New kinetic theory for nonequilibrium dense gases by the time coarse-graining method.

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The validity of the Boltzmann equation was well verified for dilute gases experimentally. Moreover the equation has been derived by starting from the Liouville equation. However its extension to the case of dense gases is not succeeded; it is well known that difficulty of re-collision is unavoidable in successive collisions, which occur in a process of irreversible momentum-transfer in far nonequilibrium dense gases.[1,2,3] Here the limitation of the Liouville equation is examined. It will be clarified that the Liouville equation is not applicable to nonequilibrium dense gases in which successive collisions are not negligible. Lastly a new ensemble for dealing with dense gases will be proposed.

Usually kinetic theory starts from the Liouville equation; the equation is defined on ensemble average of closed systems. However physical meaning of ensemble average must be reexamined because the structure of the ensemble is not clear. The usual statistical mechanics is assumed to be based on the ergodic theorem; "a macroscopic quantity is time average of a microscopic quantity, which has a large number of degrees of freedom, over an infinite time, and through the ergodic theorem this time average can be replaced by a statistical average taken over an ensemble uniformly distributed over an energy surface" [4]. The validity of the ergodic hypothesis has been proved

by Sinai however for rather small systems of N hard spheres ($N \geq 2$). Moreover chaos has been clarified recently to appear in systems of a few degrees of freedom (though some nonlinearity has been attached). These facts imply that the ergodic hypothesis based on infinite time average might be necessary for static or steady state, but cannot possibly be sufficient for dynamical states. The concept of ensemble in the Liouville equation, which cannot be supported by infinite time average, must thus be reexamined from the first principle.

1. Ensemble average

Once if a closed system consisting of definite (but huge) number N of particles is considered then a phase space $X=(x_1,\cdot\cdot,x_N)$ is defined naturally where $x_i=(r_i,p_i)$ denotes the coordinate and momentum of the i-th particle. Initial condition of the system is supposed to be unknown due to the huge number of particles. Thus the system loses identity, so that systems X_K $(k=1,2,\cdot\cdot)$ which have the same Hamiltonian as each other constitute an ensemble on an identical phase point. The phase distribution $D_N(X,t)$ is defined on ensemble average as

$$D_N(X,t) = \sum_k \psi_k / \sum_k 1, \quad \psi_k = \delta(X-X_k), \tag{1.1}$$

where δ is the delta function and summation is taken over the whole systems at each phase point; D_N is normalized to unity in the whole phase space.

The ensemble defined at each phase point is not always mechanical like a mass-point occupying a point in physical space. For example, though two systems which are just mutually reverse are represented by an identical phase point, they do not always accompany in phase space because they do not encounter with the wall of the container at the same time. Thus the member of

ensemble at a phase point changes in time though the ensemble at each phase point includes mutually reverse systems always. In order that ensemble at each phase point may be mechanical thus two conditions must be imposed on each ensemble; ensemble must have no extent in phase space and ensemble must be reversible.

The first condition that ensemble must not have any extent in phase space is caused for ensuring the definition (1.1) with the usual continuous time; the relative angular momentum of system $\hat{M}_N^{(r)}$ must vanish on ensemble average always as

$$\hat{M}_N^{(r)} = \hat{M}_N - \hat{M}_N^{(c)} = 0, \tag{1.2}$$

where $\hat{M}_N$ and $\hat{M}_N^{(c)}$ denote the total and center-of-mass angular momentum on ensemble average respectively, which are expressible by using Ψ_k of (1.1). Of course angular momentum of each system in ensemble is not conserved in such non-conserved field as the wall of the container. However, $\hat{M}_N^{(r)}$ can be conserved on ensemble average because of existence of reverse system. We call (1.2) the embedding condition because systems can be embedded into phase space under (1.2).

The second condition is that ensemble located at a phase point must be reversible like mass-point in physical space. For a closed system as seen above there exists its just reverse system among ensemble always. Thus for any pair of two particles there exists its just reverse pair in other system always; forward and reverse pairs coexist in D_N always. Then it is easily seen that particle-interchange in a pair in D_N can be identified with an operation of time reversal in the pair. Thus D_N must be symmetric always as

$$D_N(\cdots,x_i,\cdots,x_j,\cdots) = D_N(\cdots,x_j,\cdots,x_i,\cdots). \tag{1.3}$$

From (1.3) D_N is independent of the directions of relative vectors between any two particles: $k_{ij}=r_{ij}/|r_{ij}|$ and $\varrho_{ij}=p_{ij}/|p_{ij}|$ where $r_{ij}=r_i-r_j$ and $p_{ij}=(p_i-p_j)/2$. The following hold always:

$$\partial D_N/\partial k_{ij} = 0, \quad \partial D_N/\partial \varrho_{ij} = 0. \tag{1.4}$$

Under the conditions (1.2) and (1.3) the distribution D_N can be integral of motion as $dD_N/dt=0$; the Liouville equation is written as

$$\partial D_N/\partial t = (H_N, D_N), \tag{1.5}$$

where H_N is the Hamiltonian and ( ) denote the Poisson brackets.

The symmetry (1.3) must be compatible with the embedding condition (1.2). If $\hat{M}_N^{(r)}$ of (1.2) has a form making every particle connect with each other deterministically under (1.3) then any decomposition of D_N becomes impossible; such connection among particles can be easily proved. It can be proved that symmetry of the relative angular momentum $\hat{M}_2^{(r)}$ of a pair can be sustained by symmetry of $\hat{M}_2^{(r)}$ of the other every pair; once if symmetry even in a pair is disturbed by decomposition of D_N symmetry in every pair is disturbed. Thus any decomposition of D_N is prohibited under (1.2) and (1.3) generally. It is thus concluded that D_N must remain as mechanical forever.

It is seen however from the above discussion that, if $\hat{M}_2^{(r)}$ of a pair vanishes, $\hat{M}_2^{(r)}$ of every pair must vanish, that is, decomposition of a pair causes decomposition of every pair. For gases, in which intrinsic angular momentum of molecules vanishes with spherical potential, decomposition of D_N is permitted in a limited situation that $\hat{M}_2^{(r)}$ of every pair of two particles vanish simultaneously as

$$k_{ij} \times \Omega_{ij} = 0, \quad \text{or} \quad (k_{ij} \cdot \Omega_{ij}) = \pm 1. \tag{1.6}$$

From (1.6) the Stosszahlansatz or the Dyson perturbation series [5] is caused naturally. Due to (1.6) however inlet reaction (negative sign in (1.6)) and outlet one (positive sign in (1.6)) are impossible to be distinguished.

It is seen from (1.6) that the density expansion method in the B-B-G-K-Y hierarchy equation [6,7] is effective only for the first approximation but is not assured for the higher order approximations because all the higher orders of correlation are already disturbed by the first approximation. The same fact can be said for the binary collision expansion method [7].

Owing to the restriction (1.6) k_{ij} and Ω_{ij} become parallel to each other so that time interval becomes explicit correspondingly to spatial distance between two particles though the direction of motion or time is uncertain. Then if the direction of time is made implicit by introducing a finite-time average, (1.6) can play a role of gauge in phase space so that collision between particles can be drawn as if in physical space. Under (1.6) the first collision occurs in a pair of two particles locating nearest each other in time. This situation is utterly different from the usual understanding that collisions occur in any pair of two particles at random at any time [6,7]. Therefore, frequency of collisions in time process is not related to the density of particles but related to the time interval needed for collision to occur. In order to express such collisions as stochastic process we will introduce a finite-time average over collisions in Sec. 2.

However, though binary collisions can be expressed stochastically by a method of finite-time average, causality in successive binary collisions is disturbed completely. Causality in collisions can be held only in a space where metric is explicit; even if (1.6) is introduced the metric between three particles is implicit in phase space generally. Thus we will introduce a new ensemble defined in μ-space in Sec. 3.

2. Coarse-graining of space and time

Now owing to (1.6) the Liouville equation can be mapped onto μ-space. Here the mapping of the equation is performed, and space and time coarse-graining are introduced. Since every pair of two particles has been truncated as (1.6) r_i and p_i are expressible as

$$r_i = r_i(r_{ij}^{(c)}, k_{ij}, |r_{ij}|), \quad p_i = p_i(p_{ij}^{(c)}, \Omega_{ij}, |p_{ij}|). \tag{2.1}$$

where $r_{ij}^{(c)}=(r_i+r_j)/2$ and $p_{ij}^{(c)}=p_i+p_j$. Thus $\partial D_N/\partial r_i$ and $\partial D_N/\partial p_i$ in (1.5) can be written by using (2.1) as

$$\frac{\partial D_N}{\partial r_i} = \frac{\partial r_{ij}^{(c)}}{\partial r_i}\cdot\frac{\partial D_N}{\partial r_{ij}^{(c)}} + \frac{\partial k_{ij}}{\partial r_i}\cdot\frac{\partial D_N}{\partial k_{ij}} + \frac{\partial |r_{ij}|}{\partial r_i}\cdot\frac{\partial D_N}{\partial |r_{ij}|}, \tag{2.2}$$

$$\frac{\partial D_N}{\partial p_i} = \frac{\partial p_{ij}^{(c)}}{\partial p_i}\frac{\partial D_N}{\partial p_{ij}^{(c)}} + \frac{\partial \Omega_{ij}}{\partial p_i}\frac{\partial D_N}{\partial \Omega_{ij}} + \frac{\partial |p_{ij}|}{\partial p_i}\frac{\partial D_N}{\partial |p_{ij}|}. \tag{2.3}$$

In the last terms in (2.2) and (2.3) the following hold:

$$\partial |r_{ij}|/\partial r_i = k_{ij}, \quad \partial |p_{ij}|/\partial p_i = \Omega_{ij}/2. \tag{2.4}$$

The streaming and the collision terms in (1.5) are thus written by using (1.4), (2.2), (2.3) and (2.4) as

$$\frac{p_i}{m}\cdot\frac{\partial D_N}{\partial r_i} + \frac{p_j}{m}\cdot\frac{\partial D_N}{\partial r_j} = \frac{p_{ij}^{(c)}}{M}\cdot\frac{\partial D_N}{\partial r_{ij}^{(c)}} + (k_{ij}\cdot\Omega_{ij})\frac{|p_{ij}|}{\mu}\frac{\partial D_N}{\partial |r_{ij}|}, \tag{2.5}$$

$$\Theta_{ij} = \frac{\partial \Phi_{ij}}{\partial r_i}\cdot\left(\frac{\partial D_N}{\partial p_i} - \frac{\partial D_N}{\partial p_j}\right) = (k_{ij}\cdot\Omega_{ij})\frac{\partial \Phi_{ij}}{\partial |r_{ij}|}\frac{\partial D_N}{\partial |p_{ij}|}, \tag{2.6}$$

where the interaction potential $\Phi_{ij}=\Phi(|r_{ij}|)$, $M=2m$ and $\mu=m/2$.

Now let us map the Liouville equation (1.5) onto μ-space. In μ-space extent of particles is explicit, so symmetry (1.3) is disturbed when two particles approach in the interaction range r_0, or $|r_{ij}|\leq r_0$. Therefore, mapping onto μ-space causes coarse-graining of μ-space naturally.

The distribution $F_s(y_1,\cdots,y_s,t)$ in μ-space is defined as

$$F_s= V^s\int dx_1\cdots\int dx_N \prod_{k=1}^{s}\Big[\sum_{i=1}^{N}\delta(y_k-x_i)\Big/\sum_{i=1}^{N}1\Big]D_N, \tag{2.7}$$

where $y_k=(r_k',p_k')$ denote values of the coordinate of μ-space, V the volume of the system and $\int\cdots\int dy_1\cdots dy_s F_s=V^s$. As seen from (1.6) it is not convenient to discuss the term $p_i\cdot\partial F_1/\partial r_i$ directly, therefore we treat the equation for pairs of two particles F_2. By applying (2.7) to (1.5) and by using (2.5) and (2.6) we obtain as

$$\frac{\partial F_2}{\partial t}+\frac{p_{12}^{(c)'}}{M}\cdot\frac{\partial F_2}{\partial r_{12}^{(c)'}}+(k_{12}'\cdot\Omega_{12}')\frac{|p_{12}'|}{\mu}\frac{\partial F_2}{\partial|r_{12}'|}=$$

$$=(k_{12}'\cdot\Omega_{12}')\frac{\partial\Phi_{12}}{\partial|r_{12}'|}\frac{\partial F_2}{\partial|p_{12}'|}+\frac{N-2}{V}\int dy_3[\theta_{13}'+\theta_{23}']F_3. \tag{2.8}$$

The hierarchy structure of (2.8) is unavoidable under the symmetry (1.3), which gives a picture that collisions occur in any pair of two particles at random at any time. In order that F_2 of (2.8) may be symmetric according to D_N, μ-space must be coarse-grained by particle-extent as

$$\partial F_2/\partial|r_{12}'|=0,\quad \partial F_2/\partial|p_{12}'|=0\quad \text{for } |r_{12}'|\leq r_0. \tag{2.9}$$

The former of (2.9) corresponds to the assumption of homogeneous collision in the definition of cross section and the latter means that collision occurs only on the surface of potential. Under the condition (2.9) binary collisions can be expressed by the cross section. However, even if (2.9) is applied to (2.8) the unknown factor $(k'_{12}\cdot\Omega'_{12})$ remains yet for $|r'_{12}|>r_0$ in (2.8); it is seen that coarse-graining of μ-space can be attained by making the factor $(k'_{12}\cdot\Omega'_{12})$ in (2.8) implicit.

Equation (2.8) is invariant for an operation of time reversal $t\to -t$, $p_{12}^{(c)'}\to -p_{12}^{(c)'}$ and $(k'_{12}\cdot\Omega'_{12})\to -(k'_{12}\cdot\Omega'_{12})$, whereas the sign of $(k'_{12}\cdot\Omega'_{12})$ changes from negative to positive naturally as the reaction proceeds from inlet to outlet. That is, the two events of time reversal and progress of reaction cannot be distinguished at all in (2.9). To make $(k'_{12}\cdot\Omega'_{12})$ implicit thus time average over $(k'_{12}\cdot\Omega'_{12})$ is needed. Then we introduce a finite-time average in a interval τ as

$$\langle F_2\rangle = \frac{1}{\tau}\int_0^{\tau} du F_2(y_1,y_2,t+u). \tag{2.10}$$

2.1. The Boltzmann equation

The triple collision term on the right hand side of (2.8) is usually neglected by the density expansion method. Certainly in a dilute gas where triple collisions scarcely occur the approximation is applicable; thus the Boltzmann equation is obtained, strictly speaking, by imposing an isotropy condition. However the density expansion method has no sense in the case of dense gases; however in successive binary collisions in dense gases the higher terms will be shown next to become large.

2.2. Successive binary collisions

The time-average interval τ has been set to cover only an isolated binary collision in Sec. 2.1. Here τ will be extended over the 3rd particle in

successive binary collisions in the case of dense gases; this trial cannot help being performed intuitively because the usual binary collision expansion method is not inapplicable as discussed in Sec. 1.

In coarse-grained μ-space "particles" are regarded as if a mass-point with no extent. Thus any binary collision of two particles can be regarded to occur on a two-dimensional plane by twisting the trajectories at collision suitably. Because the inlet and outlet reactions cannot be distinguished from each other under $(k'_{ij}\cdot\Omega'_{ij})=\pm 1$ the sign of p'_{ij} can be taken twofold: $p'^{*}_{ij}=-p'_{ij}$ and $p'^{*}_{ij}=p'_{ij}$ ($|p_{ij}|$ is conserved) where * denotes after collision; these are rewritten as

$$p_i'^{*} = p_j', \qquad p_j'^{*} = p_i', \tag{2.11}$$

$$p_i'^{*} = p_i', \qquad p_j'^{*} = p_j'. \tag{2.11'}$$

(2.11) gives a picture of normal head-on-collision between mass-points, while (2.11') gives a picture of grazing collision. Both the pictures of (2.11) and (2.11') appear at the same time and survive even after either of the pair has collided with third ones.

When binary collisions occur successively, every collisions can be laid on an identical two-dimensional plane by twisting trajectories as Fig. 1 because the probability of successive binary collision does not depend on its configuration as far as particles can be treated as mass-point. However, the pairs of particles (1,2) and (1,3) in Fig. 1 cannot be distinguished when they are isotropic as discussed in (2.11); Fig. 1 can be drawn only when there exists anisotropy as

$$F_3 = \psi_1\psi_2\psi_3 + \sum_{ijk}^{3} \Omega_{ij}\cdot J_{ij}\psi_k, \tag{2.12}$$

where Ψ_i denotes isotropic distribution and J_{ij} vector function independent Ω_{ij} and the summation of ijk is taken cyclic over the three particles. Thus the triple collision term in (2.8) is written as

$$\langle\int dy_2\int dy_3\sum_{ij}^{3}\theta'_{ij}F_3\rangle = \langle\int dy_2\int dy_3\sum_{ij}^{3}\frac{1}{|p_{ij}|}\frac{\partial\Phi_{ij}}{\partial r_i}\cdot\frac{\partial F_3}{\partial\Omega_{ij}}\rangle$$

$$= \langle\int dy_2\int dy_3\sum_{ijk}^{3}\frac{1}{|p_{ij}|}\frac{\partial\Phi_{ij}}{\partial r_i}\cdot J_{ij}\psi_k\rangle = \langle\int dy_2\int dy_3\sum_{ijk}^{3}\frac{\partial J_{ij}}{\partial t}|_\sigma\psi_k\rangle, \qquad (2.13)$$

where, in the second term, (2.6) with (2.3) have been used by assuming the isotropy in (1.4) has been broken and, in the third term, (2.12) has been used. In the last term of (2.13) the force term has been replaced by time derivative on the potential surfaces σ because of the definition of coarse-graining (2.9). However in the case of successive collisions the surfaces are regarded to be distributed continuously due to the integration $/dy_2/dy_3$. Thus self-collision occurs as Fig. 1; the particle 1 can arrive at (γ) in two ways of grazing collision at (α) and successive collisions at (α) and (β). Collision at (β) induces self-collision at (γ) inevitably when the momenta p'_i satisfy the relation $p'_{12}//p'_{23}$ or $p'_{12}//p'_{13}$, which constitutes two-dimensional triangle as Fig. 1. Thus occurrence of self-collision at (γ) is proportional to the frequency of collision at (β), i.e., the frequency of collision occurring between (α) and (γ), which is written as $d\Omega/\Omega$ where Ω is length of the interval (α,γ) and $d\Omega$ its element. Thus (2.13) is written as

$$(2.13) \propto \sum_{ijk}\langle\frac{\partial J_{ij}}{\partial t}\psi_k\rangle\int_{r_0}^{L}d\Omega/\Omega \cong \sum_{ijk}\langle\frac{\partial J_{ij}}{\partial t}\psi_k\rangle\ln(\frac{L}{r_0}), \qquad (2.14)$$

where $L/r_0>>1$ because $L\approx\tau|p_{ij}|/\mu$ is of order of a few mean free paths. Thus it is seen from (2.14) that successive binary collisions cannot be neglected

by the density expansion method even if asymmetry is considered approximately in the Liouville equation; successive collisions cannot be treated by the usual ensemble as far as symmetry is forced. Next an alternative ensemble will be introduced to treat asymmetry.

3. New statistical ensemble

Once if closed systems consisting of definite number of particles are considered there mingle two systems which are mutually reverse in ensemble inevitably. Thus on the distribution D_N defined as ensemble average of such closed systems the embedding condition (1.2) and the symmetry (1.3) are imposed. Due to the conditions any truncation of D_N is impossible other than in the limited case of (1.6); (1.6) is indispensable for stochastic description of binary collisions but it disturbs causality in successive binary collisions. Here we will introduce a new statistical ensemble under the following conditions: not to start from closed systems and to adopt a space in which metric between particles is kept at any time and so finite-time average is definable. Thus statistical ensemble will be defined by a method of finite-time average over an open system in μ-space.

We consider an open system $X=(x_1,\cdots,x_i,\cdots)$ whose number of particles is unknown; size of the system is taken as the order of a few mean free paths. For such system neither Hamiltonian nor phase space can be defined; open system is defined in μ-space as

$$O(y,t;X) = v\sum_i \delta(y-x_i), \tag{3.1}$$

where $v=1/\rho$ (ρ: number density of gases) and summation of i is taken over the whole (unknown number of) particles. The system of (3.1) is deterministic only in a short time interval τ during which any collisions do not occur in the system; the range of potential is assumed finite. If $O(y,t;X)$ is observed

at points $y_1,\cdots,y_n$ during the interval τ then systems with the configuration $(y_1,\cdots,y_n)$ are extracted as time series in τ. The systems observed at each time step constitute ensemble because identity of systems is lost in μ-space; thus the distribution $\langle F_n(y_1,\cdots,y_n,t)\rangle_\tau$ is defined as ensemble average, or time average in τ as

$$\langle F_n\rangle_\tau = \langle\int dy \prod_{i=1}^{n} \delta(y-y_i)O(y,t;X)\rangle_\tau. \tag{3.2}$$

The extracted ensemble must be embedded into former system, condition of which will be shown below. It is noted that there never exist any two systems which are mutually mechanically reversible among the ensemble because time average is taken over only a system along (or against) direction of time; therefore symmetry is not forced on $\langle F_n\rangle_\tau$. However, because identity of particles is lost in μ-space $\langle F_n\rangle_\tau$ is symmetric in τ or $|r'_{ij}|>r_0$ as

$$\langle F_n(\cdots,y_i,\cdots,y_j,\cdots)\rangle_\tau = \langle F_n(\cdots,y_j,\cdots,y_i,\cdots)\rangle_\tau. \tag{3.3}$$

If τ is extended over collisions the symmetry (3.3) is broken; $\partial F_n/\partial\Omega'_{ij}$ does not vanish in collisions in contrast with (1.4) or (2.6).

As seen from the definition (3.2), $\langle F_n\rangle_\tau$ does not change even if the observing time at y_i is slid in τ, so that extracted system is defined by coordinates with spatial deviation; by the definition of $\langle F_n\rangle_\tau$ spatial domains or cells are produced around each "particle" at r'_i. The cells do not overlap each other, so they are supposed to occupy identical volume v_τ ($<$ v) as

$$\int dy_1\cdots\int dy_n\langle F_n\rangle_\tau = (v_\tau)^n, \tag{3.4}$$

in which v_τ tends to v when τ is extended over collisions and the cell are fused into one.

The values $(y_1,\cdots,y_n)$ in $\langle F_n\rangle_\tau$ can be regarded to construct a virtual 6n-dimensional "phase space" because each "particle" y_i has its own spatial cell as seen above. Thus physical quantities in μ-space can be defined by spatial-average over the cells; we define cell-average α_n for a quantity $A(y_1,\cdots,y_n)$:

$$\alpha_n(A\langle F_n\rangle_\tau) = \prod_{i=1}^{n}\frac{1}{v_\tau}\int_{v_\tau} dr_i' A\langle F_n\rangle_\tau. \tag{3.5}$$

Isolated state of the extracted systems is assured by angular momentum conservation on cell-average:

$$\alpha_n(M_n'\langle F_n\rangle_\tau) = \text{constant}. \tag{3.6}$$

The conscrvation laws of center-of-mass and angular momenta are expressed by applying (3.3) to (3.6) in τ as

$$\alpha_n(M_n^{(c)'}\langle F_n\rangle_\tau) = \text{constant}, \quad \alpha_n(M_n^{(r)'}\langle F_n\rangle_\tau) = 0, \tag{3.7}$$

where the former expresses isolation of systems and the latter corresponds to the embedding condition (1.2). Since isolated state has been defined equation of motion for $\langle F_n\rangle_\tau$ can be written by putting $A\langle F_n\rangle_\tau=\langle dF_n/dt\rangle_\tau=0$ in (3.5) as

$$\alpha_n\langle\frac{\partial F_n}{\partial t}\rangle_\tau = \alpha_n\langle\{H_n',F_n\}\rangle_\tau, \tag{3.8}$$

which is the averaged Liouville equation corresponding to (1.5) (the wall potential of containers may be neglected). Extension of τ over collisions must be performed by checking the embedding condition of (3.7), and also by keeping the "Liouville theorem" in the virtual "phase space". The "Liouville

theorem" is defined as: F_n of (3.8) integrated over the whole "phase space" to be conserved at every time as

$$\left\langle \int \cdots \int \prod_{i=1}^{n} dp_i \alpha_n (\partial F_n / \partial t) \right\rangle_\tau = 0. \tag{3.9}$$

Under (3.9) the time and the cell averages become commutable, which situation corresponds to Kirkwood's definition of macroscopic quantity [9]; the length of τ can be determined self-consistently under (3.9).

4. Systems of three particles

Here we will treat a moderately dense gas far from equilibrium, in which genuine triple collisions may be neglected and successive binary collisions are sufficient to be considered. Then we will consider the case of F_3 in (3.8) and derive a kinetic equation for $\langle F_1 \rangle_1$ from the equation.

Equation (3.8) with n=3 is written as

$$\left\langle \alpha_3^{(r)} \frac{\partial F_3}{\partial t} \right\rangle_3 = \left\langle \alpha_3^{(r)} \left(- \frac{P_1}{m_1} \cdot \frac{\partial F_3}{\partial R_1} - \frac{P_2}{m_2} \cdot \frac{\partial F_3}{\partial R_2} + \Theta_{12} F_3 + \sum_{i=1}^{2} \Theta_{i3} F_3 \right) \right\rangle_3. \tag{4.1}$$

where $\langle \ \rangle_3$ denotes time average in τ_3 (τ_3: the time interval in which any collision does not occur in system of three particles) and

$$R_1 = r_1 - r_2, \quad P_1 = (p_1 - p_2)/2, \quad R_2 = R_2^{(c)} - r_3, \quad P_2 = (P_2^{(c)} - 2p_3)/3, \tag{4.2}$$

in which $R_2^{(c)} = (r_1 + r_2)/2$ and $P_2^{(c)} = p_1 + p_2$. In (4.1) variables concerning the center-of-mass of systems have disappeared due to the isolation condition (3.7); the variables can revive when the embedding condition (3.9) is fulfilled. Because genuine triple collisions may be neglected the first collision in (4.1) is written as

$$\theta_{12}F_3 = \frac{\partial U_{12}}{\partial R_1}\cdot\frac{\partial F_3}{\partial P_1} = \frac{\partial U_{12}}{\partial R_1}\cdot\left(\mathfrak{Q}_1\frac{\partial F_3}{\partial |P_1|} + \frac{1}{|P_1|}\frac{\partial F_3}{\partial \mathfrak{Q}_1}\right), \tag{4.3}$$

where $\mathfrak{Q}_1 = P_1/|P_1|$. The second and third collisions in (4.1) can be written as

$$\sum_{i=1}^{2}\theta_{i3}F_3 = \frac{1}{2}\frac{\partial(U_{13}+U_{23})}{\partial R_2}\cdot\frac{\partial F_3}{\partial P_2}. \tag{4.4}$$

In the interval τ_3 any interactions do not occur. In τ_2 binary collision of (4.3) occurs, and in τ_1 collisions with the third particle (4.4) occur. In the usual theory anisotropy $\partial F_3/\partial \mathfrak{Q}_1$ in (4.3) vanishes by the symmetry of the distribution, but in the present theory symmetry is not imposed in collision; thus momentum-transfer in collision can be expressed. For lack of symmetry however coarse-graining of μ-space or introduction of cross sections is not assured directly. This matter will be solved by introducing an average force field.

In the interval τ_1, both $\theta_{12}F_3$ and $\theta_{i3}F_3$ (i=1,2) in (4.1) appear as (4.3) and (4.4). If τ_1 is set arbitrarily long to fuse three cells into one, and if the coarse-graining (2.9) is applied to the inside of the fused cell, $\theta_{i3}F_3$ in (4.4) is expressed in the similar form as (2.9). Thus the chaotic situation

$$\langle F_3\rangle_k = \langle F_1(y_1,t)F_1(y_2,t)F_1(y_3,t)\rangle_k, \tag{4.5}$$

which holds naturally in τ_3 or k=3, is extended over every collision, so that symmetry holds everywhere in the fused cell; this situation causes difficulty of self-collision (see Sec. 2.2.). It can be thus recognized that fusion of cells must be restricted only to between two cells of the first collision and the second collisions must not be included inside the fused cell.

The coarse-graining (2.9) is applicable only to the state satisfying $\partial F_3/\partial \mathfrak{Q}_1 = 0$ (because (2.9) was able to be obtained under the symmetry of the

distribution) and moreover self-collision occurs only when P_1 is parallel or similar to P_2 as $P_1//P_2$ (see Sec. 2.2). Then we introduce an average force field for cancelling $\partial F_3/\partial \Omega_1$ and also for stopping the third particle just on the fused cell including the first collision, which is expressed in Θ_{i3} of (4.4) by applying the law of action and reaction to between the center-of-mass of the first two particles and the third particle as

$$\frac{1}{2}\frac{\partial(U_{13}+U_{23})}{\partial R_2} = \frac{\partial}{\partial t}\left(\frac{\int d\Omega_1 \int d\Omega_2 P_2 F_3}{\int d\Omega_1 \int d\Omega_2 F_3}\right), \tag{4.6}$$

where $\Omega_i = P_i/|P_i|$. The above discussion for setting (4.6) will be confirmed soon below in examining the Liouville theorem (3.9). By using (4.6) equation of motion (4.1) is written as

$$\langle \alpha_3^{(r)} \frac{\partial F_3}{\partial t} \rangle_1 = \langle \alpha_3^{(r)} \{ - \frac{P_1}{m_1}\cdot\frac{\partial F_3}{\partial R_1} - \frac{P_2}{m_2}\cdot\frac{\partial F_3}{\partial R_2} + \Theta_{12}F_3 + \frac{\partial}{\partial t}\left(\frac{\int d\Omega P_2 F_3}{\int d\Omega F_3}\right)\cdot\frac{\partial F_3}{\partial P_2}\} \rangle_1, \tag{4.7}$$

where $d\Omega = d\Omega_1 d\Omega_2$ and $\langle\ \rangle_3$ has been replaced by $\langle\ \rangle_1$ because time-average interval has been extended over three cells though their fusion is controlled by the average force field.

The average force field (4.6) begins to work when either of the particle 1 or 2 collides with the particle 3 as

$$r_i - r_3 = R_2 \pm R_1/2 = r_0 e \quad \text{for } i=1,2, \tag{4.8}$$

where e is the unit vector originating from the third particle, and the case i=1 corresponds to positive sign and vice versa. When the interaction with the third particle begins, the second term on the right hand side of (4.7) is written by using (4.8) as

$$\int dR_2 \frac{P_2}{m_2}\cdot\frac{\partial F_3}{\partial R_2} = \int \frac{dR_1}{\pm 2}\,\frac{P_2}{m_2}\cdot\frac{\partial F_3}{\partial(\pm R_1/2 - r_0 e)} = \int dR_1 \frac{P_2}{m_2}\cdot\frac{\partial F_3}{\partial R_1}, \tag{4.9}$$

which means that the fused cell has been extended on the surface of the third particle.

Now on the basis of (3.9) with n=3 and (4.7) we can examine similarity between P_1 and P_2; in order that (3.9) may hold in τ_1 the following must hold on the right hand side of (4.7) as

$$\left\langle \int dP_1 \int dP_2 \alpha_3^{(r)} \left(-\frac{P_1}{m_1}\cdot\frac{\partial F_3}{\partial R_1} - \frac{P_2}{m_2}\cdot\frac{\partial F_3}{\partial R_2}\right)\right\rangle_1 \propto -\left\langle \int dP_1 \int dP_2 \int dR_1 \left(\frac{P_1}{m_1}+\frac{P_2}{m_2}\right)\cdot\frac{\partial F_3}{\partial R_1}\right\rangle_1 = 0, \tag{4.10}$$

$$\left\langle \int dP_1 \int dP_2 \alpha_3^{(r)} \left\{\frac{1}{|P_1|}\,\frac{\partial U_{12}}{\partial R_1}\cdot\frac{\partial F_3}{\partial \Omega_1} + \frac{\partial}{\partial t}\left(\frac{\int d\Omega P_2 F_3}{\int d\Omega F_3}\right)\cdot\frac{\partial F_3}{\partial P_2}\right\}\right\rangle_1 = 0, \tag{4.11}$$

in which (4.9), (4.3) and the coarse-graining (2.9) have been used. In (4.10) $dR_2=\pm dR_1/2$ of (4.8) has been used in the second term and the needless $\int dR_1$ has been removed. In (4.11) the first term of (4.3) has vanished by using (2.9). It is seen that both (4.10) and (4.11) hold under a similarity between P_1 and P_2:

$$\left\langle \int d\Omega_1 \int d\Omega_2 \left(\frac{P_1}{m_1}+\frac{P_2}{m_2}\right) F_3\right\rangle_1 = 0. \tag{4.12}$$

The reason why (4.11) holds under (4.12) is as follows; replacing both P_2's in the second term of (4.11) by $-m_2/m_1 P_1$ the first and the second terms in (4.11) cancel each other owing to Newton's second law averaged over Ω ($|P_1|$ and $|P_2|$ are conserved). It is noted that (4.12) is equivalent to the state $p_{12}//p_{23}$ or $p_{12}//p_{13}$ under which self-collision is caused (see Fig. 1); the average force field (4.6) excludes self-collision from τ_1. It is seen that the

similarity of P_1 and P_2, (4.12) not only fulfills the "Liouville theorem" (3.9) with n=3 but also prevents self-collision.

By substituting (4.12) into the average force field in (4.7) we obtain as

$$\langle\alpha_3^{(r)}\frac{\partial F_3}{\partial t}\rangle_1 = \langle\alpha_3^{(r)}(-\frac{P_1}{m_1}\cdot\frac{\partial F_3}{\partial R_1} - \frac{P_2}{m_2}\cdot\frac{\partial F_3}{\partial R_2} + \Theta_{12}F_3)\rangle_1$$

$$+ \alpha_3^{(r)}\langle\frac{m_2}{m_1}\frac{\partial}{\partial t}(\frac{\int d\Omega P_1 F_3}{\int d\Omega F_3})\rangle_1\cdot\langle\frac{\partial F_3}{\partial P_2}\rangle_1, \qquad (4.13)$$

Consequently, (4.13) holds under a restriction that the average force field (4.6) can be defined definitely, that is, anisotropy is restricted to the first order as

$$F_1(x_i,t) = (1/4\pi)\Psi_i(r_i,p_i,t)[1 + 3\omega_i\cdot j_i(r_i,p_i,t)], \qquad (4.14)$$

where

$$\Psi_i = \int d\omega_i F_1(y_i,t), \quad j_i = \int d\omega_i \omega_i F_1(y_i,t)/\Psi_i. \qquad (4.15)$$

After some calculations an extended Boltzmann equaion is obtained from (4.13) as

$$\langle\frac{\partial F_1}{\partial t}\rangle_1 + \langle\frac{p_1}{m}\cdot\frac{\partial F_1}{\partial r_1}\rangle_1 = C.I. - \frac{1}{4\pi}\langle\frac{\partial j_1}{\partial t}\rangle_1\cdot\langle j_1\Psi_1\rangle_1$$

$$+ \frac{1}{(4\pi)^2 v}\int dy_2\langle\frac{\partial j_2}{\partial t}\rangle_1\cdot\langle j_2\Psi_2\Psi_1\rangle_1, \qquad (4.16)$$

where C.I. denotes the Boltzmann collision integral. Lastly we introduce a coarse-grained time t_c with the unit τ_1 as

$$\left\langle \frac{\partial \cdot}{\partial t} \right\rangle_1 = \frac{\partial \langle \cdot \rangle_1}{\partial t_c}. \qquad (4.17)$$

Thus except for the third term of (4.16), which may be neglected, this result coincides with a transport equation reported previously.[10]

5. Conclusions

The usual Liouville equation has been examined. It has been pointed out that point in phase point cannot have mechanical property like that of mass-point in physical space because phase space is only fictitious so even metric between particles cannot be definite in phase space. For the equation to be defined definitely then two conditions have been required: the embedding condition (1.2) and the symmetry condition (1.3). Under the two conditions it has been clarified that, if the symmetry is disturbed even in a pair of two particles in D_N, symmetry of D_N is disturbed completely; thus any partial truncation of D_N is not permitted generally. However, only in the limited case of (1.6), every pair of two particles in D_N can be truncated even under the two conditions. These facts means that the usual density expansion or binary collision expansion method cannot treat mechanical sequence like momentum-transfer occurring in triple collisions or successive binary collisions.

Owing to the truncation condition (1.6) it has been pointed out that mapping of D_N onto μ-space becomes possible so coarse-graining of μ-space is caused naturally, and the Stosszahlansatz or the Dyson perturbation series is assured. Moreover it has been found that the usual understanding that collisions occur at random in any pair of two particles in the Liouville equation at any time is not always true in short time interval but collision occurs in a pair of two particles locating nearest in time. In order to describe such distance in time and also in order to express collisions with

indistinguishable direction as stochastic process, finite-time average has been shown to be indispensable.

Then for the case of dilute gases in which only binary collisions are effective the Boltzmann equation with coarse-grained time has been clarified to be derived; the equation is applicable only to quasi-isotropic gases but time-average interval is impossible to be determined self-consistently in it.

For the case of anisotropic dense gases it has been shown that, if time-average interval is extended over successive binary collisions, difficulty of self-collisions is unavoidable and the situation is inevitable as far as ensemble of closed systems is adopted. In order to treat such successive collisions in nonequilibrium dense gases we have proposed a new statistical ensemble defined by finite-time average over open subsystem in μ-space. The new ensemble has been brought by a new method of applying the Liouville theorem to μ-space.

In Sec. 4 systems of three particles is extracted from the new ensemble and successive binary collisions have been discussed; for treating the anisotropy $\partial F_3/\partial \mathfrak{Q}_1$ of (4.3) in binary collisions an average force field has been introduced.

Spatial coarse-graining is indispensable for introducing the cross section, but anisotropy $\partial F_3/\partial \mathfrak{Q}_1$ hinders coarse-graining of μ-space. Then an average force field has been introduced for cancelling out the anisotropy $\partial F_3/\partial \mathfrak{Q}_1$ inside the fused cell of the first collision, so that coarse-graining of μ-space has been able to be brought inside the fused cell and also momentum transfer in collisions has been described.

The average force field in (4.16) plays multi-fold roles: (1) to exclude self-collision from the time average, by which the time-average interval τ_1 is determined self-consistently so time is coarse-grained, (2) to conserve the anisotropy $\partial F_3/\partial \mathfrak{Q}_1$ during τ_1 and to transfer it to the next time interval as the whole and (3) to conserve the volume of the virtual "phase space", or the

"Liouville theorem" during τ_1. Owing to the role (3) the isolation condition with n=3 in (3.7) is assured in τ_1 (third particles are not disturbed); the chaotic situation (4.5) is assured in the coarse-grained μ-space localized by the average force field. Thus the extended Boltzmann equation (4.16) is applicable to dense gases under only the condition that anisotropy of F_1 is restricted by the first order of ω_1 (4.14); the fact contrasts with the restriction that the usual Boltzmann equation can treat only quasi-isotropic distribution.

Recently, the self-similarities or fractals in turbulances and various mesoscopic phenomena have been found. If the scheme of fluid mechanics is re-examined on the basis of the extended Boltzmann equation some aspects of such phenomena will be clarified. Other problems still remain concerning more dense gases or gases of non-spherical molecules.

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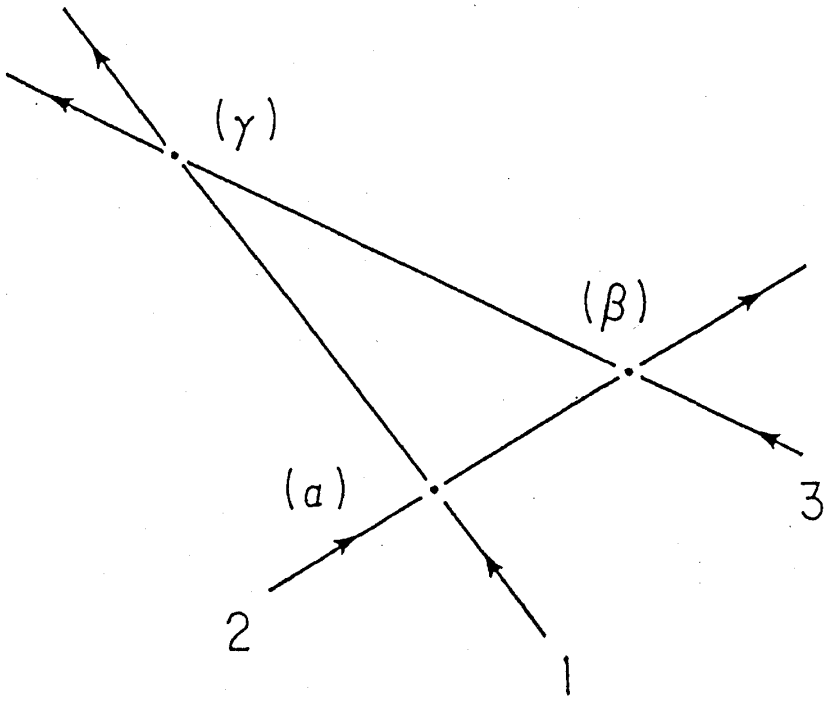

Fig. 1. Schematic draw of self-collision in coarse-grained μ-space. In coarse-grained μ-space particles behave like mass-point and cause self-collision as follows; the particle 1 makes collision at (α) in double form: grazing collision (2.11') toward (γ) and normal head-on-collision (2.11) toward (β). If the latter counterpart of the particle 1 makes normal head-on-collision at (β) then a self-collision happens at (γ). For drawing recollision triangle $p_1't_1=p_2't_2+p_3't_3$ ($t_1=t_2+t_3$: the time interval between the points (α) and (γ)), parallel of relative momenta $p_{12}'//p_{23}'$ and/or $p_{12}'//p_{13}'$ are needed. In order to judge the form of collision at (α) the direction of p_{12}' must be known; it is impossible however in the usual theory as seen from (1.4).

おことわり。この原稿を書き上げた後に、論理の起ち上げに１ステップ落ちていることが分かったが、時間がないのでそのままにした。一応の流れは読み取れると思う。