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On Fluctuations in μ Space

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A master equation is derived microscopically to describe the fluctuating motion of the particle density in μ space. This equation accounts for the drift motion of particles and is valid for any inhomogeneous gas. The Boltzmann equation is obtained from the first moment of this equation by neglecting the second cumulant (the pair correlation function). The successive moments form coarse-grained BBGKY-like hierarchy equations, in which small spatial regions with $r_{ij} \lesssim$ the force range are smeared out. These hierarchy equations are convenient for investigating the nonequilibrium long-range pair correlation function, which arises mainly from sequences of isolated binary collisions and gives rise to the much-discussed long-time tail and the logarithmic term in the density expansion of transport coefficients. It is shown to have a spatial long tail, like the Coulombic potential, in a steady laminar flow. The stochastic nature of the nonlinear Boltzmann–Langevin equation is also investigated; the random source term is found to be expressed as a linear superposition of Poisson random variables and to become Gaussian in special cases.

KEY WORDS: Master equation for μ-space fluctuations; Boltzmann–Langevin equation; molecular chaos; nonequilibrium long-range correlations.

1. INTRODUCTION

The system we consider is a classical gas with short-ranged, repulsive, and pairwise interaction. When the system is sufficiently dilute, the Boltzmann equation is known to provide a good description of the average motion of the particle density in the six-dimensional $(\mathbf{r}, \mathbf{v})$ space (μ space). This equation is closed in the one-body distribution function $f(\mathbf{r}, \mathbf{v}, t)$, which is the average quantity defined by

$$f(\mathbf{r}, \mathbf{v}, t) = \int dx^N \, \rho(x^N) \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i(t)) \, \delta(\mathbf{v} - \mathbf{v}_i(t)) \tag{1}$$

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The vector $(\mathbf{r}_i(t), \mathbf{v}_i(t))$ represents the position and velocity of the ith particle at time t, and $\rho(x^N)$ is an initially given phase-space distribution function. The actual particle density in μ space, on the other hand, exhibits fluctuations around the mean value $f(\mathbf{r}, \mathbf{v}, t)$. To describe these phase-space fluctuations, some authors consider that the distribution of the particle numbers f_i (where μ space is divided into cells) obeys a master equation essentially equivalent to[1-5]

$$\frac{\partial}{\partial t} P(\{f\}, t) = \tfrac{1}{2} \sum_{i,j,k,l} A_{ij}^{kl}(f_i + 1)(f_j + 1) \times P(f_i + 1, f_j + 1, f_k - 1, f_l - 1, \{f'\}, t) - \tfrac{1}{2} \sum_{i,j,k,l} A_{ij}^{kl} f_i f_j P(\{f\}, t) \tag{2}$$

Here, $\{f'\}$ is the set of the particle numbers other than i, j, k, and l; $P(\{f\}, t)$ gives the probability of finding the particle numbers with values $\{f\}$; A_{ij}^{kl} is the transition probability for the binary collision with initial state (i, j) and final state (k, l); and the factor $1/2$ reflects the indistinguishability of identical particles. The particle numbers $\{f\}$ follow the Markovian stochastic process determined by Eq. (2). The first moment of Eq. (2) is the equation for the one-body distribution function

$$\frac{\partial}{\partial t}\langle f_i \rangle = \sum_{i,j,k,l} A_{ij}^{kl}[\langle f_k f_l \rangle - \langle f_i f_j \rangle] \tag{3}$$

where the bracket $\langle \cdots \rangle$ represents the average over $P(\{f\}, t)$. If we neglect the pair correlation function

$$g_{ij} = \langle f_i f_j \rangle - \langle f_i \rangle \langle f_j \rangle \tag{4}$$

then Eq. (3) reduces to the Boltzmann equation for spatially homogeneous cases. The master equation (2) neglects completely the drift motion of particles, which causes spatial inhomogeneities of the system, so that it cannot be used to treat transport phenomena and spatial molecular correlations. In this paper we derive "microscopically" a master equation similar to Eq. (2) and applicable to any inhomogeneous case.

Next we mention the treatment of phase-space fluctuations by the Boltzmann–Langevin equation,[5-13] which is of the form

$$\left[\frac{\partial}{\partial t} + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}}\right] F(\mathbf{r}, \mathbf{v}, t) = \Gamma(\mathbf{r}, \mathbf{v}; F, F) + R(\mathbf{r}, \mathbf{v}, t) \tag{5}$$

where Γ is the collision term in the Boltzmann equation and R is the random source term. This form of the equation is suggested by the fact that the actual hydrodynamic variables obey hydrodynamic equations with random stress

and heat current that are Markovian and Gaussian stochastic processes.[14] The fluctuating kinetic equation (5) should give a finer description than the fluctuating hydrodynamic equations, so that the latter must be derivable from the former.

However, both the physical and mathematical meanings of Eq. (5) have been obscure; that is, the stochastic nature of the random source term has not been specified explicitly. Moreover, only the linearized version of Eq. (5) has been treated around the Maxwell distribution function $f_M(v)$ or the mean value $f(\mathbf{r}, \mathbf{v}, t)$. It should be remarked that the stochastic nature of Eq. (5) can be examined only on the basis of microscopic arguments of the collision processes. This is done in this paper. Furthermore, we also reveal the role of the nonlinearity appearing in the collision term of Eq. (5), which in fact gives rise to long-range molecular correlations. Finally, we note the relation between the two approaches to the phase-space fluctuations, one through the master equation and the other through the Boltzmann–Langevin equation. They are shown to be equivalent to each other.

2. BOLTZMANN–LANGEVIN EQUATION

The Liouville operator of our system is written as

$$i\mathscr{L}_N = -\sum_{i=1}^{N} \mathbf{v}_i \frac{\partial}{\partial \mathbf{r}_i} + \sum_{i<j} \theta_{ij} \tag{6}$$

$$\theta_{ij} = \frac{1}{m} \frac{\partial}{\partial \mathbf{r}_i} V(\mathbf{r}_{ij}) \cdot \left[\frac{\partial}{\partial \mathbf{v}_i} - \frac{\partial}{\partial \mathbf{v}_j} \right] \tag{7}$$

The pair potential $V(r_{ij})$ will be assumed to be short-ranged and repulsive. The particle density in μ space is usually defined by

$$N(\mathbf{r}, \mathbf{v}, t) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i(t)) \, \delta(\mathbf{v} - \mathbf{v}_i(t)) \tag{8}$$

This quantity obeys the so-called Klimontovich equation

$$\left[\frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} \right] N(\mathbf{r}_1, \mathbf{v}_1, t)$$

$$= \int d\mathbf{r}_2 \, d\mathbf{v}_2 \, \theta_{12} [N(\mathbf{r}_1, \mathbf{v}_1, t) N(\mathbf{r}_2, \mathbf{v}_2, t)$$

$$- \delta(\mathbf{r}_1 - \mathbf{r}_2) \, \delta(\mathbf{v}_1 - \mathbf{v}_2) N(\mathbf{r}_1, \mathbf{v}_1, t)] \tag{9}$$

which is a closed equation for the particle density in μ space, and determines completely the precise microscopic motion of the indistinguishable N-particle

system. What is the relation between this microscopic equation and the fluctuating kinetic equation (5), which is of course approximate? Mori answered that a stochastic kinetic equation like Eq. (5) describes the motion of the spatially coarse-grained particle density in μ space.[13] He performed the spatial coarse-graining by replacing the spatial δ function in the definition of the fine-grained particle density (8) by the following function with a finite width of the peak:

$$\Delta(\mathbf{r} - \mathbf{r}_i(t)) = \int_{q<\lambda^{-1}} \frac{dq}{(2\pi)^3} \exp[i\mathbf{q}\cdot(\mathbf{r} - \mathbf{r}_i(t))] \tag{10}$$

where the cutoff length λ satisfies

$$a \ll \lambda \ll l \tag{11}$$

a being the force range of the potential and l the mean free path. It is clear that the approximate equation (5) does not describe the short-wavelength part of the fine-grained particle density $N(\mathbf{r}, \mathbf{v}, t)$.

We denote the coarse-grained particle density by $F(\mathbf{r}, \mathbf{v}, t)$:

$$F(\mathbf{r}, \mathbf{v}, t) = \sum_{i=1}^{N} \Delta(\mathbf{r} - \mathbf{r}_i(t))\, \delta(\mathbf{v} - \mathbf{v}_i(t)) \tag{12}$$

The quantity $F(\mathbf{r}, \mathbf{v}, t)$ is a dynamical variable dependent on the phase-space configuration of the N-particle system and obeys the equation

$$\left[\frac{\partial}{\partial t} + \mathbf{v}_1\cdot\frac{\partial}{\partial \mathbf{r}_1}\right] F(\mathbf{r}_1, \mathbf{v}_1, t) = S(1, t) \tag{13}$$

where

$$S(1, t) = \int d1'\, \Delta(\mathbf{r}_1 - \mathbf{r}_1')\, \delta(\mathbf{v}_1 - \mathbf{v}_1') \times \int d2'\, \theta_{1'2'}[N(1', t)N(2', t) - \delta(1' - 2')N(1', t)] \tag{14}$$

Here $1 = (\mathbf{r}_1, \mathbf{v}_1)$, $1' = (\mathbf{r}_1', \mathbf{v}_1')$,... represent points in μ space. This equation is not closed in $F(\mathbf{r}, \mathbf{v}, t)$, so that we must relate the right-hand side of Eq. (13) to $F(\mathbf{r}, \mathbf{v}, t)$ to construct a closed equation in $F(\mathbf{r}, \mathbf{v}, t)$. This will be shown to be possible if the system is sufficiently dilute and the dominant interaction process is an isolated binary collision. It is convenient to integrate Eq. (13) over a small time interval to examine the collision term $S(1, t)$:

$$F(1, t + \Delta t) = F(\mathbf{r}_1 + \Delta t\mathbf{v}_1, \mathbf{v}_1, t) + \Delta S(1, t) \tag{15}$$

where

$$\Delta S(1, t) = \int_0^{\Delta t} d\tau \{\exp[-(\Delta t - \tau)\mathbf{v}_1 \cdot \partial/\partial \mathbf{r}_1]\} S(1, t + \tau) \tag{16}$$

The time difference Δt is chosen to satisfy

$$t_c \ll \Delta t \ll t_{mf} \tag{17}$$

where $t_c \sim a/v_{\text{th}}$ is the duration time of a binary collision and $t_{\text{mf}} \sim l/v_{\text{th}}$ is the mean free time, with v_{th} the thermal velocity. The nature of the collision increments $\Delta S(1, t)$ can be examined by considering their moments

$$\begin{aligned} &\langle \Delta S(1, t) \rangle \\ &\langle \Delta S(1, t)\, \Delta S(2, t) \rangle \\ &\langle \Delta S(1, t)\, \Delta S(2, t)\, \Delta S(3, t) \rangle \\ &\vdots \end{aligned} \tag{18}$$

where $\langle \cdots \rangle$ represents an average over a nonequilibrium ensemble in general. These moments can be expanded in powers of Δt if the binary collision is assumed to take place instantaneously compared with Δt and the leading terms in Δt can be related to the average $\langle FF \rangle$. Kirkwood considered only the first moment and obtained an expression in which the two-body distribution function at large spatial separation is involved.[15] By introducing the approximation

$$g(1, 2, t) = f(1, 2, t) - f(1, t) f(2, t) = 0 \qquad \text{for} \quad |\mathbf{r}_1 - \mathbf{r}_2| \gg a \tag{19}$$

the first moment becomes the Boltzmann collision term multiplied by Δt. This is the molecular chaos hypothesis and expresses no long-range pair correlation. In this paper, however, we consider the fluctuations of $F(1, t)$ around $f(1, t)$ and therefore retain the long-range pair correlation. We readily notice that the long-range pair correlation function coincides with the second cumulant of F by its definition, that is,

$$\begin{aligned} g(1, 2, t) = &\langle F(1, t) F(2, t) \rangle \\ &- \langle F(1, t) \rangle \langle F(2, t) \rangle \qquad \text{for} \quad |\mathbf{r}_1 - \mathbf{r}_2| \gg a \end{aligned} \tag{20}$$

All the moments in Eq. (18) must be calculated to relate $\Delta S(1, t)$ to $F(1, t)$ [Kirkwood related the average $\langle \Delta S(1, t) \rangle$ to the average $f(1, t)$ using the molecular chaos hypothesis]. This program is much facilitated by introducing the characteristic functional of $\Delta S(1, t)$ defined by

$$C(\{\alpha\}) = \langle e^{\Delta X} \rangle \tag{21}$$

where

$$\Delta X = \int d1\, \alpha(1)\, \Delta S(1, t)$$

$$= \int d1 \int_0^{\Delta t} d\tau\, \alpha(\mathbf{r}_1 + (\Delta t - \tau)\mathbf{v}_1, \mathbf{v}) S(1, t + \tau) \tag{22}$$

Here, $\alpha(1)$ is an arbitrary function having only long-wavelength components ($k < \lambda^{-1}$) corresponding to the spatial coarse-graining. The increment ΔX is written in terms of the molecular positions and velocities as

$$\Delta X = -\sum_{i<j} \int_0^{\Delta t} d\tau\, \beta(i(t + \tau), j(t + \tau)) \tag{23}$$

where

$$\beta(1, 2) = \theta_{12}[\alpha(\mathbf{r}_1 + (\Delta t - \tau)\mathbf{v}_1, \mathbf{v}_1) + \alpha(\mathbf{r}_2 + (\Delta t - \tau)\mathbf{v}_2, \mathbf{v}_2)] \tag{24}$$

Thus,

$$e^{\Delta X} = 1 + \sum_{r=1}^{\infty} \frac{(-1)^r}{r!} \int_0^{\Delta t} d\tau_1 \cdots \int_0^{\Delta t} d\tau_r \sum_{i_1<j_1} \cdots \sum_{i_r<j_r} \beta(i_1(t + \tau_1), j_1(t + \tau_1))$$
$$\cdots \beta(i_r(t + \tau_r), j_r(t + \tau_r)) \tag{25}$$

In the above approximation the number of particles labeled $(i_1, j_1),\ldots,(i_r, j_r)$ extends from at least two to at most $2r$. The terms involving two particles are characterized by

$$(i_1, j_1) = (i_2, j_2) = \cdots = (i_r, j_r) \tag{26}$$

and represent one binary collision. These terms are proportional to Δt when averaged over a realistic nonequilibrium ensemble, because the collision is assumed to take place almost instantaneously. The averages of the other terms involving more than three particles are higher in Δt or in the density for the system concerned, so that these terms can be neglected. Picking up the terms representing one binary collision, the characteristic functional C can be written as

$$C(\{\alpha\}) = 1 + \sum_{i<j} \sum_{r=1}^{\infty} \frac{(-1)^r}{r!} \int_0^{\Delta t} d\tau_1 \cdots \int_0^{\Delta t} d\tau_r$$
$$\times \langle \beta(i(t + \tau_1), j(t + \tau_1)) \cdots \beta(i(t + \tau_r), j(t + \tau_r)) \rangle$$
$$= 1 + \sum_{i<j} \left\langle \exp\left[-\int_0^{\Delta t} d\tau\, \beta(i(t + \tau), j(t + \tau)) \right] - 1 \right\rangle \tag{27}$$

The colliding pair can be assumed to suffer no interaction from the other

$N - 2$ particles in the small time interval $t \sim t + \Delta t$. Then, the problem is reduced to two-body dynamics. We find the relation

$$\begin{aligned}\beta(i(t+\tau), j(t+\tau)) &= \int d1\, d2\, \delta(1 - i(t))\, \delta(2 - j(t)) \\ &\quad \times [\exp(-i\mathscr{L}_{12}\tau)]\theta_{12}\{\exp[-i\mathscr{L}^0_{12}(\Delta t - \tau)]\} \\ &\quad \times [\alpha(1) + \alpha(2)] \\ &= -\frac{\partial}{\partial\tau}\int d1\, d2\, \delta(1 - i(t))\, \delta(2 - j(t))[\exp(-i\mathscr{L}_{12}\tau)] \\ &\quad \times \{\exp[-i\mathscr{L}^0_{12}(\Delta t - \tau)]\}[\alpha(1) + \alpha(2)] \end{aligned} \tag{28}$$

where

$$i\mathscr{L}_{12} = i\mathscr{L}^0_{12} + \theta_{12} \tag{29}$$

$$i\mathscr{L}^0_{12} = -\mathbf{v}_1 \cdot \partial/\partial\mathbf{r}_1 - \mathbf{v}_2 \cdot \partial/\partial\mathbf{r}_2 \tag{30}$$

Therefore, the integration with respect to τ can be performed to give

$$C(\{\alpha\}) = 1 + \int d1 \int d2\, (e^{\gamma(1,2)} - 1)\left\langle \sum_{i<j} \delta(1 - x_i(t))\, \delta(2 - x_j(t)) \right\rangle \tag{31}$$

where

$$\begin{aligned}\gamma(1,2) &= [\exp(-i\mathscr{L}_{12}\Delta t) - \exp(-i\mathscr{L}^0_{12}\Delta t)][\alpha(1) + \alpha(2)] \\ &= \alpha(\mathbf{r}_1(\Delta t), \mathbf{v}_1(\Delta t)) + \alpha(\mathbf{r}_2(\Delta t), \mathbf{v}_2(\Delta t)) \\ &\quad - \alpha(\mathbf{r}_1 + \Delta t\mathbf{v}_1, \mathbf{v}_1) - \alpha(\mathbf{r}_2 + \Delta t\mathbf{v}_2, \mathbf{v}_2) \end{aligned} \tag{32}$$

The quantity $\gamma(1, 2)$ is not zero only when the collision takes place in the time interval $t \sim t + \Delta t$, so that the small spatial region $r_{12} \lesssim v_{12}\, \Delta t$ contributes in the spatial integration in Eq. (31). Taking for the $\mathbf{r}_2$ integration cylindrical coordinates with the axis in the direction of the relative velocity $\mathbf{v}_2 - \mathbf{v}_1$ and denoting the coordinate along the axis by ξ and the polar coordinates by b and ψ, we integrate over $\mathbf{r}_2$ to obtain approximately

$$\begin{aligned}C(\{\alpha\}) &= 1 + \tfrac{1}{2}\int d1 \int d\mathbf{v}_2 \int db\, b\, d\psi \int_{-\infty}^{\infty} d\xi\, (e^{\gamma(1,2)} - 1) f(1, 2, t) \\ &\simeq 1 + \tfrac{1}{2}\Delta t \int d_1 \int d\mathbf{v}_2 \int db\, b\, d\psi\, \mathbf{v}_{12}(e^{\gamma^*(1,2)} - 1) f(1, 2, t) \end{aligned} \tag{33}$$

where

$$\gamma^*(1,2) = \alpha(\mathbf{r}_1, \mathbf{v}_1') + \alpha(\mathbf{r}_1, \mathbf{v}_2') - \alpha(\mathbf{r}_1, \mathbf{v}_1) - \alpha(\mathbf{r}_1, \mathbf{v}_2) \tag{34}$$

with $\mathbf{v}_1'$ and $\mathbf{v}_2'$ the velocities after the collision characterized by the impact parameter b and the azimuthal angle ψ.

Use has been made of the fact that the function $a(1)$ varies slowly in space, and the positions $\mathbf{r}_1(\Delta t)$, $\mathbf{r}_2(\Delta t)$, $\mathbf{r}_1 + \Delta t\, \mathbf{v}_1$, and $\mathbf{r}_2 + \Delta t\, \mathbf{v}_2$ in $\gamma(1, 2)$, Eq. (32), are set equal to $\mathbf{r}_1$ in Eq. (33). We note that the spatial region $a \ll |\mathbf{r}_1 - \mathbf{r}_2| \ll l$ gives the main contribution in Eq. (33), so that the two-body distribution function can be replaced by the second moment of $F(t)$:

$$f(1, 2, t) = \langle F(\mathbf{r}_1, \mathbf{v}_1, t) F(\mathbf{r}_1, \mathbf{v}_2, t) \rangle \qquad \text{for} \quad a \ll |\mathbf{r}_1 - \mathbf{r}_2| \ll l \tag{35}$$

Equation (33) can be rewritten in a more symmetric form by introducing the transition probability defined by

$$\begin{aligned} A_{12}^{1'2'} = {} & \sigma(v_{12}, \chi)\, \delta(\mathbf{r}_1 - \mathbf{r}_2)\, \delta(\mathbf{r}_1 - \mathbf{r}_1')\, \delta(\mathbf{r}_2 - \mathbf{r}_2') \\ & \times \delta(\tfrac{1}{2}(\mathbf{v}_1 + \mathbf{v}_2) - \tfrac{1}{2}(\mathbf{v}_1' + \mathbf{v}_2'))\, \delta(v_1^2 + v_2^2 - v_1'^2 - v_2'^2) \end{aligned} \tag{36}$$

where $\sigma(v_{12}, \chi)$ is the differential cross section and χ the deflection angle. The two δ functions in the velocity subspace represent the conservation of energy and momentum. The inverse collision process has the same transition probability, i.e.,

$$A_{12}^{1'2'} = A_{1'2'}^{12} \tag{37}$$

Then, Eq. (33) becomes

$$\begin{aligned} C(\{\alpha\}) &= \left\langle \exp\left[\int d1\, \alpha(1)\, \Delta S(1, t) \right] \right\rangle \\ &= 1 + \tfrac{1}{2}\Delta t \int d1\, d2\, d1'\, d2'\, A_{12}^{1'2'} \{\exp[\alpha(1') + \alpha(2') - \alpha(1) - \alpha(2)] - 1\} \\ &\quad \times \langle F(1, t) F(2, t) \rangle + \cdots \end{aligned} \tag{38}$$

Functional differentiation of the above equation with respect to $\alpha(1)$ yields

$$\begin{aligned} &\langle \Delta S(1, t) \cdots \Delta S(r, t) \rangle \\ &\quad = \tfrac{1}{2}\Delta t \int d\bar{1}\, d\bar{2}\, d\bar{1}'\, d\bar{2}'\, A_{\bar{1}\bar{2}}^{\bar{1}'\bar{2}'} \\ &\qquad \times \prod_{i=1}^{r} [\delta(i - \bar{1}') + \delta(i - \bar{2}') - \delta(i - \bar{1}) - \delta(i - \bar{2})] \\ &\qquad \times \langle F(\bar{1}, t) F(\bar{2}, t) \rangle + \cdots \end{aligned} \tag{39}$$

The first term ($r = 1$) is nothing but the Boltzmann collision term multiplied by Δt. Equation (38) relates the collision increment $\Delta S(1, t)$ statistically to the product $F(1, t)F(2, t)$.

We will adopt the assumption that $\Delta S(1, t)$ is a random variable whose distribution is dependent on the product $F(1, t)F(2, t)$ via Eq. (38); then, the starting equation (15) becomes closed in "the random variable F." For small Δt, Eq. (15) can be written as the following stochastic differential equation:

$$\Delta F(1, t) + \Delta t\, \mathbf{v}_1 \cdot (\partial/\partial \mathbf{r}_1) F(1, t) = \Delta S(1, t) \tag{40}$$

The incremental change of $F(1, t)$ arises from the drift motion and the binary collision separately. The random force may be defined by

$$\Delta R(1, t) = \int_0^{\Delta t} d\tau\, R(1, t + \tau) = \Delta S(1, t) - \Delta t\, \Gamma(1; F(t), F(t)) \tag{41}$$

where Γ is the Boltzmann collision term, quadratic in $F(t)$. The characteristic functional of the random increment $\Delta R(1, t)$ is written as

$$\begin{aligned} &\left\langle \exp\left[\int d1\, \alpha(1)\, \Delta R(1, t)\right]\right\rangle \\ &\quad = 1 + \tfrac{1}{2}\Delta t \int d1\, d2\, d1'\, d2'\, A_{12}^{1'2'} \\ &\qquad \times \{\exp[\alpha(1') + \alpha(2') - \alpha(1) - \alpha(2)] - \alpha(1') - \alpha(2') + \alpha(1) + \alpha(2) - 1\} \\ &\qquad \times \langle F(1, t)F(2, t)\rangle + \cdots \end{aligned} \tag{42}$$

The average of the random source term vanishes by its definition in any nonequilibrium situation; in general, the random source term is statistically independent of the past values of F, i.e.,

$$\langle R(1, t)\Phi(\{F(s)\}; s < t)\rangle = 0 \tag{43}$$

where $\Phi(\{F(s)\}; s < t)$ represents an arbitrary functional of the past values of F. Clearly, the random force conserves the number, momentum, and energy, i.e.,

$$\int dv \begin{Bmatrix} 1 \\ \mathbf{v} \\ v^2 \end{Bmatrix} R(\mathbf{r}, \mathbf{v}, t) = 0 \tag{44}$$

which is easily seen from the definition of the transition probability, Eq. (36). The second moment of $R(1, t)$ may be defined by

$$\langle R(1, t_1)R(2, t_2)\rangle = (1/\Delta t_1\, \Delta t_2)\langle \Delta_1 R(1, t_1)\, \Delta_2 R(2, t_2)\rangle \tag{45}$$

where $\Delta_1 R(1, t_1)$ is the random increment in the time interval $t_1 \sim t_1 + \Delta t_1$ and $\Delta_2 R(2, t_2)$ is that in the time interval $t_2 \sim t_2 + \Delta t_2$. The right-hand

side of Eq. (45) does not vanish only when the two time intervals overlap. Let Δt be the overlapping time; then, Eq. (45) is written as

$$\langle R(1, t_1)R(2, t_2)\rangle = \frac{\Delta t}{\Delta t_1\, \Delta t_2}\frac{1}{\Delta t}\langle \Delta R(1, t_1)\, \Delta R(2, t_1)\rangle \tag{46}$$

where $\Delta R(1, t_1)$ and $\Delta R(2, t_2)$ are the random increments in the same time interval of width Δt. In the limit of small time intervals we can prove the mathematical relation

$$\Delta t/(\Delta t_1\, \Delta t_2) = \delta(t_1 - t_2) \tag{47}$$

Therefore, using Eq. (42) we obtain the second moment in the form

$$\begin{aligned}&\langle R(1, t_1)R(2, t_2)\rangle \\ &= \tfrac{1}{2}\delta(t_1 - t_2)\int d\bar{1}\, d\bar{2}\, d\bar{1}'\, d\bar{2}'\, A_{\bar{1}\bar{2}}^{\bar{1}'\bar{2}'} \\ &\quad \times \prod_{i=\bar{1}}^{\bar{2}} [\delta(i - \bar{1}') + \delta(i - \bar{2}') - \delta(i - \bar{1}) - \delta(i - \bar{2})]\langle F(\bar{1}, t_1)F(\bar{2}, t_2)\rangle\end{aligned} \tag{48}$$

In equilibrium this expression is written in the form

$$\langle R(1, t_1)R(2, t_2)\rangle_{\mathrm{eq}} = 2\delta(t_1 - t_2)\, \delta(\mathbf{r}_1 - \mathbf{r}_2)\langle \mathbf{v}_1|J_0|\mathbf{v}_2\rangle \tag{49}$$

where $\langle \mathbf{v}_1|J_0|\mathbf{v}_2\rangle$ is the integral kernel of the linearized Boltzmann collision operator around the Maxwell distribution function $f_{\mathrm{M}}(v)$. Use has been made of the relation

$$\langle F(1, t)F(2, t)\rangle_{\mathrm{eq}} = f_{\mathrm{M}}(\mathbf{v}_1)f_{\mathrm{M}}(\mathbf{v}_2) \qquad \text{for} \quad |\mathbf{r}_1 - \mathbf{r}_2| \gg a \tag{50}$$

The higher moments may be defined by

$$\langle R(1, t_1) \cdots R(r, t_r)\rangle = (1/\Delta_1 t \cdots \Delta_2 t)\langle \Delta_1 R(1, t_1) \cdots \Delta_r R(r, t_r)\rangle \tag{51}$$

which do not take simple forms. This is because the higher moments ($r \geqslant 3$) involve up to $r - 1$ collisional events which have correlations among one another.

3. MASTER EQUATION AND COARSE-GRAINED HIERARCHY EQUATION

We can consider the distribution functional of the coarse-grained particle density $F(1, t)$ because it evolves obeying Eq. (40). It is convenient to introduce here the characteristic functional of $F(1, t)$ by

$$Q(\{\eta\}, t) = \left\langle \exp\left[\int d1\, \eta(1)F(1, t)\right]\right\rangle \tag{52}$$

where $\langle\cdots\rangle$ represents a nonequilibrium average in general. The distribution functional of the random variable $F(1, t)$ will be denoted by $P(\{f\}, t)$, which gives the probability for $F(1, t)$ to take the value $f(1 - t)$. The time evolution of $Q(\{\eta\}, t)$ can be written from Eq. (40) as

$$\begin{aligned}\frac{\partial}{\partial t} Q(\{\eta\}, t)&\\ &= \lim_{\Delta t \to 0} \frac{1}{\Delta t} \left\langle \left\{ \exp\left[\int d1\, \eta(1)\, \Delta F(1, t) \right] - 1 \right\} \exp\left[\int d1\, \eta(1) F(1, t) \right] \right\rangle \\ &= -\left\langle \int d1\, \eta(1) \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} F(1, t) \exp\left[\int d1\, \eta(1) F(1, t) \right] \right\rangle \\ &\quad + \lim_{\Delta t \to 0} \frac{1}{\Delta t} \left\langle \left\{ \exp\left[\int d1\, \eta(1)\, \Delta S(1, t) \right] - 1 \right\} \exp\left[\int d1\, \eta(1) F(1, t) \right] \right\rangle \end{aligned} \tag{53}$$

Equation (38) says that the distribution of the collisional increment $\Delta S(1, t)$ is determined completely by the instantaneous value of $F(1, t)$, so that the second term on the right-hand side of Eq. (53) is written as

$$\begin{aligned}&\tfrac{1}{2} \int d1\, d2\, d1'\, d2'\, A_{12}^{1'2'} \{\exp[\eta(1') + \eta(2') - \eta(1) - \eta(2)] - 1\} \\ &\qquad \times \left\langle F(1, t) F(2, t) \exp\left[\int d1\, \eta(1) F(1, t) \right] \right\rangle \end{aligned} \tag{54}$$

Thus, Eq. (53) can be expressed in the form

$$(\partial/\partial t) Q(\{\eta\}, t) = \mathscr{D}(\eta, \delta/\delta\eta) Q(\{\eta\}, t) \tag{55}$$

with

$$\begin{aligned}\mathscr{D}\left(\eta, \frac{\delta}{\delta\eta}\right) &= -\int d1\, \eta(1) \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} \frac{\delta}{\delta \eta(1)} \\ &\quad + \tfrac{1}{2} \int d1\, d2\, d1'\, d2'\, A_{12}^{1'2'} \{\exp[\eta(1') + \eta(2') - \eta(1) - \eta(2)] - 1\} \\ &\quad \times \frac{\delta^2}{\delta\eta(1)\, \delta\eta(2)} \end{aligned} \tag{56}$$

On the other hand, the distribution functional $P(\{f\}, t)$ is governed by

$$(\partial/\partial t) P(\{f\}, t) = \mathscr{D}(-\delta/\delta f, f) P(\{f\}, t) \tag{57}$$

with

$$\mathscr{D}\left(-\frac{\delta}{\delta f}, f\right) = \int d1 \, \frac{\delta}{\delta f(1)} \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} f(1)$$
$$+ \tfrac{1}{2} \int d1 \, d2 \, d1' \, d2' \, A_{12}^{1'2'}$$
$$\times \left\{ \exp\left[-\frac{\delta}{\delta f(1')} - \frac{\delta}{\delta f(2')} + \frac{\delta}{\delta f(1)} + \frac{\delta}{\delta f(2)} \right] - 1 \right\} f(1) f(2) \tag{58}$$

The operator $\exp[\delta/\delta f(1)]$ has the meaning

$$\{\exp[\delta/\delta f(1)]\} P(\{f(1')\}) = P(\{f(1') + \delta(1 - 1')\}) \tag{59}$$

The operator $\mathscr{D}(-\delta/\delta f, f)$, Eq. (58), is obtained by the following replacement in the expression of $\mathscr{D}(\eta, \delta/\delta\eta)$:

$$\eta(1) \to -\delta/\delta f(1) \qquad \text{and} \qquad \delta/\delta\eta(1) \to f(1) \tag{60}$$

The first term of Eq. (58) represents the drift motion; the second term represents the binary collision, which is capable of an intuitive explanation by dividing μ space into cells. The second term reads

$$\tfrac{1}{2} \sum_{i,j,k,l} A_{ij}^{kl} (f_i + 1)(f_j + 1) P(f_i + 1, f_j + 1, f_k - 1, f_l - 1, \{f'\}, t)$$
$$- \tfrac{1}{2} \sum_{i,j,k,l} A_{ij}^{kl} f_i f_j P(\{f\}, t) \tag{61}$$

This term is explained in Section 1. We note that the distribution functional $P(\{f\}, t)$ has no definite limit as a functional of $f(1)$ in the limit of small cell division. However, the master equation (57) shows that the average of any functional of $F(1, t)$, say $A(\{F(t)\})$, obeys the equation

$$\frac{\partial}{\partial t} \langle A(\{F(t)\}) \rangle = \left\langle \mathscr{D}\left(\frac{\delta}{\partial F(t)}, F(t) \right) A(\{F(t)\}) \right\rangle \tag{62}$$

This quantity may well be expected to be well-defined even when the continuous limit of cell division is taken.

Next, we introduce the r-body distribution functional by[16]

$$Q = 1 + \sum_{r=1}^{\infty} \frac{1}{r!} \int d1 \cdots dr \, \zeta(1) \cdots \zeta(r) f(1, \ldots, r, t) \tag{63}$$

where

$$\zeta(1) = e^{\eta(1)} - 1 \tag{64}$$

The characteristic functional Q can be regarded as the generating functional of the r-body distribution functions; Q, as a functional of $\zeta(1)$, obeys the equation

$$\left[\frac{\partial}{\partial t} + \int d1\ \zeta(1)\mathbf{v}_1 \cdot \frac{\delta}{\partial \mathbf{r}_1} \frac{\delta}{\delta\zeta(1)}\right] Q(\{\zeta\}, t)$$

$$= \tfrac{1}{2} \int d1\ d2\ d1'\ d2'\ A_{12}^{1'2'}\{[\zeta(1') + 1][\zeta(2') + 1]$$

$$- [\zeta(1) + 1][\zeta(2) + 1]\} \frac{\delta^2}{\delta\zeta(1)\ \delta\zeta(2)} Q(\{\zeta\}, t) \tag{65}$$

Functional differentiation with respect to $\zeta(1)$ yields the following BBGKY-like hierarchy equations:

$$\left[\frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1}\right] f(1, t) = \int d2\ T_{12}^{(0)} f(1, 2, t)$$

$$\vdots$$

$$\left[\frac{\partial}{\partial t} + \sum_{i=1}^{r} \mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} - \sum_{1 \leqslant i \leqslant j \leqslant r} T_{ij}^{(0)}\right] f(1,\ldots,r, t) \tag{66}$$

$$= \sum_{i=1}^{r} \int d(r+1) T_{ir+1}^{(0)} f(1,\ldots,r+1, t)$$

where $T_{ij}^{(0)}$ is the operator on i and j defined by

$$T_{ij}^{(0)}\alpha(i, j) = \int di'\ dj'\ A_{ij}^{i'j'}[\alpha(i', j') - \alpha(i, j)]$$

$$= \delta(\mathbf{r}_i - \mathbf{r}_j) \int d\Omega\ v_{ij}\sigma(v_{ij}, x)[\alpha(i', j') - \alpha(i, j)] \tag{67}$$

where $\alpha(i, j)$ is an arbitrary function of i and j. The r-body distribution functions are defined in the usual way by

$$f(1,\ldots,r, t) = \sum_{(i_1,\ldots,i_r)} \langle \delta(1 - i_1(t)) \cdots \delta(r - i_r(t)) \rangle \tag{68}$$

The above functions change rapidly in space and time in a complicated way in the small region $r_{ij} \leqslant a$ because of short-range correlations and slowly in the remaining region. On the other hand, the r-body distribution functions defined by Eq. (63) change slowly in space in the whole spatial region. That is, the small spatial region $r_{ij} \leqslant a$ is smeared out in the new distribution

functions; therefore, we may call them the coarse-grained distribution functions. The hierarchy equations for the cumulant correlation functions are also obtained by setting

$$Q(\{\zeta\}, t) = \exp\Big[\int d1\ \zeta(1) f(1, t) + \tfrac{1}{2}\int d1\ d2\ \zeta(1)\zeta(2) g(1, 2, t) + (1/3!)\int d1\ d2\ d3\ \zeta(1)\zeta(2)\zeta(3) h(1, 2, 3, t) + \cdots\Big] \tag{69}$$

where $g(1, 2, t)$ is the pair correlation function, $h(1, 2, 3, t)$ is the three-body cumulant correlation function, etc. The equilibrium solution is given by

$$Q_{\mathrm{eq}}(\{\zeta\}) = \exp\Big[\int d1\ \zeta(1) f_{\mathrm{M}}(v_1)\Big] \tag{70}$$

$f_{\mathrm{M}}(v)$ being the Maxwell distribution function. The Boltzmann equation is obtained if we neglect cumulant correlation functions higher than the second (no long-range correlation); in this case, the distribution of the particle number in a cell of μ space is Poissonian, independent of one another. The cumulant correlation function does not vanish in general in nonequilibrium. The long-range pair correlation function is investigated in Section 5.

4. STOCHASTIC NATURE OF THE RANDOM FORCE

We show that the collision increment $\Delta S(1, t)$ determined by Eq. (38) can be expressed as a linear superposition of random variables obeying a Poisson distribution independent of one another (multi-Poissonian). This fact was already argued by Kogan and Shul'man intuitively on the analogy of shot noise.[11] Let us consider the number of binary collisions occurring in the small time interval $t \sim t + \Delta t$ such that the two colliding particles are located initially in cells Δ_1 and Δ_2 and transferred finally to cells Δ_1' and Δ_2'. This number will be denoted by $\Delta J_{12}^{1'2'}(t)$. The increments $\Delta S(1, t)$ and ΔX are expressed as

$$\int_{\Delta_1} d\bar{1}\ \Delta S(\bar{1}, t) = \sum_{\Delta_2}\sum_{\Delta_1'}\sum_{\Delta_2'} [-\Delta J_{12}^{1'2'}(t) + \Delta J_{1'2'}^{12}(t)] \tag{71}$$

$$\Delta X(t) = \tfrac{1}{2}\sum_{\Delta_1}\sum_{\Delta_2}\sum_{\Delta_1'}\sum_{\Delta_2'} [\alpha(1') + \alpha(2') - \alpha(1) - \alpha(2)]\, \Delta J_{12}^{1'2'}(t) \tag{72}$$

where the integration with respect to $\bar{1}$ is limited to within Δ_1 and the function $\alpha(1)$ is assumed not to vary appreciably in one cell. It is natural to

expect that the collision numbers $\Delta J_{12}^{1'2'}(t)$ obey a Poisson distribution with mean value

$$\Delta t \int_{\Delta_1} d\bar{1} \int_{\Delta_2} d\bar{2} \int_{\Delta_{1'}} d\bar{1}' \int_{\Delta_{2'}} d\bar{2}' \, A_{\bar{1}\bar{2}}^{\bar{1}'\bar{2}'} \langle F(1, t)F(2, t)\rangle \tag{73}$$

This is equivalent to the assumption that the binary collisions in the time interval $t \sim t + \Delta t$ take place randomly and independent of one another. We note that the characteristic functional of a Poissonian random variable, say x, is

$$\langle e^{\alpha x}\rangle = e^{(e^{\alpha}-1)\langle x\rangle} \tag{74}$$

and that the collision numbers $\Delta J_{12}^{1'2'}(t)$ are doubly counted in Eq. (72) because of the relation

$$\Delta J_{12}^{1'2'}(t) = \Delta J_{1'2'}^{12}(t) \tag{75}$$

Now, we can write down the characteristic functional of $\Delta S(1, t)$ in the same form as Eq. (38)

$$\begin{aligned}
&\langle \exp(\Delta X)\rangle \\
&\quad = \exp\Bigg(\tfrac{1}{2} \sum_{\Delta_1} \sum_{\Delta_2} \sum_{\Delta_{1'}} \sum_{\Delta_{2'}} \{\exp[\alpha(1') + \alpha(2') - \alpha(1) - \alpha(2)] - 1\} \\
&\qquad \times \langle \Delta J_{12}^{1'2'}(t)\rangle\Bigg) \\
&\quad = 1 + \tfrac{1}{2} \sum_{\Delta_1} \sum_{\Delta_2} \sum_{\Delta_{1'}} \sum_{\Delta_{2'}} \{\exp[\alpha(1') + \alpha(2') - \alpha(1) - \alpha(2)] - 1\} \\
&\qquad \times \langle \Delta J_{12}^{1'2'}(t)\rangle + \cdots
\end{aligned} \tag{76}$$

where $\langle \Delta J_{12}^{1'2'}(t)\rangle$ is considered as infinitesimal.

We recall here that the theory of generalized Brownian motion has usually assumed the Gaussian nature of the random force.[17,18] However, our expressions (38) and (42) contain $\alpha(1)$ in an exponential manner, showing that $\Delta S(1, t)$ is multi-Poissonian. The phase-space random increment $\Delta R(1, t)$ can be approximated as Gaussian in two special cases. One is the case in which all of the particle numbers in one cell are much larger than unity.[3,4,19,20] If this holds, the distribution $P(\{f\}, t)$ suffers only a small change from a single binary collision. The collisional change of $P(\{f\}, t)$ Eq. (61), can be expanded as

$$\begin{aligned}
&\tfrac{1}{2} \sum_{i,j,k,l} A_{ij}^{kl} \Bigg[\left(\frac{\partial}{\partial f_i} + \frac{\partial}{\partial f_j} + \frac{\partial}{\partial f_k} - \frac{\partial}{\partial f_l} \right) \\
&\qquad + \frac{1}{2} \left(\frac{\partial}{\partial f_i} + \frac{\partial}{\partial f_j} - \frac{\partial}{\partial f_k} - \frac{\partial}{\partial f_l} \right)^2 \Bigg] f_i f_j P(\{f\}, t)
\end{aligned} \tag{77}$$

Therefore, the master equation for $P(\{f\}, t)$ reduces to a Fokker–Planck equation which contains the derivatives $\delta/\delta f$ up to the second power. It is well known that gross variables with a Gaussian random source are governed by a Fokker–Planck equation. The condition $f_i \gg 1$ is interpreted as

$$\Delta N = n\lambda^3(\Delta v/v_{\rm th})^3 \gg 1 \tag{78}$$

where λ is the linear spatial size satisfying Eq. (11), Δv is the linear size in the velocity subspace, n is the average number density, and $v_{\rm th}$ is the thermal velocity. We note, however, that the number ΔN may be either greater or smaller than unity. The sole condition on λ, Eq. (11), does not determine the magnitude of ΔN. Furthermore, the linear size in the velocity subspace Δv can be chosen arbitrarily. Our results so far obtained do not depend on the magnitude of Δv.

The second special case is the weak coupling case, in which small-angle collisions are dominant. The quantity $\alpha(1') + \alpha(2') - \alpha(1) - \alpha(2)$ in Eq. (42) can be considered to be small when the cross section is large for small deflection angle (an example is given by the Coulombic interaction). In this case Eq. (42) can be expanded as

$$\begin{aligned}
&\left\langle \exp\left[\int d1\, \alpha(1)\, \Delta R(1, t)\right]\right\rangle \\
&\quad = 1 + \tfrac{1}{4}\Delta t \int d1\, d2\, d1'\, d2'\, A_{12}^{1'2'}[\alpha(1') + \alpha(2') - \alpha(1) - \alpha(2)]^2 \\
&\qquad \times \langle F(1, t)F(2, t)\rangle + \cdots \\
&\quad = 1 + \frac{1}{16}\Delta t \int d1\, d2\, d1'\, d2'\, A_{12}^{1'2'} \sum_{\mu,\nu} \Delta_\mu \Delta_\nu \left[\frac{\partial}{\partial v_{1\mu}}\alpha(1) - \frac{\partial}{\partial v_{2\mu}}\alpha(2)\right] \\
&\qquad \times \left[\frac{\partial}{\partial v_{1\nu}}\alpha(1) - \frac{\partial}{\partial v_{2\nu}}\alpha(2)\right]\langle F(1, t)F(2, t)\rangle + \cdots
\end{aligned} \tag{79}$$

where

$$\boldsymbol{\Delta} = 2(\mathbf{v}_1' - \mathbf{v}_1) = 2(\mathbf{v}_2 - \mathbf{v}_2') \tag{80}$$

is the collisional change in the relative velocity, and use has been made of the expansions

$$\begin{aligned}
\alpha(\mathbf{r}_1, \mathbf{v}_1') &= \alpha(\mathbf{r}_1, \mathbf{v}_1) + \tfrac{1}{2}\boldsymbol{\Delta}\cdot(\partial/\partial\mathbf{v}_1)\alpha(\mathbf{r}_1, \mathbf{v}_1) + \cdots \\
\alpha(\mathbf{r}_2, \mathbf{v}_2') &= \alpha(\mathbf{r}_2, \mathbf{v}_2) - \tfrac{1}{2}\boldsymbol{\Delta}\cdot(\partial/\partial\mathbf{v}_2)\alpha(\mathbf{r}_2, \mathbf{v}_2) + \cdots
\end{aligned} \tag{81}$$

The second moment of the random force is given by

$$\langle R(1, t_1)R(2, t_2)\rangle$$
$$= \delta(t_1 - t_2) \sum_{\mu,\nu} \frac{\partial^2}{\partial v_{1\mu}\, \partial v_{2\nu}} \Big[\delta(1 - 2) \int d\bar{1}\, B_{\mu\nu}(1, \bar{1}) \langle F(1, t)F(\bar{1}, t)\rangle$$
$$- B_{\mu\nu}(1, 2)\langle F(1, t)F(2, t)\rangle \Big] \tag{82}$$

where the tensor $B_{\mu\nu}(1, 2)$ is defined by

$$B_{\mu\nu}(1, 2) = \tfrac{1}{4}\delta(\mathbf{r}_1 - \mathbf{r}_2)v_{12}(v_{12}^2\, \delta_{\mu\nu} - v_{12\mu}v_{12\nu})$$
$$\times\, 2\pi \int_0^\pi d\chi\, (\sin\chi)\sigma(v_{12}, \chi)(1 - \cos\chi) \tag{83}$$

In general, the random force is Gaussian when the potential is much smaller than the kinetic energy of one particle, because the random increment itself can be expanded in the potential. Examples are an assembly of colloidal particles suspended in fluids, electrons coupled with acoustic phonons, and plasmas with sufficiently small plasma parameter.

5. LONG-RANGE CORRELATION IN NONEQUILIBRIUM

The coarse-grained hierarchy equations (66), which are related to the characteristic functional of $F(1, t)$ by Eqs. (63) and (64), can describe long-range molecular correlations extending much farther than the force range, if we are not interested in short-range correlations. They exist generally in nonequilibrium and give rise to the deviation of molecular chaos. In what follows we examine the long-range pair correlation function $g(1, 2, t)$ by neglecting the third cumulant correlation function $h(1, 2, 3, t)$. This is the simplest approximation. The cumulant correlation functions are defined by

$$f(1, 2, t) = f(1, t)f(2, t) + g(1, 2, t) \tag{84}$$

$$f(1, 2, 3, t) = f(1, t)f(2, t)f(3, t) + f(1, t)g(2, 3, t)$$
$$+ f(2, t)g(3, 1, t) + f(3, t)g(1, 2, t) + h(1, 2, 3, t) \tag{85}$$

It is plausible, except for a turbulent state, to assume that higher order cumulant correlation functions are smaller than the products of those of lower order. Of course, this assumption is invalid in small spatial regions $|\mathbf{r}_1 - \mathbf{r}_j| \lesssim a$. However, these regions are smeared out and do not appear in

Eqs. (66); this allows the truncation of Eqs. (66). Then, we obtain coupled equations for $f(1, t)$ and $g(1, 2, t)$:

$$\left[\frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1}\right] f(1, t) = \int dx_2 \, T_{12}^{(0)}[f(1, t) f(2, t) + g(1, 2, t)] \tag{86}$$

$$\left[\frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} + \mathbf{v}_2 \cdot \frac{\partial}{\partial \mathbf{r}_2} + J(1, t) + J(2, t) - T_{12}^{(0)}\right] g(1, 2, t)$$
$$= T_{12}^{(0)} f(1, t) f(2, t) \tag{87}$$

where $J(1, t)$ is the linearized collision operator around $f(1, t)$ and is written as

$$J(1, t)\alpha(1) = -\int dx_2 \, T_{12}^{(0)}[\alpha(1) f(2, t) + \alpha(2) f(1, t)] \tag{88}$$

where $\alpha(1, t)$ is an arbitrary function. Integration of Eq. (87) is performed to give

$$g(1, 2, t) = U(1, 2, t, t_0) g(1, 2, t_0) + \int_{t_0}^{t} d\tau \, U(1, 2, t, \tau) T_{12}^{(0)} f(1, \tau) f(2, \tau) \tag{89}$$

where the propagation operator $U(1, 2, t, \tau)$ is defined as the solution of the operator equation

$$\frac{\partial}{\partial t} U(1, 2, t, \tau) = -\left[\mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} + J(1, t) + \mathbf{v}_2 \cdot \frac{\partial}{\partial \mathbf{r}_2} + J(2, t) - T_{12}^{(0)}\right] U(1, 2, t, \tau)$$
$$U(1, 2, \tau, \tau) = 1 \tag{90}$$

The first term on the right-hand side of Eq. (89) represents the propagation of the initial pair correlation and decays after a sufficiently long time; the second represents the creation of long-range pair correlations, which is effective only when the one-body distribution function deviates from Maxwellian. It is easily verified from the definition of $T_{12}^{(0)}$, Eq. (67), that the right-hand side of Eq. (87) vanishes when $f(1, t)$ is Maxwellian. However, $f(1, t)$ deviates from Maxwellian in nonequilibrium and the right-hand side of Eq. (87) does not vanish. As the second term of Eq. (89) indicates, correlation between two particles is created when they encounter, and then propagates in space and time. The operator $\mathbf{v} \cdot \partial/\partial \mathbf{r} + J$ expressed damped propagation of a single particle suffering isolated binary collisions with other particles. Equation (86) differs from the ordinary Boltzmann equation by the presence of the pair correlation function in the collision integral. The collision term involving $g(1, 2, t)$ accounts for sequences of correlated binary collisions taking place over a large spatial region and for a long time compared with the force range and the collision duration time, respectively. We consider the following two special cases briefly.

5.1. Small Deviations from Equilibrium

We can derive the so-called ring operator first introduced by Kawasaki and Oppenheim[21] by linearizing Eqs. (86) and (89) around equilibrium. The small deviation $\delta f(1, t) = f(1, t) - f_M(1)$ obeys the linear equation

$$\left[\frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} + J_0(1)\right] \delta f(1, t) + \int_{t_0}^{t} d\tau \int dx_2 \, M(1, 2, t - \tau) \, \delta f(2, \tau) = \mathscr{D}(1, t) \tag{91}$$

where $J_0(1)$ is the linearized Boltzmann collision operator and the term $\mathscr{D}(1, t)$ expresses the effect of the initial pair correlation coming from the first term of Eq. (89) and vanishes after a long time. The memory function $M(1, 2, t)$ is nothing but the ring operator and its Laplace transformation is written as

$$\begin{aligned} &\int dx_2 \, M(1, 2, \epsilon)\alpha(2) \\ &\quad = \int_0^\infty dt \, e^{-\epsilon t} \int dx_2 \, M(1, 2, t)\alpha(2) \\ &\quad = \int dx_2 \, T_{12}^{(0)} \left[\frac{1}{\epsilon + \mathbf{v}_1 \cdot \partial/\partial \mathbf{r}_1 + J_0(1) + \mathbf{v}_2 \cdot \partial/\partial \mathbf{r}_2 + J_0(2) - T_{12}^{(0)}}\right. \\ &\qquad \left. - \frac{1}{\epsilon + \mathbf{v}_1 \cdot \partial/\partial \mathbf{r}_1 + \mathbf{v}_2 \cdot \partial/\partial \mathbf{r}_2}\right] T_{12}^{(0)}[\alpha(1) f_M^{(2)}(2) + \alpha(2) f_M(1)] \end{aligned} \tag{92}$$

where, using the relation

$$T_{12}^{(0)} \frac{1}{\epsilon + \mathbf{v}_1 \cdot \partial/\partial \mathbf{r}_1 + \mathbf{v}_2 \cdot \partial/\partial \mathbf{r}_2} T_{12}^{(0)} = 0 \tag{93}$$

we have subtracted the second term in the bracket of Eq. (92). This relation comes from the fact that a recollision of two particles occurs only when they are scattered by other particles and assures that the operator $M(1, \epsilon)$, whose integral kernel is $M(1, 2, \epsilon)$, is of higher order than $J_0(1)$ in the density. The ring operator gives rise to the long tail in various flux time correlation functions[22] and the logarithmic term in the density expansion of transport coefficients.[21,23]

5.2. Steady States

We now examine the pair correlation function in a steady laminar flow. Equations (86) and (87) have various solutions corresponding to various macroscopic boundary conditions on the system. It is always assumed in

deriving the hydrodynamic equations from the Boltzmann equation that the one-body distribution function is given by the local equilibrium Maxwell distribution function in the limit of small velocity and temperature gradients. Then, the creation rate of the pair correlation, the right-hand side of Eq. (87), vanishes in the zeroth order of the inhomogeneities of the system and starts from the first order. In particular, there is no creation rate at equilibrium, and there is a constant source in a steady flow in which steady velocity and temperature gradients are set up. We assume that the number density $n(\mathbf{r})$, the velocity field $\mathbf{u}(\mathbf{r})$, and the temperature $T(\mathbf{r})$ vary slowly in space compared with the mean free path and there is no enhanced hydrodynamic fluctuation due to instabilities. Then, the steady one-body distribution function $f_s(1)$ is given in the zeroth order of the inhomogeneities of the system by the local equilibrium Maxwellian

$$f_l(1) = n(\mathbf{r}_1)\left[\frac{2\pi T(\mathbf{r}_1)}{m}\right]^{-d/2} \exp\left\{-\frac{m}{2T(\mathbf{r}_1)}[\mathbf{v} - \mathbf{u}(\mathbf{r}_1)]^2\right\} \tag{94}$$

The steady pair correlation function is given, from Eq. (87), by

$$g_s(1, 2) = \left[\mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} + J_s(1) + \mathbf{v}_2 \cdot \frac{\partial}{\partial \mathbf{r}_2} + J_s(2)\right]^{-1} T_{12}^{(0)}[f_s(1)f_s(2) + g_s(1, 2)] \tag{95}$$

Exact treatment of the above equation is difficult, so we consider $g_s(1, 2)$ for $l < r_{12} < L$. Here, l is the mean free path and L the characteristic length over which the hydrodynamic variables change appreciably. In this region the pair correlations arise from hydrodynamic origin, as will be shown in what follows. We first note that the operator $\mathbf{v}_1 \cdot \partial/\partial \mathbf{r}_1 + J_s(1)$ takes small values when it operates on functions of the form

$$\begin{Bmatrix} 1 \\ \mathbf{v}_1 \\ v_1^2 \end{Bmatrix} f_s(\mathbf{r}_1, \mathbf{v}_1)\beta(\mathbf{r}_1) \tag{96}$$

where $\beta(\mathbf{r}_1)$ is a slowly varying function in space. Therefore, Eq. (95) may be approximated as

$$\begin{aligned} g_s(1, 2) = &\left[\mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} + J_s(1) + \mathbf{v}_2 \cdot \frac{\partial}{\partial \mathbf{r}_2} + J_s(2)\right]^{-1} \\ &\times \sum_{1 \le i, j \le d+2} \alpha_i(1)\alpha_j(2) \frac{1}{n(1)} f_s(1) \frac{1}{n(2)} f_s(2) \\ &\times \int d\mathbf{v}_1\, d\mathbf{v}_2\, \alpha_i(1)\alpha_j(2) T_{12}^{(0)}[f_s(1)f_s(2) + g_s(1, 2)] \end{aligned} \tag{97}$$

where the $\alpha_i(1)$ are linear combinations of 1, $\mathbf{v}_1$, and ${v_1}^2$ satisfying the normalization condition

$$\int d\mathbf{v}_1\, \alpha_i(1)\alpha_j(1) f_s(1) = \delta_{ij} \tag{98}$$

Using the relation

$$\int d\mathbf{v}_1\, d\mathbf{v}_2\, [\alpha_i(1) + \alpha_i(2)][\alpha_j(1) + \alpha_j(2)] T_{12}^{(0)}[\cdots] = 0 \tag{99}$$

and Eq. (86) we obtain

$$\int d\mathbf{v}_1\, d\mathbf{v}_2\, \alpha_i(1)\alpha_j(2) T_{12}^{(0)}[f_s(1)f_s(2) + g_s(1, 2)]$$
$$= -\delta(\mathbf{r}_1 - \mathbf{r}_2) \int d\mathbf{v}_1\, \alpha_i(1)\alpha_j(1)\mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} f_s(1) \tag{100}$$

To first order in the inhomogeneities we can set

$$\mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} f_s(1) \simeq \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} f_l(1)$$
$$\simeq \left[\left(\frac{m}{2T(\mathbf{r}_1)} {c_1}^2 - \frac{d+2}{2} \right) \mathbf{c}_1 \frac{1}{T(\mathbf{r}_1)} \frac{\partial}{\partial \mathbf{r}_1} T(\mathbf{r}_1) \right.$$
$$\left. + \frac{m}{T(\mathbf{r}_1)} \left(\mathbf{c}_1 \mathbf{c}_1 - \frac{1}{d} {c_1}^2 I \right) : \frac{\partial}{\partial \mathbf{r}_1} \mathbf{u}(\mathbf{r}_1) \right] f_l(1) \tag{101}$$

where

$$\mathbf{c}_1 = \mathbf{v}_1 - \mathbf{u}(\mathbf{r}_1) \tag{102}$$

is the relative velocity with respect to the flow. Equation (100) can be obtained from the hydrodynamic equations without dissipative fluxes. Therefore, $g_s(1, 2)$ is written as

$$g_s(1, 2) = \left[\mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} + J_s(1) + \mathbf{v}_2 \cdot \frac{\partial}{\partial \mathbf{r}_2} + J_s(2) \right]^{-1} \delta(\mathbf{r}_1 - \mathbf{r}_2) f_l(1) f_l(2)$$
$$\times \left\{ \mathbf{c}_1 \mathbf{c}_2 : A(\mathbf{r}_1) + \left[\left(\frac{m}{T(\mathbf{r}_1)} {c_2}^2 - d \right) \mathbf{c}_1 + \left(\frac{m}{T(\mathbf{r}_1)} {c_1}^2 - d \right) \mathbf{c}_2 \right] \cdot \mathbf{B}(\mathbf{r}_1) \right\} \tag{103}$$

where the tensor A and the vector B are defined by

$$A_{\alpha\beta}(\mathbf{r}) = -\frac{m}{n(\mathbf{r})T(\mathbf{r})} \left[\frac{\partial}{\partial x_\alpha} u_\beta(\mathbf{r}) + \frac{\partial}{\partial x_\beta} u_\alpha(\mathbf{r}) - \frac{2}{d} \delta_{\alpha\beta} \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{u}(\mathbf{r}) \right] \tag{104}$$

$$B_\alpha(\mathbf{r}) = -\frac{dt^2}{2d} \frac{1}{n(\mathbf{r})T(\mathbf{r})} \frac{\partial}{\partial x_\alpha} T(\mathbf{r}) \tag{105}$$

If the spatial separation r_{12} does not exceed the distance L over which the hydrodynamic variables change appreciably, the system can be considered homogeneous in the first approximation. The static pair correlation function $g_s(1, 2)$ is thus Fourier-transformed in relative spatial coordinates as

$$\begin{aligned} g_{s\mathbf{k}} &= \int d(\mathbf{r}_2 - \mathbf{r}_1)\{\exp[i\mathbf{k}\cdot(\mathbf{r}_2 - \mathbf{r}_1)]\}g_s(1, 2) \\ &\simeq [i\mathbf{k}\cdot(\mathbf{c}_1 - \mathbf{c}_2) + J_l(1) + J_l(2)]^{-1} f_l(1) f_l(2) \\ &\quad \times \left\{ \mathbf{c}_1\mathbf{c}_2 : A + \left[\left(\frac{m}{T} c_2^2 - d \right)\mathbf{c}_1 + \left(\frac{m}{T} c_1^2 - d \right)\mathbf{c}_2 \right]\mathbf{B} \right\} \end{aligned} \tag{106}$$

Here, $g_s(1, 2)$ is considered as a function of $\mathbf{r}_2 - \mathbf{r}_1$, $\frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$, $\mathbf{c}_1$, and $\mathbf{c}_2$, and J_s is replaced by J_l, which is the linearized Boltzmann operator around f_l. The operator $i\mathbf{k}\cdot\mathbf{v} + J_l$ has five (four) discrete eigenfunctions with small eigenvalues given by $\pm ick + \frac{1}{2}\Gamma k^2$, νk^2, and λk^2 up to the second power of k in three (two) dimensions.[24] Therefore, $g_{s\mathbf{k}}$ is proportional to k^{-2} for $L^{-1} < k < l^{-1}$ and $g_s(1, 2)$ behaves for $l < r_{12} < L$ like the Coulombic potential,

$$g_s(1, 2) \simeq \begin{cases} \log(1/\mathbf{r}_{12}) & \text{for } d = 2 \\ 1/r_{12} & \text{for } d = 3 \end{cases} \tag{107}$$

The inhomogeneities are not neglected for $r_{12} > L$.

After detailed calculation we obtain

$$\begin{aligned} g_s(1, 2) = \frac{1}{4\pi}\left(\log\frac{1}{r_{12}}\right) f_l(1) f_l(2) \Bigg\{ & \left(\frac{1}{\nu} + \frac{1}{\Gamma} \right)\mathbf{c}_1\mathbf{c}_2 : A \\ & + \frac{1}{2(\nu + \lambda)} \left[\left(\frac{m}{T} c_1^2 - 4 \right)\mathbf{c}^2 + \left(\frac{m}{T} c_2^2 - 4 \right)\mathbf{c}_1 \right]\cdot\mathbf{B} \\ & + \frac{m}{2\Gamma T}(c_1^2\mathbf{c}_2 + c_2^2\mathbf{c}_1)\cdot\mathbf{B} \Bigg\} \end{aligned} \tag{108}$$

for $d = 2$; and

$$\begin{aligned} g_s(1, 2) = \frac{1}{32\pi}\frac{1}{r_{12}} f_l(1) f_l(2) \Bigg\{ & \frac{1}{\nu}(\mathbf{c}_1 + \mathbf{c}_1^{\parallel})(\mathbf{c}_2 + \mathbf{c}_2^{\parallel}) + \frac{1}{\Gamma}\mathbf{c}_1^{\perp}\mathbf{c}_2^{\perp} \\ & - \left[\frac{1}{2}\left(\frac{1}{\nu} + \frac{1}{\Gamma} \right)\left(\mathbf{c}_1^{\perp}\cdot\mathbf{c}_2^{\perp} + \frac{2m}{15\Gamma T} \right) c_1^2 c_2^2 \right] \frac{\mathbf{r}_{12}\mathbf{r}_{12}}{r_{12}^2} \Bigg\} : A \\ & + \frac{1}{40\pi}\frac{1}{r_{12}} f_l(1) f_l(2) \Bigg\{ \frac{3}{\nu + \lambda} \left[\left(\frac{m}{T} c_1^2 - 5 \right)(\mathbf{c}_2 + \mathbf{c}_2^{\parallel}) \right. \\ & \left. + \left(\frac{m}{T} c_2^2 - 5 \right)(\mathbf{c}_1 + \mathbf{c}_1^{\parallel}) \right] + \frac{2m}{\Gamma T}(c_1^2\mathbf{c}_2^{\perp} + c_2^2\mathbf{c}_1^{\perp}) \Bigg\}\cdot\mathbf{B} \end{aligned} \tag{109}$$

for $d = 3$, where

$$\begin{aligned} \mathbf{c}_1^{\parallel} &= (\mathbf{r}_{12}/r_{12}^2)(\mathbf{r}_{12}\cdot\mathbf{c}_1), \qquad c_1^{\perp} = \mathbf{c}_1 - \mathbf{c}_1^{\parallel} \\ \mathbf{c}_2^{\parallel} &= (\mathbf{r}_{12}/r_{12}^2)(\mathbf{r}_{12}\cdot\mathbf{c}_2), \qquad \mathbf{c}_2^{\perp} = \mathbf{c}_2 - \mathbf{c}_2^{\parallel} \end{aligned} \tag{110}$$

and ν is the kinetic viscosity, $\lambda = \kappa/\rho c_p$ is the thermal diffusivity, and Γ is the sound attenuation constant.

This result shows that the pair correlation extends much farther than the mean free path at nonequilibrium, although the behavior for $r_{12} > L$ is not considered.

We can readily note from Eq. (93) that the long-range pair correlation function is given approximately by its projection on the hydrodynamic variables, that is,

$$g_s(1, 2) \simeq \sum_{1 \leqslant i,j \leqslant d+2} \alpha_i(1)\alpha_j(2) f_i(1) f_i(2) \langle A_i(\mathbf{r}_1, t) A_j(\mathbf{r}_2, t) \rangle \tag{111}$$

where the α_i are linear combinations of 1, $\mathbf{v}$, and v^2 chosen to satisfy Eq. (98), and the A_i are the hydrodynamic variables defined by

$$A_i(\mathbf{r}, t) = \int d\mathbf{v}\, \alpha_i(\mathbf{v}) F(\mathbf{r}, \mathbf{v}, t) \tag{112}$$

where $F(\mathbf{r}, \mathbf{v}, t)$ is the coarse-grained density in μ space, Eq. (12). The nonequilibrium averages $\langle A_i(1) A_j(2) \rangle$ can be calculated from Eq. (103) by considering its first $(d + 2) \times (d + 2)$ moments. We note that the same result can be obtained from the nonlinear fluctuating hydrodynamic equations by linearizing them around mean values, and the long-range behavior of $g_s(1, 2)$ for $r_{12} > L$ may be calculated from them. The above arguments clearly indicate that long-range molecular correlations such as Eqs. (108) and (109) exist generally in nonequilibrium fluids irrespective of density, although our discussion is limited to dilute gases.

6. REMARKS

We must treat the collision in a probabilistic way in order to be able to write down intuitively the collision term of the Boltzmann equation; the following assumptions are involved:

(i) In each binary collision only the initial and final states of two particles are considered and the intermediate details are not followed. The impact parameter b and the azimuthal angle ψ are assumed to take various values with equal probabilities.

(ii) The collision rate is assumed to be proportional to the product $f(\mathbf{r}, \mathbf{v}_1, t) f(\mathbf{r}, \mathbf{v}_2, t)$, where $\mathbf{v}_1$ and $\mathbf{v}_2$ are the initial velocities of the two particles. This is the molecular chaos hypothesis.

The first assumption can be justified if we assume that the multibody distribution functions change slowly in space and time compared with the force range a and the collision duration time, respectively; this procedure is called the coarse-graining of the BBGKY hierarchy equations in Section 3. The molecular chaos hypothesis, on the other hand, has not been used in this paper. The resultant equations are the coarse-grained hierarchy equations (66), which take into account sequences of correlated binary collisions and neglect genuine multiple collisions. Genuine multiple collisions, in which more than three particles interact simultaneously, can be neglected as long as the system is sufficiently dilute and give contributions to transport coefficients analytic in the density. Moreover, the Enskog equation accounts for a large part of the genuine multiple collisions,[25] and long-range correlations arise mainly from sequences of correlated binary collisions.

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