(\mathbf{r}_j - \mathbf{r})\, \mathbf{P}_j F^{(s)}(x^{(s)}; t), \tag{4.2}$$

energy density:

$$\rho(\mathbf{r}, t)\, e(\mathbf{r}, t) = \nu \sum_{j=1}^{s} V^{-s} \int d\Gamma^{(s)} \delta(\mathbf{r}_j - \mathbf{r}) \times \left[\mathbf{P}_j^2/2m_j + \frac{1}{2} \nu \sum_{j \neq k}^{s} V_{jk}(\mathbf{r}_j - \mathbf{r}_k) \right] F^{(s)}(x^{(s)}; t), \tag{4.3}$$

where ν is the number of sybsystems, and we have dropped the subscript denoting subsystems from $F^{(s)}$. Note that ν^2 appears in the potential contribution to the energy density since the additional factor ν is due to the "charging" of the interaction potentials of the subsystems. The reason for the presence of the factor ν is that we have divided the whole system into ν sybsystems which are allowed over the entire volume. Since dividing the system into subsystems and allowing them over the whole volume amount to thinning the number of degrees of freedom and thus density, it is necessary to counterbalance this thinning effect by multiplying ν to the average quantities of macroscopic variables. Note that ν becomes N if $s = 1$ in agreement with the theory of Choh and Uhlenbeck [10a].

Let us denote the collision integral in (2.36) by a more compact symbol as follows:

$$C\left[\prod_{\beta} F_{\beta}^{(s)}\right] \equiv V^{-N+s} \int d\Gamma^{(N-s)} T_{12\ldots\nu}(z) \prod_{\beta=1}^{\nu} F_{\beta}^{(s)}(x^{(s)}; t). \tag{4.4}$$

Now we consider the case of 0-class functions, i.e., the functions which satisfy the equation,

$$\mathscr{L}^{(0)} \prod_{\beta=1}^{\nu} F_{\beta}^{(s)}(x^{(s)}; t) = 0. \tag{4.5}$$

Such a function will be denoted by $F_0^{(N)} \equiv \prod_{\beta=1}^{\nu} F_{\beta 0}^{(s)}$. This condition is equivalent to the spatial homogeneity of the system in the case of Boltzmann's equation.

Since we have the relation

$$\mathscr{R}_{\nu}(z) = \mathscr{R}^{(0)}(z) - \mathscr{R}_{\nu}^{(0)}(z)\, T_{12\ldots\nu}(z)\, \mathscr{R}_{\nu}^{(0)}(z), \tag{4.6}$$

the integrand of the collision integral in (2.36) may be written as

$$T_{12\ldots\nu}(z) \prod_{\beta=1}^{\nu} F_{\beta}^{(s)}(x^{(s)}; t) = -\mathscr{R}_{\nu}^{(0)-1}[\mathscr{R}_{\nu}(z) - \mathscr{R}_{\nu}^{(0)}(z)]\, \mathscr{R}_{\nu}^{(0)-1} \prod_{\beta=1}^{\nu} F_{\beta}^{(s)}(x^{(s)}; t). \tag{4.7}$$

We would like to make a remark that the operator relation on the right hand side of (4.7) is completely equivalent to the so-called intertwining relation [18]

$$\Omega_{12\ldots\nu}\mathscr{L}^{(0)} = \mathscr{L}\Omega_{12\ldots\nu}$$

or its equivalent

$$\mathscr{L}^{(0)}\Omega_{12\ldots\nu} - \Omega_{12\ldots\nu}\mathscr{L}^{(0)} = T_{12\ldots\nu}\,.$$

If the function is in the 0-class, then we have

$$\begin{aligned} T_{12\ldots\nu}(z)\, F_0^{(N)} &= (i\epsilon)\, \mathscr{R}_{\nu}^{(0)-1}[\mathscr{R}_{\nu}(z) - \mathscr{R}_{\nu}^{(0)}(z)]\, F_0^{(N)} \\ &= i\epsilon[F_0^{(N)}(x^{(N)*}; t) - F_0^{(N)}(x^{(N)}; t)] \end{aligned} \tag{4.8}$$

where the asterisk denotes the change in phases due to the collisions between the subsystems beyond their changes owing to the "internal" interactions. The second line of (4.8) is obtained by making use of the fact that the resolvent operators are propagators [13, 14, 17, 19] in phase space which transform one phase into another, i.e.,

$$\begin{aligned} -i\epsilon\mathscr{R}(i\epsilon)\, F_0^{(N)}(x^{(N)}; t) &= F_0^{(N)}(x^{(N)*}; t) \\ -i\epsilon\mathscr{R}_{\nu}^{(0)}(i\epsilon)\, F_0^{(N)}(x^{(N)}; t) &= F_0^{(N)}(x^{(N)}; t). \end{aligned} \tag{4.9}$$

We stress here the operational meaning of the asterisk used to differentiate the change in phases due to intersubsystem interactions (collisions) and that due to intrasubsystem interactions (collisions).

With (4.8) the collision integral takes the form,

$$C\left[\prod_{\beta=1}^{\nu} F_{\beta 0}^{(s)}\right] \equiv C[F_0^{(N)}] = \frac{i\epsilon}{V^{N-s}} \int d\Gamma^{(N-s)}[F_0^{(N)}(x^{(N)*}; t) - F_0^{(N)}(x^{(N)}; t)]. \quad (4.10)$$

It is now possible to show that the integral over the phases is finite in the limit $\epsilon \to +0$,

$$\lim_{\epsilon \to +0} \epsilon \int d\Gamma^{(N-s)} \int d\Gamma^{(s)} \cdots = V \int db\, d\Omega_{3N-6}\, b^{3N-5} \left|\frac{P}{\mu}\right| \cdots \quad (4.10b)$$

where the notations for the various symbols on the right hand side of (4.10a) are defined in Appendix. We simply note that this is an N-body extension of the three-body phase integrals discussed previously by the author [18]. Here b is the N-body analog of the impact parameter and $d\Omega_{3N-6}$ the N-body analog of the solid angle in two-body collisions.

Equation (4.10a) implies that the phase volume representative of non-virtual collisions of N particles made up by ν subsystems grows linearly with respect to time on the time scale on which ϵ has a meaning.

This result can be verified for lower order collisions by using the cluster expansion discussed previously and mass-normalized coordinate systems [18] for many-particle collisions. The energy conservation law must be imposed on the collision of subsystems, since otherwise the collision may be virtual. A more systematic investigation will be made of (4.10a) especially in connection with density expansion in future. At the moment it is sufficient to know that the integral is finite.

Now, we define the entropy $S(t)$ such that

$$S(t) = -k_B \sum_{\alpha=1}^{\nu} V^{-s} \int d\Gamma_\alpha^{(s)} F_\alpha^{(s)}(x^{(s)}; t) \log F_\alpha^{(s)}(x^{(s)}; t) \quad (4.11)$$

where $\Gamma_\alpha^{(s)}$ collectively denotes the phases of subsystem α and k_B the Boltzmann constant. We regard $F_\alpha^{(s)}$ as belonging to the 0-class functions. Then by using (4.10) and the kinetic equation (2.36), we obtain the following inequality:

$$\begin{aligned}
\frac{dS}{dt} &= -\frac{k_B}{V^s} \sum_{\alpha=1}^{\nu} \int d\Gamma_\alpha^{(s)} \log F_\alpha^{(s)} \frac{\partial F_\alpha^{(s)}}{\partial t} \\
&= i \frac{k_B}{V^s} \sum_{\alpha=1}^{\nu} \int d\Gamma_\alpha^{(s)} C\left[\prod_{\beta=1}^{\nu} F_\beta^{(s)}\right] \log F_\alpha^{(s)} \\
&= \frac{k_B \epsilon}{V^N} \int d\Gamma^{(N)} \left[\prod_{\alpha=1}^{\nu} F_\alpha^{(s)}(x^{(s)*}; t) - \prod_{\alpha=1}^{\nu} F_\alpha^{(s)}(x^{(s)}; t)\right] \log\left[\prod_{\alpha=1}^{\nu} \left(\frac{F_\alpha^{(s)}(x^{(s)*}; t)}{F_\alpha^{(s)}(x^{(s)}; t)}\right)\right] \\
&\geqslant 0. \qquad (4.12)
\end{aligned}$$

Here Eq. (4.10a) is understood for the phase integral. We have followed the well-known procedure on the original H-theorem in order to obtain (4.12). This is a generalized H-theorem for correlated macroscopic systems which can be described

by the kinetic equation (2.36), provided that the distribution function belongs to the 0-class functions. The equality holds only when

$$\prod_{\alpha=1}^{\nu} F_\alpha^{(s)}(x^{(s)*}; t) = \prod_{\alpha=1}^{\nu} F_\alpha^{(s)}(x^{(s)}; t) \tag{4.13}$$

or

$$\sum_{\alpha=1}^{\nu} \log F_\alpha^{(s)} = \text{constant in time.}$$

Equation (4.13) implies that $F_0^{(N)}$ consists of constants of motion, $H \equiv \sum_{\alpha=1}^{\nu} H_\alpha^{(s)}$, $\mathbf{P} \equiv \sum_{\alpha=1}^{\nu} \sum_{j=1}^{s} \mathbf{P}_j$, $M = \sum_{i=1}^{N} m_i$. Moreover, the unique solution to (4.13) is

$$\begin{aligned} F_0^{(N)} &\equiv \prod_{\alpha=1}^{\nu} F_{\alpha 0}^{(s)} = \exp\left[-\theta^{-1}\left(\sum_{\alpha=1}^{\nu}\sum_{j=1}^{s} \frac{|\,\mathbf{P}_j - m_j\mathbf{u}\,|^2}{2m_j} + \nu \sum_{\alpha=1}^{\nu}\sum_{j<k}^{s} V_{jk}\right)\right](QN!)^{-1} \\ &\equiv \exp[-\theta^{-1}\mathscr{H}(\mathbf{P}, \mathbf{r}; \mathbf{u})](QN!)^{-1} \end{aligned} \tag{4.14}$$

where

$$Q = \frac{V^{-N}}{N!} \int d\Gamma^{(N)} \exp\left[-\theta^{-1} \sum_{\alpha=1}^{\nu}\sum_{j=1}^{s}\left(\frac{|\,\mathbf{P}_j - m_j\mathbf{u}\,|^2}{2m_j} + \nu \sum_{k<j}^{s} V_{jk}\right)\right]. \tag{4.15}$$

Here $\theta = k_B T$, k_B being the Boltzmann constant. The solution of (4.13) follows the standard procedure in kinetic theory by making use of the definitions of the macroscopic variables ρ, $\mathbf{u}$ and the kinetic temperature [see Eq. (5.18) below for the definition of kinetic temperature]. The distribution function given above is simply the local equilibrium distribution in Gibbs' ensemble, when N and s are large. This form of distribution function arises uniquely as a consequence of the H-theorem for the kinetic equation (2.36). Within the validity of the approximation

$$H = \sum_{\alpha=1}^{\nu} H_\alpha^{(s)}$$

where $H_\alpha^{(s)}$ is the Hamiltonian of the subsystem α of s particles which is "charged," the function $\mathscr{H}(\mathbf{P}, \mathbf{r}; \mathbf{u})$ in (4.14) may be replaced by

$$\begin{aligned} H &= H(\mathbf{P}, \mathbf{r}; \mathbf{u}) \\ &= \sum_{j=1}^{N} \frac{(\mathbf{P}_j - m_j\mathbf{u})^2}{2m_j} + \sum_{j<k}^{N}\sum V_{jk}\,. \end{aligned} \tag{4.16}$$

Thus, it is consistent to define

$$Q = \frac{V^{-N}}{N!} \int d\Gamma^{(N)} \exp\left[-\theta^{-1}\left(\sum_{j=1}^{N} \frac{(\mathbf{P}_j - m_j\mathbf{u})^2}{2m_j} + \sum_{j<k}^{N}\sum V_{jk}\right)\right].$$

When (4.14) is combined with (4.16), some allowance must be made regarding the meaning of N, since if the N is rigorously meant for the total N of the system which

is isolated, then there arises a conceptual difficulty with (4.14), since the energy of the entire system is fixed at a value. Therefore, it is important to remember that since $F_0^{(N)}$ is a product of $F_{\alpha 0}^{(s)}$'s which are canonical distributions at equilibrium, it is only valid in the limit of large N and s as well as ν and if such a large system is in equilibrium with still another subsystem. A similar situation arises in Boltzmann's theory, since the total distribution function may be written as $\prod_{i=1}^{N} F_i^{(1)}$ and $F_i^{(1)}$ are exponential functions of the kinetic energy at equilibrium.

This way, the present kinetic theory is seen to put a bridge between kinetic theory of dense fluids and the equilibrium statistical mechanics of Gibbs and consequently thermodynamics of nonideal fluids. This conncetion has been lacking so far in many existing kinetic theories of dense fluids and constitutes an important result of the present kinetic theory. From this viewpoint of irreversibility one can set aside all the subtle points regarding the "derivation" of the kinetic equation (2.36) and *regard it as a conjecture that connects kintic phenomena to thermodynamics* and also enables us to develop the theory of transport processes for dense fluids.

At complete equilibrium, $\mathbf{u} = 0$. Then, we have

$$F_0^{(N)} = e^{-H\beta}/QN!, \qquad H = H(\mathbf{P}, \mathbf{r}; 0), \tag{4.17}$$

which, when used in (4.11), gives rise to the entropy formula of the system at equilibrium. It is trivial to verify this statement. We will further elaborate the discussion along this line later when solution of the kinetic equation is discussed. We now turn to other properties of the collision integral.

The collision integral $C[\prod_{\beta=1}^{\nu} F_\beta^{(s)}]$ has five right eigenfunctions at zero eigenvalue, i.e., the integral equation.

$$C\left[\prod_{\beta=1}^{\nu} F_\beta^{(s)}\right] = 0 \tag{4.18}$$

is solved by M, $\mathbf{P} = (P_x, P_y, P_z)$, and H. If we put

$$\prod_{\beta=1}^{\nu} F_\beta^{(s)} = F_0^{(N)} \psi_{R_i} \tag{4.19}$$

where

$$\psi_R \equiv \{M, P_x, P_y, P_z, H\} \equiv \{\psi_1, \psi_2, \psi_3, \psi_4, \psi_5\} \tag{4.20}$$

and $F_0^{(N)}$ is given by (4.17), then it is easy to show that (4.18) holds. We simply note that the argument for the proof goes similarly to what was used for (4.8) and (4.10) and that ψ_i are collisional invariants, which do not change due to collisions of ν subsystems.

The left eigenfunctions for zero eigenvalue of $C[\prod_\beta F_\beta^{(s)}]$ are given by

$$\psi_L = \{\psi_{LM}, \Psi_{LP}, \psi_{LH}\} \tag{4.21}$$

where

$$\psi_{LM} = \nu \sum_{j=1}^{s} m_j \delta(\mathbf{r}_j - \mathbf{r}), \tag{4.22}$$

$$\boldsymbol{\psi}_{LP} = \nu \sum_{j=1}^{s} \mathbf{P}_j \delta(\mathbf{r}_j - \mathbf{r}) \tag{4.23}$$

$$\psi_{LH} = \nu \sum_{j=1}^{s} \left[\frac{\mathbf{P}_j^2}{2m_j} + \frac{1}{2} \nu \sum_{k \neq j}^{s} V_{jk} \right] \delta(\mathbf{r}_j - \mathbf{r}). \tag{4.24}$$

We prove [20] the above statement with the example of energy density. The proofs for others proceed similarly.

By using the definition of energy density (4.3), we obtain

$$\begin{aligned}
\frac{d}{dt} E(\mathbf{r}, t) &\equiv \frac{d}{dt} \rho(\mathbf{r}, t)\, e(\mathbf{r}, t) \\
&= V^{-s} \int d\Gamma_1^{(s)} \nu \sum_{j=1}^{s} \left[\frac{\mathbf{P}_j^2}{2m_j} + \frac{1}{2} \nu \sum_{k \neq j}^{s} V_{jk} \right] \delta(\mathbf{r}_j - \mathbf{r}) \left(\frac{\partial}{\partial t} + i\mathscr{L}_s^{(1)} \right) F_1^{(s)} \\
&= - \frac{-i}{V^s} \int d\Gamma_1^{(s)} \nu \sum_{j=1}^{s} \left[\frac{\mathbf{P}_i^2}{2m_j} + \frac{1}{2} \nu \sum_{k \neq j} V_{ij} \right] \delta(\mathbf{r}_j - \mathbf{r})\, C \left[\prod_{\beta=1}^{\nu} F_\beta^{(s)} \right] \\
&= \frac{-i}{V^N} \int d\Gamma^{(N)} \prod_{\beta=1}^{\nu} F_\nu^{(s)}(x^{(s)}; t)\, T_{12\ldots\nu}^{\dagger} \nu \sum_{j=1}^{s} \left[\frac{\mathbf{P}_j^2}{2m_j} + \frac{1}{2} \nu \sum_{k \neq j}^{s} V_{jk} \right] \delta(\mathbf{r}_j - \mathbf{r}).
\end{aligned} \tag{4.25}$$

By virtue of the symmetry of $T_{12\ldots\nu}$ with respect to the interchange of subsystems and the fact that for a large s the sum of the subsystem energies is equal to the total energy of the system, we may write

$$\begin{aligned}
&T_{12\ldots\nu}^{\dagger} \nu \sum_{j=1}^{s} \left[\frac{\mathbf{P}_j^2}{2m_j} + \frac{1}{2} \nu \sum_{k \neq j}^{s} V_{jk} \right] \delta(\mathbf{r}_j - \mathbf{r}) \\
&\quad = T_{12\ldots\nu}^{\dagger} \sum_{j=1}^{N} \left[\frac{\mathbf{P}_j^2}{2m_j} + \frac{1}{2} \sum_{k \neq j}^{N\prime} V_{jk} \right] \delta(\mathbf{r}_j - \mathbf{r})
\end{aligned} \tag{4.26}$$

where $T_{12\ldots\nu}^{\dagger}$ is the adjoint of $T_{12\ldots\nu}$ and the prime on the summation sign means that the intersubsystem interactions are excluded so that the operand in (4.26) is the energy density of the entire set of subsystems separated from each other (and thus mutually independent). This interpretation is consistent with (2.8) and (2.9). Since the energy of the system must be conserved, the left hand side of (4.25) must be equal to zero [20]. Since the distribution function is positive definite, we conclude that

$$T_{12\ldots\nu}^{\dagger} \sum_{j=1}^{N} \left[\frac{\mathbf{P}_i^2}{2m_j} + \frac{1}{2} \sum_{k=j}^{N\prime} V_{jk} \right] \delta(\mathbf{r}_j - \mathbf{r}) = 0 \tag{4.27}$$

for which we have used (4.26). This means that ψ_{LH} is left eigenfunction of the collision operator in (2.36), i.e.,

$$C\left[\sum_{j=1}^{N}\left(\frac{\mathscr{P}_i^2}{2m_j}+\frac{1}{2}\sum_{k\neq j}^{N}{}' V_{jk}\right)\delta(\mathbf{r}_j-\mathbf{r})\right]=0.$$

This is the necessary condition for the energy $E(r, t)$ to conserve. It means that the total energy of the system observed at r is a collisional invariant. This must be true since from the viewpoint of an observer located at point r the total energy of the system must be the same before and after the collision of ν subsystems, the effect of which will be displacements of particles and changes in velocities of particles without changing the total energy of the system as a whole. Therefore we also see that (4.27) is the sufficient condition for

$$\frac{dE(r, t)}{dt}=0.$$

This proves that ψ_{LH} is an eigenfunction of the collision integral for zero eigenvalue. In fact, an equivalent argument can be made with (4.10) which makes it quite obvious. Similar arguments apply for other components of ψ_L. These properties will be used for deriving macroscopic equations for the system from the kinetic equation (2.36) presented above.

V. Macroscopic Equations of Change

The kinetic equation (2.36) can be used to derive macroscopic equations of change for density, momentum and energy. We first note that

$$\int d\Gamma_1^{(s)}\psi_{Li}C\left[\prod_{\beta=1}^{\nu}F_\beta^{(s)}\right]=0 \tag{5.1}$$

where $i=M, \mathbf{P}, H$ [see (4.20)–(4.24)].

By multiplying ψ_{LM} from left on (2.36) and integrating the resulting equation over $\Gamma_1^{(s)}$, we obtain the equation of continuity:

$$\frac{\partial}{\partial t}\rho(\mathbf{r}, t)=V^{-s}\int d\Gamma_1^{(s)}\nu\sum_{j=1}^{s}m_j\delta(\mathbf{r}_j-\mathbf{r})(-i)\,\mathscr{L}_s^{(1)}F_1^{(s)}(x^{(s)}; t)$$

$$+V^{-s}\int d\Gamma^{(s)}\nu\sum_{j=1}^{s}m_j\delta(\mathbf{r}_j-\mathbf{r})(-i)\,C\left[\prod_{\beta=1}^{\nu}F_\beta^{(s)}\right].$$

The second term is equal to zero by (5.1) and the first term is easily calculated:

$$\text{First term}=V^{-s}\int d\Gamma_1^{(s)}\nu\sum_{j=1}^{s}\left[\frac{\partial}{\partial\mathbf{r}_j}\cdot\mathbf{P}_j\delta(\mathbf{r}_j-\mathbf{r})\right]F_1^{(s)}(x^{(s)}; t)$$

$$=-\frac{\partial}{\partial\mathbf{r}}\cdot\rho(\mathbf{r}, t)\,\mathbf{u}(\mathbf{r}, t),$$

where the property of delta functions and the definition of momentum (4.1) have been used to obtain the second equatlity. Note that the interaction term in $\mathscr{L}_s^{(1)}$ simply integrates to zero. By combining the two equations above, we obtain the equation of continuity

$$\frac{\partial}{\partial t}\rho(\mathbf{r}, t) + \frac{\partial}{\partial \mathbf{r}} \cdot \rho(\mathbf{r}, t)\,\mathbf{u}(\mathbf{r}, t) = 0, \tag{5.2}$$

or if substantial derivative,

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{u} \cdot \frac{\partial}{\partial \mathbf{r}} \tag{5.3}$$

is used, we have

$$\frac{D\rho}{Dt} = -\rho \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{u}(\mathbf{r}, t). \tag{5.2a}$$

In order to obtain the equation of change for momentum, we multiply ψ_{LP} on (2.36) from left and integrate it over $\Gamma_1^{(s)}$. Since the collision integral contributes nothing on integration according to (5.1), we obtain

$$\frac{\partial}{\partial t}\rho(\mathbf{r}, t)\,\mathbf{u}(\mathbf{r}, t) = -iV^{-s}\int d\Gamma_1^{(s)}\psi_{LP}\mathscr{L}_1^{(s)}(x^{(s)}; t). \tag{5.3}$$

The right hand side contains kinetic and potential parts. The kinetic part may be calculated as below:

$$\begin{aligned} &-V^{-s}\int d\Gamma_1^{(s)}\psi_{LP}\sum_{j=1}^{s}\frac{\mathbf{P}_j}{m_j}\cdot\frac{\partial}{\partial \mathbf{r}_j}F_1^{(s)}(x^{(s)}; t) \\ &\quad = -\frac{\partial}{\partial \mathbf{r}}\cdot V^{-s}\int d\Gamma_1^{(s)}\nu\sum_{j-1}^{s}\frac{\mathbf{P}_j\mathbf{P}_j}{m_j}\delta(\mathbf{r}_j - \mathbf{r})\,F_1^{(s)}(x^{(s)}; t) \\ &\quad = -\frac{\partial}{\partial \mathbf{r}}\cdot\mathbf{u}\mathbf{u}\rho - \frac{\partial}{\partial \mathbf{r}}\cdot\mathscr{P}_\kappa \end{aligned} \tag{5.4}$$

where

$$\mathscr{P}_\kappa = V^{-s}\int d\Gamma_1^{(s)}\nu\sum_{j=1}^{s} m_j\left(\frac{\mathbf{P}_j}{m_j} - \mathbf{u}\right)\left(\frac{\mathbf{P}_j}{m_j} - \mathbf{u}\right)\delta(\mathbf{r}_j - \mathbf{r})\,F_1^{(s)}(x^{(s)}; t), \tag{5.5}$$

the kinetic part of stress tensor. The potential part is given by

$$\begin{aligned} &\frac{1}{2}\nu V^{-s}\int d\Gamma_1^{(s)}\psi_{LP}\sum_{j\neq k}^{s}\sum\left(\frac{\partial V_{jk}}{\partial \mathbf{r}_j}\cdot\frac{\partial}{\partial \mathbf{P}_j} + \frac{\partial V_{jk}}{\partial \mathbf{r}_k}\cdot\frac{\partial}{\partial \mathbf{P}_k}\right)F_1^{(s)}(x^{(s)}; t) \\ &\quad = -\frac{1}{2}\nu^2 V^{-s}\int d\Gamma_1^{(s)}\sum_{i=1}^{s}\sum_{j\neq k}^{s}\sum\left[\left(\frac{\partial V_{jk}}{\partial \mathbf{r}_j}\cdot\frac{\partial}{\partial \mathbf{P}_j} + \frac{\partial V_{jk}}{\partial \mathbf{r}_k}\cdot\frac{\partial}{\partial \mathbf{P}_k}\right)\mathbf{P}_i\delta(\mathbf{r}_i - \mathbf{r})\right]F_1^{(s)}(x^{(s)}; t) \\ &\quad = -\frac{1}{2}\nu^2 V^{-s}\int d\Gamma_1^{(s)}\sum_{j\neq k}^{s}\sum\frac{\partial V_{jk}}{\partial \mathbf{r}_j}\cdot 1[\delta(\mathbf{r}_j - \mathbf{r}) - \delta(\mathbf{r}_k - \mathbf{r})]\,F_1^{(s)}(x^{(s)}; t). \end{aligned} \tag{5.6}$$

Since [22]

$$\delta(\mathbf{r}_j - \mathbf{r}) - \delta(\mathbf{r}_k - \mathbf{r}) = (\mathbf{r}_j - \mathbf{r}_k) \cdot \frac{\partial}{\partial \mathbf{r}} \mathscr{D}_{jk} \delta(\mathbf{r}_k - \mathbf{r})$$

where

$$\mathscr{D}_{jk} = \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+1)!} \left[(\mathbf{r}_j - \mathbf{r}_k) \cdot \frac{\partial}{\partial \mathbf{r}}\right]^n. \tag{5.7}$$

the right-hand side of (5.6) takes the form,

$$-\frac{\partial}{\partial \mathbf{r}} \cdot \mathscr{P}_v, \tag{5.8}$$

where

$$\mathscr{P}_v = -\frac{1}{2} \nu^2 V^{-s} \int d\Gamma_1^{(s)} \sum_{j \neq k}^{s} \sum \frac{\partial V_{jk}}{\partial \mathbf{r}_j} (\mathbf{r}_j - \mathbf{r}_k)[\mathscr{D}_{jk} \delta(\mathbf{r}_k - \mathbf{r})] F_1^{(s)}(x^{(s)}; t). \tag{5.9}$$

By combining (5.4) and (5.8) with (5.3), we-obtain the hydrodynamic equation,

$$\frac{\partial}{\partial t} \rho \mathbf{u} = -\frac{\partial}{\partial \mathbf{r}} \cdot [\mathbf{u}\mathbf{u}\rho + \mathscr{P}] \tag{5.10}$$

where

$$\mathscr{P} = \mathscr{P}_\kappa + \mathscr{P}_v \tag{5.11}$$

or in the substantial derivative form,

$$\rho \frac{D\mathbf{u}}{Dt} = -\frac{\partial}{\partial \mathbf{r}} \cdot \mathscr{P}. \tag{5.11a}$$

By integrating (5.9) over particle phases j and k and making use of the symmetry with respect to particles, we may rewrite (5.9) in the form

$$\mathscr{P}_v = -\frac{1}{2} \frac{\nu^2 s(s-1)}{V^2} \int dx_1\, dx_2 \frac{\partial V_{12}}{\partial \mathbf{r}_1} \mathbf{r}_{12}[\mathscr{D}_{12} \delta(\mathbf{r}_2 - \mathbf{r})] f_{12}(x_1 x_2\,; t) \tag{5.12}$$

where

$$f_{12}(x_1 x_2\,; t) = V^{-s+2} \int dx_3 \cdots dx_s F_1^{(s)}; \qquad \mathbf{r}_{21} = \mathbf{r}_2 - \mathbf{r}_1\,. \tag{5.13}$$

Therefore, in the thermodynamic limit

$$\mathscr{P}_v = -\frac{1}{2} n^2 \int dx_1\, dx_2 \frac{\partial V_{12}}{\partial \mathbf{r}_1} \mathbf{r}_{12}[\mathscr{D}_{12} \delta(\mathbf{r}_2 - \mathbf{r})] f_{12}(x_1 x_2\,; t), \tag{5.13a}$$

since $\nu^2 s(s-1)/V^2 = N(N-\nu)/V^2 \to n^2$. We observe that this form for $\mathscr{P}_v$ leads to the familiar potential contribution [21] to the pressure if the system is at equilibrium. This definition for $\mathscr{P}_v$ is also consistent with that by Irving and Kirkwood [22].

The energy transport equation can be derived by multiplying ψ_{LH} on (2.36) and then integrating over $\Gamma_1^{(s)}$. The collision term again vanishes and we obtain

$$\frac{\partial}{\partial t} E(r, t) = -iV^{-s} \int d\Gamma_1^{(s)} \psi_{LH} \mathscr{L}_s^{(1)} F_1^{(s)}(x^{(s)}; t).$$

By using a procedure similar to those for other equations of change, we obtain the following equation:

$$\frac{\partial}{\partial t} E(r, t) + \frac{\partial}{\partial \mathbf{r}} \mathbf{u} E(r, t) = -\frac{\partial}{\partial \mathbf{r}} \cdot (\mathbf{q} + \mathbf{u} \cdot \mathscr{P}) \tag{5.14}$$

where

$$\mathbf{q} = \mathbf{q}_\kappa + \mathbf{q}_v \tag{5.15}$$

$$\mathbf{q}_\kappa = V^{-s} \int d\Gamma_1^{(s)} \nu \sum_{j=1}^{s} \frac{1}{2} m_j \left| \frac{\mathbf{P}_j}{m_j} - \mathbf{u} \right|^2 \left(\frac{\mathbf{P}_j}{m_j} - \mathbf{u} \right) \delta(\mathbf{r}_j - \mathbf{r}) F_1^{(s)}(x^{(s)}; t), \tag{5.16}$$

$$\mathbf{q}_v = V^{-s} \int d\Gamma_1^{(s)} \frac{\nu^2}{2} \sum_{j \neq k}^{s} \sum [(\mathbf{P}_k/m_k) - \mathbf{u}]$$

$$\times \left[V_{jk}(\mathbf{r}_j - \mathbf{r}) - \mathbf{r}_{jk} \frac{\partial V_{jk}}{\partial \mathbf{r}_j} \mathscr{D}_{jk} \right] \delta(\mathbf{r}_k - \mathbf{r}) F_1^{(s)}(x^{(s)}; t), \tag{5.17}$$

These definitions are also consistent with those by Irving and Kirkwood [22].

Lastly, we present the equation of change for kinetic temperature. Since the procedure is the same as for the other, we will simply give the result only.

Kinetic temperature is defined by

$$\tfrac{3}{2} n k_B T = V^{-s} \int d\Gamma_1^{(s)} \nu \sum_{j=1}^{s} \tfrac{1}{2} m_j |(\mathbf{P}_j/m_j) - \mathbf{u}|^2 \delta(\mathbf{r}_j - \mathbf{r}) F_1^{(s)}(x^{(s)}; t). \tag{5.18}$$

Then we obtain the equation of change for T

$$\frac{\partial}{\partial t} \left(\frac{3}{2} n k_B T \right) = -\frac{\partial}{\partial \mathbf{r}} \cdot \left(\frac{3}{2} n k_B T \mathbf{u} + \mathbf{q}_\kappa + \mathbf{q}_{vf} \right) - \mathscr{P} \cdot \frac{\partial \mathbf{u}}{\partial \mathbf{r}} + C_T \tag{5.19}$$

where

$$\mathbf{q}_{vf} = \frac{1}{2} \nu^2 V^{-s} \int d\Gamma_1^{(s)} \sum_{j \neq k}^{s} \sum \left(\frac{\mathbf{P}_j}{m_j} - \mathbf{u} \right) \cdot \mathbf{r}_{jk} \frac{\partial V_{jk}}{\partial \mathbf{r}_j} [\mathscr{D}_{jk} \delta(\mathbf{r}_k - \mathbf{r})] F_1^{(s)}(x^{(s)}; t) \tag{5.20}$$

$$C_T = -iV^{-s} \int d\Gamma_1^{(s)} \nu \sum_{j=1}^{s} \frac{m_j}{2} \left| \frac{\mathbf{P}_j}{m_j} - \mathbf{u} \right|^2 C \left[\prod_{\beta=1}^{\nu} F_\beta^{(s)} \right]. \tag{5.21}$$

In the substantial derivative form

$$n\frac{D}{Dt}\left(\frac{3}{2}k_BT\right) = -\mathscr{P}:\frac{\partial \mathbf{u}}{\partial \mathbf{r}} - \frac{\partial}{\partial \mathbf{r}}\cdot(\mathbf{q}_\kappa + \mathbf{q}_{vf}) + C_T. \tag{5.19a}$$

Since the kinetic energy is not conserved, the collision integral does not disappear. This is the reason for the presence of C_T in (5.19) and (5.19a).

VI. Solution of the Kinetic Equation

The kinetic equation (2.36) must be solved in order to calculate various transport coefficients for dense fluids.

The equation is highly nonlinear and is defined in a $6N$-dimensional space. Certainly, the most difficult problem resides in the transition operator $T_{12\ldots\nu}$ which is an N-particle operator whose precise structure and functional dependence on collision parameters are not known to all orders of density. In view of these difficulties and in order to gain some insights into the problem, we shall study the solution of (2.36) in the crudest approximation, leaving a more systematic and mathematically satisfying investigation to the following paper. The present study at least enables us to investigate the density dependence of some transport coefficients without being unnecessarily encumbered by the complex molecular interaction effects which a more rigorous solution method would inevitably be compelled to include. The present solution method, albeit limited, can show the density dependence of kinetic parts of transport coefficients in a rather concise manner and also demonstrate the general features of the collision integral appearing in this theory.

Since the 0-class function is shown to fulfil the H-theorem for the kinetic equation and the function at equilibrium is the canonical ensemble distribution function, we may expand the distribution function $F_1^{(s)}$ into moments around the equilibrium solution of the kinetic equation. That is,

$$F_1^{(s)}(x^{(s)};t) = F_{01}^{(s)}\left[a_0 + \mathbf{a}_1 : \sum_{j=1}^{s}[\mathbf{W}_j\mathbf{W}_j]^{(2)} + \mathbf{a}_2\cdot\sum_{j=1}^{s}\mathbf{W}_j(W_j^2 - \tfrac{5}{2}) + \cdots\right], \tag{6.1}$$

where

$$F_{01}^{(s)} = \exp\left\{-\beta\left[\sum_{j=1}^{s} m_j\left(\frac{\mathbf{P}_j}{m_j} - \mathbf{u}\right)^2/2 + \frac{1}{2}\nu\sum_{j\neq k}^{s}\sum V_{jk}\right]\right\} Q_1^{-1} \tag{6.2}$$

$$Q_1 = V^{-s}\int d\Gamma_1^{(s)} \exp\left\{-\beta\left[\sum_{j=1}^{s}\frac{m_j}{2}\left(\frac{\mathbf{P}_j}{m_j} - \mathbf{u}\right)^2 + \frac{1}{2}\nu\sum_{j\neq k}^{s}\sum V_{jk}\right]\right\} \tag{6.3}$$

$$\begin{aligned} \beta &= (k_BT)^{-1} \equiv \theta^{-1} \\ \mathbf{W}_j &= \left(\frac{m_j}{2\theta}\right)^{1/2}\left(\frac{\mathbf{P}_j}{m_j} - \mathbf{u}\right) \end{aligned} \tag{6.4}$$

and a_i are constants which can be determined by the procedure in the moment method [23, 24]. They are

$$a_0 = 1$$

$$\mathbf{a}_1 = \frac{1}{n\theta}\mathring{\mathscr{P}}_\kappa \equiv \mathring{\mathbf{\Pi}}_\kappa \equiv [\mathscr{P}_\kappa]^{(2)}$$

$$\mathbf{a}_2 = \frac{8}{5}\left(\frac{m}{2\theta}\right)^{3/2}\rho^{-1}\mathbf{q}_\kappa \equiv \mathscr{Q}_\kappa, \qquad (\rho = nm,\ m = m_i).$$

Therefore, the distribution function to thirteen moments is

$$F_1^{(s)} = F_{01}^{(s)}\left(1 + \mathring{\mathbf{\Pi}}_\kappa : \sum_{j=1}^{s}[\mathbf{W}_j\mathbf{W}_j]^{(2)} + \mathscr{Q}_\kappa \cdot \sum_{j=1}^{s}\mathbf{W}_j(W_j^2 - \tfrac{5}{2})\right). \tag{6.5}$$

This mode of expansion does not include the potential contributions, the neglect of which would limit us to calculations of kinetic contributions to various transport coefficients. When $F_\alpha^{(s)}$'s are multiplied out for all α, the distribution function for the whole system is given in the form,

$$F^{(N)} = F_0^{(N)}\left(1 + \mathring{\mathbf{\Pi}}_\kappa : \sum_{j=1}^{N}[\mathbf{W}_j\mathbf{W}_j]^{(2)} + \mathscr{Q}_\kappa \cdot \sum_{j=1}^{N}\mathbf{W}_j(W_j^2 - \tfrac{5}{2}) + \cdots\right). \tag{6.6}$$

The equations of change for $\mathring{\mathscr{P}}_\kappa$ and $\mathbf{q}_\kappa$ can be obtained by the standard procedure in the moment method. We only present the results below:

$$\frac{\partial}{\partial t}\mathring{\mathscr{P}}_\kappa + \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{u}\mathring{\mathscr{P}}_\kappa + \frac{4}{5}\left[\frac{\partial}{\partial \mathbf{r}}\mathbf{q}_\kappa\right]^{(2)} + 2\left[\mathring{\mathscr{P}}_\kappa \cdot \frac{\partial \mathbf{u}}{\partial \mathbf{r}}\right]^{(2)} + 2n\theta\left[\frac{\partial \mathbf{u}}{\partial \mathbf{r}}\right]^{(2)} = C_t[\mathring{\mathscr{P}}_\kappa] \tag{6.7}$$

and

$$\frac{\partial}{\partial t}\mathbf{q}_\kappa + \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{u}\mathbf{q}_\kappa + \left(\frac{D\mathbf{u}}{Dt}\right)_\kappa \cdot \left(\mathring{\mathscr{P}}_\kappa + \frac{5}{2}n\theta\mathscr{U}\right) + \mathbf{q}_\kappa \cdot \frac{\partial \mathbf{u}}{\partial \mathbf{r}}$$
$$+ \frac{\partial}{\partial \mathbf{r}} \cdot \left[\frac{5}{2}\rho\left(\frac{\theta}{m}\right)^2\mathscr{U} + \frac{7}{2m}\theta\mathring{\mathscr{P}}_\kappa\right] + \left(\frac{\widetilde{\partial \mathbf{u}}}{\partial \mathbf{r}}\right) : \left(\frac{2}{3}\mathscr{U}\mathscr{U} + \frac{4}{5}\mathbf{T}^{(4,1)}\right)\mathbf{q}_\kappa = C_v[\mathbf{q}_\kappa], \tag{6.8}$$

where $\mathscr{U}$ is the unit second rank tensor and [10e]

$$(\mathbf{T}^{(4,1)})_{ijkl} = \tfrac{1}{2}(\delta_{il}\delta_{jk} + \delta_{ik}\delta_{jl}) - \tfrac{1}{3}\delta_{ij}\delta_{kl},$$
$$\rho\left(\frac{D\mathbf{u}}{Dt}\right)_\kappa = -\frac{\partial}{\partial \mathbf{r}} \cdot \mathscr{P}_\kappa \tag{6.9}$$

$$C_t[\mathring{\mathscr{P}}_\kappa] = -iV^{-s}\int d\Gamma_1^{(s)}\nu\sum_{j=1}^{s}\left[\left(\frac{\mathbf{P}_j}{m_j} - \mathbf{u}\right)\left(\frac{\mathbf{P}_j}{m_j} - \mathbf{u}\right)\right]^{(2)} m_j\delta(\mathbf{r}_j - \mathbf{r})' \, C\left[\prod_{\beta=1}^{\nu}F_\beta^{(s)}\right] \tag{6.10}$$

and

$$C_v[\mathbf{q}_\kappa] = -iV^{-s}\int d\Gamma_1^{(s)}\nu \sum_{j=1}^{s}\frac{1}{2}m_j\left|\frac{\mathbf{P}_j}{m_j}-\mathbf{u}\right|^2\left(\frac{\mathbf{P}_j}{m_j}-\mathbf{u}\right)\delta(\mathbf{r}_j-\mathbf{r})\,C\left[\prod_{\beta=1}^{\nu}F_\beta^{(s)}\right]. \tag{6.11}$$

These collisional contributions can be witten in terms of analogs of the Ω integrals, if the tensorial characters of the collisional contributions are taken into consideration. Since C_t must be a symmetric traceless tensor of second rank, and C_v a tensor of first rank, we see that they must be in the following forms:

$$C_t[\mathring{\mathscr{P}}_\kappa] = \omega_1^{-1}\mathscr{P}_\kappa + \omega_2^{-1}[\mathscr{Q}_\kappa\mathscr{Q}_\kappa]^{(2)} + \omega_3^{-1}[\mathring{\mathscr{P}}_\kappa\cdot\mathring{\mathscr{P}}_\kappa]^{(2)}, \tag{6.12}$$

$$C_v[\mathbf{q}_\kappa] = \omega_4^{-1}\mathbf{q}_\kappa + \omega_5^{-1}\mathscr{Q}_\kappa\cdot\mathring{\mathbf{\Pi}}_\kappa, \tag{6.13}$$

where

$$\omega_1^{-1} = \frac{2}{5n}V^{-s}\int d\Gamma_1^{(s)}\nu\sum_{j=1}^{s}[\mathbf{W}_j\mathbf{W}_j]^{(2)}\,\delta(\mathbf{r}_i-\mathbf{r})\colon C\left[F_0^{(N)}\sum_{i=1}^{N}[\mathbf{W}_i\mathbf{W}_i]^{(2)}\right] \tag{6.14}$$

$$\omega_2^{-1} = \frac{1}{5}\left(\frac{2\theta}{m}\right)V^{-s}\int d\Gamma_1^{(s)}\nu\sum_{j=1}^{s}m_j[\mathbf{W}_j\mathbf{W}_j]^{(2)}\,\delta(\mathbf{r}_j-\mathbf{r})\colon C\left[F_0^{(N)}\sum_{i=1}^{N}\sum_{j=1}^{N}[\mathbf{W}_i\mathbf{W}_j]^2\right.$$
$$\left.\times(W_i^2-\tfrac{5}{2})(W_j^2-\tfrac{5}{2})\right], \tag{6.15}$$

$$\omega_3^{-1} = \frac{2}{27}\left(\frac{1}{n\theta}\right)^2 V^{-s}\int d\Gamma_1^{(s)}\nu\sum_{j=1}^{s}m_jW_j^2\delta(\mathbf{r}_j-\mathbf{r})\,C\left[F_0^{(N)}\sum_{i=1}^{N}\sum_{j=1}^{N}W_i^2W_j^2\right] \tag{6.16}$$

$$\omega_4^{-1} = \frac{8}{15\rho}\left(\frac{m}{2\theta}\right)^{3/2}V^{-s}\int d\Gamma_1^{(s)}\nu\sum_{j=1}^{s}\frac{1}{2}m_j\left|\frac{\mathbf{P}_j}{m_j}-\mathbf{u}\right|^2\left(\frac{\mathbf{P}_j}{m_j}-\mathbf{u}\right)\delta(\mathbf{r}_j-\mathbf{r})$$
$$\times\,C\left[F_0^{(N)}\sum_{i=1}^{N}\mathbf{W}_i(W_i^2-\tfrac{5}{2})\right] \tag{6.17}$$

and

$$\omega_5^{-1} = \frac{1}{5}V^{-s}\int d\Gamma_1^{(s)}\nu\sum_{j=1}^{s}\frac{1}{2}m_j\left|\frac{\mathbf{P}_j}{m_j}-\mathbf{u}\right|^2\left(\frac{\mathbf{P}_j}{m_j}-u\right)\delta(\mathbf{r}_j-\mathbf{r})$$
$$\times\,C\left[F_0^{(N)}\sum_{i=j}^{N}\sum_{j=1}^{N}\mathbf{W}_i:[\mathbf{W}_j\mathbf{W}_j]^{(2)}(W_i^2-\tfrac{5}{2})\right] \tag{6.18}$$

with $C[F_0^{(N)}X]$ denoting (4.4) with $\prod_\beta F_\beta^{(s)}$ replaced by $F_0^{(N)}X$ and multiplied by $-i$.

The equations of change (6.7) and (6.8) may be solved approximately by expanding $\mathring{\mathscr{P}}_\kappa$ and $\mathbf{q}_\kappa$ into series of uniformity parameter after multiplication of the parameter to all the derivatives in the equations. Then to the lowest order in uniformity parameter the solutions are as follows:

$$\mathring{\mathscr{P}}_\kappa^{(1)} = 2n\theta\omega_1\left[\frac{\partial\mathbf{u}}{\partial\mathbf{r}}\right]^{(2)} \tag{6.19}$$

and

$$\mathbf{q}_\kappa^{(1)} = \frac{5n\theta^2}{2mk_B}\omega_4 \frac{\partial T}{\partial \mathbf{r}}. \tag{6.20}$$

Therefore, by comparing these equations (6.19) and (6.20) with phenomenological constitutive equations

$$\mathring{\mathscr{P}}_\kappa = -2\eta_\kappa \left[\frac{\partial \mathbf{u}}{\partial \mathbf{r}}\right]^{(2)}$$

and

$$\mathbf{q}_\kappa = -\lambda_\kappa \frac{\partial T}{\partial \mathbf{r}},$$

we obtain the kinetic parts of viscosity and thermal conductivity coefficients:

$$\eta_\kappa = -nk_BT\omega_1 = 5k_BTI(\mathscr{T}:\mathscr{T})^{-1} \tag{6.21}$$

and

$$\lambda_\kappa = -\frac{5}{2}\frac{nk_B^2T}{m}\omega_4 = \frac{75}{8}k_B^2TI(v\cdot v)^{-1} \tag{6.22}$$

where

$$I(\mathscr{T}:\mathscr{T}) = \frac{-2}{n^2V}\int d\Gamma^{(s)}\nu \sum_{j=1}^{N} [\mathbf{W}_j\mathbf{W}_j]^{(2)}\,\delta(\mathbf{r}_j - \mathbf{r}): C\left[F_0^{(N)}\sum_{i=1}^{N}[\mathbf{W}_i\mathbf{W}_i]^{(2)}\right] \tag{6.23}$$

and

$$I(v\cdot v) = \frac{-2}{n^2V^s}\int d\Gamma^{(s)}\nu \sum_{j=1}^{s}\frac{1}{2}m_jW_j^2\mathbf{W}_j\delta(\mathbf{r}_j - \mathbf{r})\cdot C\left[F_0^{(N)}\sum_{i=1}^{N}\mathbf{W}_i\left(W_i^2 - \frac{5}{2}\right)\right]. \tag{6.24}$$

Here we emphasize that (6.23) and (6.24) are not two-body integrals, since $C(x)$ is a many-body collision operator. Since the N-body collision integral is density-dependent in general, the transport coefficients are now density-dependent. Therefore, we see that (6.21) and (6.22) can go beyond the Chapman–Enskog results. In fact, if the binary collision approximation is made to the collision integral $C[x]$, (6.21) and (6.22) lead to the Chapman–Enskog first approximation [25]. Therefore, it is reasonable to state that (6.21) and (6.22) are dense gas generalizations of the Chapman–Enskog results. We will further discuss this aspect of (6.21) and (6.22) below.

The integrals (6.23) and (6.24) may be written in the form

$$I(a\odot a) = \frac{2}{n^2}\sum_{j=1}^{N} V^{-s}\int d\Gamma_1^{(s)}a_j \odot C\left[F_0^{(N)}\sum_{i=1}^{N}a_i\right]$$

$$\equiv \frac{2}{n^2}\sum_{j=1}^{N} I_j \tag{6.25}$$

for which we have made use of particle and subsystem symmetry properties of $C[\cdots]$. Then by making use of (3.40) and (3.41), we may write I_j in the form,

$$I_j = \frac{in}{V^{2s}} \int dx_1 \cdots dx_{2s}\, a_j \odot \mathscr{T}_{j,s+1} F_0^{(2s)} \sum_{i=1}^{2s} a_i$$

$$+ i \frac{n^2}{V^{3s}} \int dx_1 \cdots dx_{3s}\, a_j \odot \mathscr{T}_{j,s+1,2s+1} F_0^{(3s)} \sum_{i=1}^{3s} a_i + \cdots$$

$$= \frac{n}{V} I_p^{(2)} + \frac{n^2}{V} I_p^{(3)} + \cdots, \qquad (p = \eta, \lambda). \tag{6.26}$$

Since the particles are equivalent, we obtain

$$I(a \odot a) = (I_p^{(2)} + n I_p^{(3)} + \cdots) \tag{6.27}$$

where

$$I_p^{(2)} = \frac{i}{V^{2s-1}} \int dx_1 \cdots dx_{2s}\, a_1 \odot \mathscr{T}_{1,s+1} \left[F_0^{(2s)} \sum_{i=1}^{2s} a_i \right] \tag{6.28}$$

and

$$I_p^{(3)} = \frac{i}{V^{3s-1}} \int dx_1 \cdots dx_{3s}\, a_1 \odot \mathscr{T}_{1,s+1,2s+1} \left[F_0^{(3s)} \sum_{i=1}^{3s} a_i \right], \tag{6.29}$$

etc.

Therefore, we finally have for the kinetic parts of shear viscosity and heat conductivity,

$$\eta_\kappa = \frac{5 k_B T}{I_\eta^{(2)}} [1 + n(I_\eta^{(3)}/I_\eta^{(2)}) + \cdots]^{-1} \tag{6.30}$$

and

$$\lambda_\kappa = \frac{75}{8} k_B{}^2 T (I_\lambda^{(2)})^{-1} [1 + n(I_\lambda^{(3)}/I_\lambda^{(2)}) + \cdots]^{-1}, \tag{6.31}$$

The structures of these results are faintly reminiscent of the kinetic parts of transport coefficients in the Enskog theory of dense gases [10e]. The density corrections are due to higher order collisions. For example, $I_\eta^{(3)}$ and $I_\lambda^{(3)}$ represent three-body collisions. These terms make a correction linear in density.

VII. Summary and Discussion

In this paper we have presented a kinetic equation for dense fluids for which there exists an H-function the time derivative of which is negative semidefinite. The equilibrium solution to the kinetic equation is shown to be canonical and this solution is unique. We have derived various conservation equations from the kinetic equation. It is also solved in a moment method by which the kinetic parts of viscosity and heat

conductivity are calculated. The transport coefficients obtained are formally shown to have density expansions in which the leading terms are the Chapman–Enskog results for the transport coefficients. The first order density correction terms are made of three-body collision integrals. We have not attempted their numerical evaluations here.

The kinetic equation presented in this paper is reminiscent of the Boltzmann equation in many respects. The basis of "derivation" of the kinetic equation is the viewpoint that the Boltzmann equation for singlet distribution functions is simply an element—in fact the lowest order element—of an invariant subset of equations whose structures stay invariant as the number of particles is increased in the *apparently identical subsystems* comprising the whole system of a macroscopic size. The subsystems are viewed sufficiently large in the thermodynamic limit so that the macroscopic Hamiltonian for an interacting system is approximately the sum of the subsystem Hamiltonians. Therefore, the kinetic equation (2.36) includes the original Boltzmann equation as a special case, i.e., the low density limit, if the subsystems contain one particle each and when the collision operator $T_{12\ldots N}$ is approximated by two-body collision operators in the low density limit. If three-body terms are retained, the kinetic equation resembles the kinetic equation proposed by Hollinger and Curtiss [13]. In fact, if the N-body collision operator $T_{12\ldots N}$ is expanded in the cluster expansion [15], then the resulting equation may be looked upon as the generalization of the Hollinger–Curtiss equation to an arbitrary order in density. However, these equations do not give rise to correlation effects and consequently are not very useful for dense fluid studies. The correlation effects are fully retained if the number of particles in subsystems is sufficiently large in Eq. (2.36).

However special a type of equation it may seem, the kinetic equation certainly gives us a way to make a connection between the kinetic theory initiated by Boltzmann and the Gibbsian equilibrium statistical mechanics (thermodynamics) for dense fluids. In this sense there seems to be a great deal to hope for with the kinetic equation presented. The Chapman–Enskog type solution method is applied and transport coefficients are formally obtained in the following paper. They are formally in agreement with the transport coefficients obtained by linear response theory for thermal phenomena except for the collision operator replacing the Liouville operator in the evolution operator $\exp(-it\mathscr{L})$ in the correlation functions. Note, however, that the two operators are intimately related to each other.

Before we close this paper, there are a few remarks to make. Firstly, our assumption on the existence of the collision operator $T_{12\ldots\nu}(z)$ may appear a little far-fetched at first glance, but we note that such an assumption is not without a precedent in many-body problems. For example, in linear response theory it is common to assume that the many-body evolution operator $\exp(-it\mathscr{L})$ has mathematical meanings, being defined in an appropriate space over a sufficiently long time duration. It has also the resolvent operator $(\mathscr{L} - i\epsilon)^{-1}$, $\epsilon > 0$, which is assumed to satisfy[28] the Lippmann–Schwinger equation. This assumption is not basically different from the assumption on the existence of the collision operator. Therefore, the assumption is not a radical departure from the common practice in modern statistical mechanics. Secondly, we

note that there are some studies available in the literature regarding the H-theorem for moderately dense gases [29] and correlated systems [30], based on either the *BBGKY* hierarchy [29] or the generalized master equation obtained from the Liouville equation by projection [30]. The kinetic equation used here in the present study is entirely different from those in the references cited. Lastly, in the proof presented for the H-theorem Eq. (4.13) has arisen as the equilibrium condition which leads to the canonical distribution function. This condition can be obtained also somewhat differently from the viewpoint of collisional invariants. Physically, the collision operator $T_{12\ldots\nu}(z)$ describes the rate of change in the quantity on which it operates. Since at equilibrium the left-hand side of the kinetic equation (2.36) must be equal to zero, we have

$$T_{12\ldots\nu}(z) \prod_{\beta=1}^{\nu} F_\beta^{(s)} = 0,$$

that is, the operand is a collisional invariant at equilibrium. This implies Eq. (4.13) quite naturally. It also means that $\prod_{\beta=1}^{\nu} F_\beta^{(s)}$ must be an (exponential) function of the basic collisional invariants such as the energy, momentum, and mass.

APPENDIX

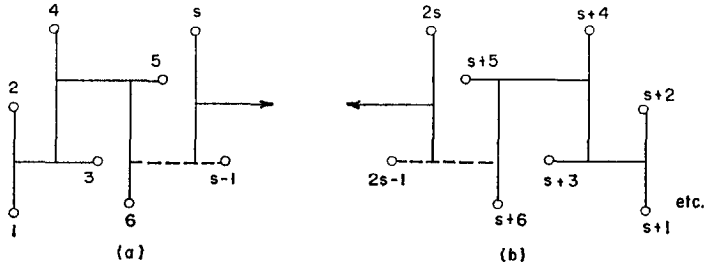
In this Appendix we show (4.10a). The problem is to express the phase volume

$$d\Gamma^{(N)} = d\Gamma^{(s)}\, d\Gamma^{(N-s)} \tag{A.1}$$

in such a way that it exhibits as clearly as possible the collision of the N-particle system and also it reduces to simpler known forms when the N-body scattering is approximated by two-, three-body scattering, etc.

Since the whole system is divided into ν s-particle subsystems, the particles are numbered consecutively as $1, 2, \ldots, s$; $s+1, \ldots, 2s; \ldots; (\nu-1)s+1, \ldots, \nu s$. Let us denote the coordinates of particles in an arbitrary frame by $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$.

Then it is convenient to introduce new coordinates such that it is possible to discuss collisions in the most economic way. For this purpose it is useful to construct the "mobile" diagram proposed by Jepsen and Hirschfelder [31] as follows:



Corresponding to these "mobile" diagrams are the new coordinates defined by

$$Q_k = \left(\frac{m_{k+1}M_k}{M_{k+1}}\right)^{1/2}(\mathbf{r}_{k+1} - \mathbf{r}_{ck})$$

$$= \left(\frac{m_{k+1}}{M_k M_{k+1}}\right)^{1/2} \sum_{j=1}^{k} m_j(\mathbf{r}_{k+1} - \mathbf{r}_j) \tag{A.2}$$

where

$$M_k = \sum_{j=1}^{k} m_j$$

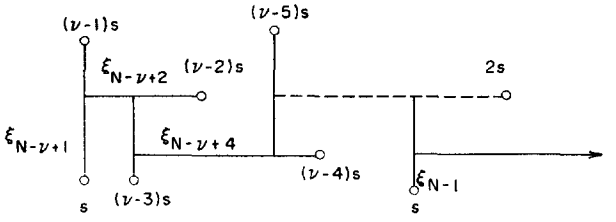
and

$$\mathbf{r}_{ck} = M_k^{-1} \sum_{j=1}^{k} m_j \mathbf{r}_j ,$$

and k denotes the indices, $1, 2, \ldots, s-1, s+1, \ldots, 2s-1$, etc. Therefore, the center of mass coordinates of the subsystems are given by

$$Q_s = M_s^{-1/2} \sum_{j=1}^{k} m_j \mathbf{r}_j \text{ , etc.} \tag{A.3}$$

Then, we construct a "mobile" diagram with Q_s , Q_{2s} ,..., Q_{vs} as follows:



where the line $\xi_{N-\nu+1}$ means the relative distance between the center of mass of the $(\nu - 4)$th subsystem and the center of mass of the previous four subsystems combined together. These relative distances are defined by

$$\xi_{N-\nu+k} = \left(\frac{M_{\nu-k}}{\bar{\mu}_k \bar{\mu}_{k+1}}\right)^{1/2} \sum_{j=1}^{k} M_{\nu-j+1}(Q_{(\nu-k)s} - Q_{(\nu-j)s}) \tag{A.4}$$

and

$$\xi_N = \bar{\mu}_\nu^{-1/2} \sum_{j=1}^{\nu} M_{\nu-j+1} Q_{(\nu-j)s} \tag{A.5}$$

where

$$\bar{\mu}_k = \sum_{j=1}^{k} M_{\nu-k} .$$

Therefore, ξ_N is the center of mass coordinate of the system as a whole and ξ_{N-1} pertains to the relative distance between the centers of mass of the subsystem 1 and the rest of the system.

Now we rearrange coordinate indices and define coordinate ξ_i for the rest of degrees of freedom as follows:

$$\begin{aligned}
&\{Q_{(\nu-1)s+1}, \ldots, Q_{s\nu-1}\} \Rightarrow \{\xi_1, \ldots, \xi_{s-1}\} \\
&\{Q_{(\nu-2)s+1}, \ldots, Q_{(\nu-1)s-1)}\} \Rightarrow \{\xi_s, \ldots, \xi_{2s-2}\} \\
&\qquad\vdots \\
&\{Q_1, \ldots, Q_{s-1}\} \Rightarrow \{\xi_{N-\nu-s+1}, \ldots, \xi_{N-\nu}\},
\end{aligned} \tag{A.6}$$

so that we finally have a set of $N\xi$ vectors.

It was shown by Jepsen and Hirschfelder [31] that the kinetic energy is diagonal in this coordinate system, i.e.,

$$T = \sum_{i=1}^{N} \frac{1}{2} \dot{\xi}_i^2 \equiv \frac{1}{2\mu} \sum_{i=1}^{N-1} P_i^2 + \frac{1}{2M} \dot{\xi}_N^2,$$

where

$$P_i = \dot{\xi}_i \mu$$

Therefore, it is possible to regard the momentum in the center of mass coordinate system in which $\dot{\xi}_N = 0$, as $(3N - 3)$ dimensional column vector in $(3N - 3)$ dimensional orthogonal space.

With the coordinate system thus defined as above, we can express the phase volume in a manner analogous to the phase volume in a two-body problem. For this purpose, we introduce the following hyperpolar coordinates [32]:

$$\begin{aligned}
\xi_{3N-3} &= \rho \cos \theta_{3N-4} \\
\xi_{3N-4} &= \rho \sin \theta_{3N-4} \cos \theta_{3N-5} \\
\xi_{3N-5} &= \rho \sin \theta_{3N-4} \sin \theta_{3N-5} \cos \theta_{3N-6} \\
&\vdots \\
\xi_2 &= \rho \prod_{i=1}^{3N-5} (\sin \theta_{3N-3-i}) \cos \theta_1 \\
\xi_1 &= \rho \prod_{i=1}^{3N-4} \sin \theta_{3N-3-i}
\end{aligned} \tag{A.7}$$

where

$$\rho^2 = \sum_{i=1}^{3N-3} \xi_i^2 \tag{A.8}$$

and θ_j are the hyperpolar angles,

$$0 \leqslant \theta_j \leqslant \pi, \qquad (j = 2,..., 3N - 4)$$
$$0 \leqslant \theta_1 \leqslant 2\pi.$$

In fact, ρ^2 is the $(N - 1)$ particle analog of the moment of inertia.

It is useful to define the generalized impact parameter b by

$$b = \left(\sum_{i=1}^{3N-4} \xi_i^2 \right)^{1/2} = \rho \sin \theta_{3N-4} . \tag{A.9}$$

It is instructive to note that if we define generalized angular momentum [33] $\mathbf{\Lambda}$ by

$$\Lambda_{ij} = \xi_i P_j - P_i \xi_j , \qquad (i, j = 1, 2,..., 3N - 3) \tag{A.10}$$

then the kinetic energy may be written as

$$T = \frac{1}{2\mu} P_\rho^2 + \frac{\Lambda^2}{2\mu\rho^2} \tag{A.11}$$

where Λ is the absolute value of the generalized angular momentum and P_ρ the "radial momentum" conjugate to ρ. The kinetic energy as given by (A.11) is completely isomorphic to the kinetic energy for two-body problems.

Then the phase volume in the hyperpolar coordinate system can be written as

$$d\Gamma^{(N)} = d\Gamma^{(C)} \rho^{3N-4} \prod_{i=2}^{3N-4} (\sin \theta_i)^{i-1} \, d\rho \, d\theta_1 \cdots d\theta_{3N-4} \, d\mathbf{P}^{(N-1)} \tag{A.12}$$

where

$$d\mathbf{P}^{(N-1)} = d\mathbf{P}_1 \, d\mathbf{P}_2 \cdots d\mathbf{P}_{N-1} .$$

It is possible to put $d\Gamma^{(C)} = 1$ in the center of mass coordinate system.

If we make use of the hypercylindrical coordinate system, which is more suitable for our purpose here, we have

$$\begin{aligned} d\Gamma^{(N-1)} &= d\Gamma^{(N)} / d\Gamma^{(C)} \\ &= b^{3N-5} \prod_{i=2}^{3N-5} (\sin \theta_i)^{i-1} \, d\xi_{3N-3} \, db \, d\theta_1 \cdots d\theta_{3N-5} \, d\mathbf{P}^{(N-1)} \end{aligned} \tag{A.13}$$

where (A.7) and (A.9) are made use of.

Since we can assume that the relative vector of approach between the subsystem 1 and the rest is parallel to the ξ_{N-3} axis, it is possible to express $d\xi_{3N-3}$ in the form,

$$d\xi_{3N-3} = | P | \mu^{-1} \, dt = | P | \mu^{-1} \tau^{-1} = | P | \mu^{-1} \epsilon^{-1} \tag{A.14}$$

if the time is sufficiently large so that the collision is finished between the subsystem 1

and the rest of the system, where τ is the collision time. Then we obtain in the limit $\epsilon \to +0$

$$\epsilon \int d\Gamma^{(s)}\, d\Gamma^{(N-s)}/d\Gamma^{(C)} = \int db\, d\Omega_{3N-6}\, b^{3N-5} \mid P \mid \mu^{-1} \cdots \tag{A.15}$$

where

$$d\Omega_{3N-6} = \prod_{i=2}^{3N-5} (\sin \theta_i)^{-1}\, d\theta_1 \cdots d\theta_{3N-5}\,. \tag{A.16}$$

This is the result used in (4.10a) and an extension of the result obtained for the three-body problems previously by the author [18].

ACKNOWLEDGMENTS

The author would like to thank Professor Jonn Ross and Professor Irwin Oppenheim for helpful discussions and useful comments on this work.

REFERENCES

1. J. W. GIBBS, "The Collected Works of J. W. Gibbs." Vol. II. "Elementary Principles in Statistical Mechanics," Longmans, Green, New York, 1928. See also, for example, R. C. TOLMAN, "Principles of Statistical Mechanics," Oxford Univ. Press, London, 1938.
2. L. BOLTZMANN, *Sitzungsber. Oesterr. Akad. Wiss.* **66**, No. 2 (1872), 275; "Lectures on Gas Theory" (S. G. Brush Trans.), Univ. of California Press, Berkeley, 1964.
3. S. CHAPMAN AND T. G. COWLING, "The Mathematical Theory of Nonuniform Gases," Cambridge Univ. Press, London, 1939.
4. See also, S. R. DE GROOT AND P. MAZUR, "Non-Equilibrium Thermodynamics," North-Holland, Amsterdam, 1962.
5. J. E. MAYER, *J. Chem. Phys.* **5** (1937), 67; J. E. MAYER AND S. F. HARRISON, *J. Chem. Phys.* **6** (1938), 87, 101; J. E. MAYER AND M. G. MAYER, "Statistical Mechanics," Wiley, New York, 1940.
6. N. N. BOGOLIUBOV, *J. Phys. (U.S.S.R.)* **10** (1946), 256, 265; N. N. BOGOLIUBOV, Problems of a Dynamical Theory in Statistical Physics, *in* "Studies in Statistical Mechanics" (J. de Boer and G. E. Uhlenbeck, Eds.), Vol. I, North-Holland, Amsterdam, 1962.
7. (a) M. BORN AND H. S. GREEN, *Proc. Royal Soc., Ser. A* **188** (1946), 10; (b) H. S. GREEN, *Proc. Royal Soc., Ser. A* **189** (1947), 103; (c) M. BORN AND H. S. GREEN, "A General Kinetic Theory of Fluids," Cambridge Univ. Press, London, 1949; (d) H. S. GREEN, "Molecular Theory of Fluids," Dover, New York, 1969.
8. J. G. KIRKWOOD, *J. Chem. Phys.* **14** (1946), 180; **14** (1946), 347.
9. J. YVON, "La Théorie Statistique des Fluids et l'Équation d'État," Herman et Cie, Paris, 1935.
10. For example, see: (a) S. T. CHOH, "The Kinetic Theory of Phenomena in Dense Gases," Ph.D. Thesis University of Michigan, Ph.D. Thesis, 1958; (b) "Lectures in Theoretical Physics" (W. E. Brittin, Ed.), Vol. 9c, Gordon and Breach, New York, 1967; (c) E. G. D. COHEN, "Fundamental Problems in Statistical Mechanics," Vol. 1, North-Holland, Amsterdam, 1962; (d) S. G. BRUSH, "Kinetic Theory," Pergamon, New York, 1966; (e) J. H. FERZIGER AND H. G. KAPER, "Mathematical Theory of Transport Processes in Gases," North-Holland, Amsterdam, 1972 for the theory of Bogoliubov.

11. See, for example, S. A. RICE AND P. GRAY, "Statistical Mechanics for Simple Liquids," Wiley–Interscience, New York, 1965, for the theory of Kirkwood.
12. (a) T. L. HILL, "Statistical Mechanics," Chap. 2, Sec. 13, McGraw–Hill, New York, 1956; (b) L. D. LANDAU AND E. M. LIFSCHITZ, "Statistical Physics," Addison–Wesley, Reading, Mass., 1958.
13. H. B. HOLLINGER AND C. F. CURTISS, *J. Chem. Phys.* **33** (1960), 1386.
14. (a) J. R. N. MILES AND J. S. DAHLER, *J. Chem. Phys.* **52** (1970), 616; (b) B. C. EU, *J. Chem. Phys.* **54** (1971), 559.
15. B. C. EU, *J. Chem. Phys.* **55** (1971), 4613.
16. B. C. EU, *J. Chem. Phys.* **54** (1971), 4246.
17. J. ROSS AND J. G. KIRKWOOD, *J. Chem. Phys.* **22** (1954), 1094.
18. B. C. EU, *Physica* **88A** (1977), 158.
19. F. ANDREWS, *Bull. Cl. Sci. Acad. Roy. Belg.* **46** (1960), 475.
20. See, L. S. GARCIA-COLIN, M. S. GREEN AND F. CHAOS, *Physica* **32** (1966), 450.
21. A. MÜNSTER, "Statistical Mechanics," Vol. I, Springer-Verlag, Heidelberg, 1956. See also Ref. 12, Chap. 6.
22. J. H. IRVING AND J. G. KIRKWOOD, *J. Chem. Phys.* **18** (1950), 817.
23. H. GRAD, *Comm. Pure Appl. Math.* **2** (1949), 311.
24. L. WALDMANN, "Handbuch der Physik" (S. Flügge, Ed.), Vol. 12, Springer-Verlag, Heidelberg, 1958.
25. That the lowest order solutions in the moment method lead to the Chapman–Enskog first approximations to transport coefficients is known through studies of some authors. See Refs. 26 and 27.
26. M. THEODOSOPULU AND J. S. DAHLER, *Phys. Fluids* **15** (1972), 1755.
27. B. C. EU AND K. W. LI, *Physica* **88A** (1977), 135.
28. For example, see (a) R. ZWANZIG, *Phys. Rev.* **129** (1963), 486; (b) U. FANO, "Lectures on the Many-body Problem" (E. R. Caianiello, Ed.), Academic, New York, 1964; (c) B. J. BERNE AND G. D. HARP, *Advan. Chem. Phys.* **17** (1970), 63.
29. YU. L. KLIMONTOVICH, *Žh. Èksp. Teor. Fiz.* **63** (1972), 150—*Sov. Phys.-JETP* **36** (1973), 78.
30. B. LEAF, *Physica* **72** (1974), 131.
31. D. W. JEPSEN AND J. O. HIRSCHFELDER, *Proc. Nat. Acad. Sci.* **45** (1959), 249.
32. A. ERDELYI, "Higher Transcendental Functions" (H. Bateman Manuscripts), Vol. 2, McGraw–Hill, New York, 1953.
33. F. T. SMITH, *Phys. Rev.* **120** (1960), 1058.