*Journal of Statistical Physics, Vol. 25, No. 1, 1981*

# Nonequilibrium Fluctuations in $\mu$ Space

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*Received June 3, 1980*

The properties of fluctuations in $\mu$ space in or outside thermal equilibrium are obtained by solving hierarchies of equations derived either from the Liouville or the Master equation. In particular we study the one-, two-, etc., time correlation functions that describe the spatial and temporal behavior of the fluctuations in $\mu$ space. Explicit solutions are obtained for a dilute gas. The Langevin approach is briefly discussed. Our results are compared with those obtained in the extensive literature, which is reviewed in some detail.

**KEY WORDS:** Fluctuations; nonequilibrium statistical mechanics; master equation; time correlation functions; hierarchy equations, master hierarchy; pair correlation function.

## 1. INTRODUCTION

In this paper we derive in a systematic way the properties of $\mu$ space fluctuations at equal or different times in gases in or outside thermal equilibrium. In fact we develop a hierarchy method in which we derive and solve hierarchies of coupled equations for these fluctuations, obtained either from the Liouville equation or from a master equation.

The hierarchy of equations derived from the Liouville equation can be solved using standard methods of kinetic theory. We will treat here in particular the case of a gas of hard spheres. This is done solely for the purpose of a simpler and more transparent treatment, since in the hard-sphere case the strong interparticle interaction can be taken into account directly, while for other strong short-range interactions resummations have

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0022-4715/81/0500-0153$03.00/0

to be performed. Nevertheless our results can readily be generalized to systems with more realistic interparticle interactions.

The hierarchy of equations derived from the master equation for a dilute gas gives a description of equal or unequal time fluctuations only on a scale large compared to the range of the interparticle forces. This master hierarchy is valid for strong short-range interactions in general and can be solved by the same simple method as used in the kinetic theory of hard spheres.

In this way we will obtain from a unified point of view many results that have been derived and rederived in the literature over and over again. In order to compare more completely with the existing literature, we discuss also the Langevin approach for deriving equations for fluctuations which uses a fluctuating Boltzmann equation as a starting point.

We will restrict ourselves to concrete results for a classical dilute gas, with short-range additive intermolecular forces. The gas may be in equilibrium or not in equilibrium; in the latter case the deviations from equilibrium are supposed to be small so that only terms linear in the gradients of the local density, energy, and velocity have to be taken into account. Furthermore, we are interested only in fluctuations on a spatial scale that is much larger than the range of the intermolecular forces, but not necessarily larger than the mean free path. Therefore, we will study fluctuations in $\mu$ space, although in case the scale of the fluctuations is much larger than the mean free path hydrodynamical equations can be used.

The hierarchy method has been traditionally developed for the calculation of distribution functions, as in the derivation of the Boltzmann equation from the Liouville equation, or for the computation of equilibrium time correlation functions, as for the evaluation of the Green–Kubo formulas for the transport coefficients. Here we show that this same method can be used to obtain multitime distribution and correlation functions both in equilibrium and nonequilibrium. Since these multitime correlation functions determine all the properties of the fluctuations in the gas, this method furnishes a theory of fluctuations at the same time.

A interesting result is that the equal time pair correlation function of a gas, not in equilibrium[3] exhibits long range correlations that decay only proportional to the inverse distance between two particles. This long range correlation in the pair correlation function has been noticed before by various authors as will be discussed in Section 3. It contributes to the correlation between density fluctuations and, thus, influences the light scattering of a gas not in equilibrium. The theory also suggests that not

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[3] In equilibrium the pair and higher correlation functions vanish at low densities and distances large compared to the range of the forces. In our considerations we use systems in which only the average number of particles is given (i.e., described by a grand canonical ensemble in the equilibrium case), so that the correlation functions do not have a long range part of $O(1/V)$.

only the pair correlation function but also all higher-order correlation functions exhibit long-range correlations in a nonequilibrium gas.

The plan of the paper is as follows. In Section 2 we develop the hierarchy method in kinetic theory for the one- and two-time distribution and correlation functions. Details of the derivation of the hierarchies are discussed in Appendix A. In Section 3 we solve the hierarchy equations in a systematic fashion for a dilute gas and for distances large compared to the range of the interparticle forces. In Section 4 we sketch how the methods employed in kinetic theory can be used in a completely analogous fashion in the master equation approach. As a typical example, we treat the equal and unequal time fluctuations in the occupation numbers of discrete cells in velocity space. In Section 5 we sketch the Langevin approach to the calculation of fluctuations. Here we start from a fluctuating Boltzmann equation and make the usual random and Gaussian assumptions on the statistical properties of the fluctuating force in this equation. In order to obtain an explicit expression for the correlation strength of the fluctuating force additional data are required that can be obtained from the hierarchy methods. A comparison of our results with corresponding results from the literature is made at the end of Sections 3, 4, and 5. In particular a proof for the equivalence of the explicit expressions given here and in the literature for the equal time correlation functions is presented in Appendix D.

Special applications of the hierarchy method are discussed in two Appendixes: the computation of the fluctuations of a tagged particle in a dilute gas not in equilibrium in Appendix B and the computation of a three-time correlation function, which gives the correlations between fluctuations at three different times, in Appendix C.

## 2. HIERARCHIES FOR DISTRIBUTION AND CORRELATION FUNCTIONS

As pointed out before, we will illustrate the derivation of the hierarchies of equations that hold for the distribution or the correlation functions on the special case of a system of hard spheres. The case of a smooth potential was discussed in another publication.$^{(1)}$

A hierarchy for the distribution functions of a hard-sphere system can be derived from that for the microscopic densities $\psi(1t)$, $\psi(12t)$, ... defined by

$$\begin{aligned} \psi(1t) &\equiv \psi(x_1 t) = \sum_{i=1}^{N} \delta(X_i(t) - x_1) \\ \psi(12t) &\equiv \psi(x_1 x_2 t) = \sum_{i \neq j}^{N} \sum^{N} \delta(X_i(t) - x_1)\delta(X_j(t) - x_2) \text{ etc.} \end{aligned} \tag{2.1}$$

by averaging over an appropriate initial ensemble. In (2.1) the lower-case variables $x_i \equiv (\mathbf{r}_i, \mathbf{v}_i)$ $(i = 1, 2, \ldots, N)$ are field variables while the capital variables $X_i(t) \equiv (\mathbf{R}_i(t), \mathbf{V}_i(t))$ represent the phase of the $i$th particle of the system at time $t$ in $\Gamma$ space. Only the dependence on the field variables is indicated explicitly in the $\psi$ functions.

A hierarchy for the $\psi$ functions in the case of a system of hard spheres can be derived using pseudo-streaming operators,$^{(2)}$ leading to the Klimontovich hierarchy$^{(3)}$ for hard spheres as shown in Appendix A:

$$\left[\frac{\partial}{\partial t} + L_0(1)\right]\psi(1t) = \int d2\, \bar{T}_-(12)\psi(12t) \tag{2.2a}$$

$$\left[\frac{\partial}{\partial t} + L_0(12) - \bar{T}_-(12)\right]\psi(12t) = \int d3\,(1 + P_{12})\bar{T}_-(12)\psi(123t) \text{ etc.} \tag{2.2b}$$

Here the operator $L_0(1)$ is defined by

$$L_0(1) \equiv L_0(x_1) = \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} \tag{2.3}$$

while $L_0(12) = L_0(1) + L_0(2)$. The binary collision operator $\bar{T}_-(12)$ is given by

$$\bar{T}_-(12) = \sigma^2 \int_{\mathbf{v}_{12}\cdot\hat{\sigma} > 0} d\hat{\sigma}\, |\mathbf{v}_{12} \cdot \hat{\sigma}| \left[\delta(\mathbf{r}_{12} - \sigma\hat{\sigma}) b_{\hat{\sigma}} - \delta(\mathbf{r}_{12} + \sigma\hat{\sigma})\right] \tag{2.4a}$$

where $\sigma$ is the diameter of the hard spheres and $\hat{\sigma}$ a unit vector that characterizes the geometry of the binary collision between the two colliding spheres 1 and 2 at contact. The operator $b_{\hat{\sigma}}$ replaces the velocities $\mathbf{v}_1$ and $\mathbf{v}_2$ of the two spheres before the collision by those after the collision $\mathbf{v}_1', \mathbf{v}_2'$:

$$\begin{aligned} b_{\hat{\sigma}}\mathbf{v}_1 &\equiv \mathbf{v}_1' = \mathbf{v}_1 - \hat{\sigma}(\hat{\sigma} \cdot \mathbf{v}_{12}) \\ b_{\hat{\sigma}}\mathbf{v}_2 &\equiv \mathbf{v}_2' = \mathbf{v}_2 + \hat{\sigma}(\hat{\sigma} \cdot \mathbf{v}_{12}) \end{aligned} \tag{2.4b}$$

where $\mathbf{v}_{12} = \mathbf{v}_1 - \mathbf{v}_2$. The permutation operator $P_{12}$ interchanges the labels of the particles 1 and 2.

The one-time distribution functions are averages of the $\psi$ functions over the phases $X_1 \ldots X_N$, taken over some initial ensemble $D(1 \ldots N, 0)$:

$$\begin{aligned} f(1t) &\equiv f(x_1 t) = \langle \psi(1t) \rangle \\ f(12t) &\equiv f(x_1 x_2 t) = \langle \psi(12t) \rangle \text{ etc.} \end{aligned} \tag{2.5}$$

where

$$\langle \psi(i \ldots jt) \rangle = \sum_N \int dX_1 \ldots \int dX_N\, D(X_1 \ldots X_N, 0)\psi(i \ldots jt) \tag{2.6}$$

Here we consider a grand ensemble in which only the average number of particles is defined and the bulk limit is understood to have been taken on the right-hand side of (2.5). The distribution function $f(1t)$ is the probability density to find a particle in phase $1 \equiv x_1$ at time $t$, etc.

A hierarchy for the one-time distribution functions can be obtained directly by averaging the hierarchy (2.2) with $D(X_1 \ldots X_N, 0)$. The result is the following $B$-$B$-$G$-$K$-$Y$ hierarchy[4] for a system of hard spheres$^{(2,4,5)}$:

$$\begin{gathered}\left[\frac{\partial}{\partial t} + L_0(1)\right] f(1t) = \int d2\, \bar{T}_-(12) f(12t) \\ \left[\frac{\partial}{\partial t} + L_0(12) - \bar{T}_-(12)\right] f(12t) = \int d3\,(1 + P_{12}) \bar{T}_-(13) f(123t) \text{ etc.}\end{gathered} \tag{2.7}$$

A hierarchy for two-time distribution functions $f(1t, 1't')$, $f(12t, 1't')$, etc. can be derived in a similar fashion from (2.2). For smooth potentials this has been done by Tolmachev,$^{(7)}$ Vineyard,$^{(8)}$ and others,$^{(9-11)}$ while for hard spheres we refer to Refs. 1, 12, and 13. The two-time distribution functions are defined by the relations

$$\begin{gathered} f(1t, 1't') \equiv f(x_1 t, x_1' t') = \langle \psi(1t) \psi(1't') \rangle \\ f(12t, 1', t') \equiv f(x_1 x_2 t, x_1' t') = \langle \psi(12t) \psi(1't') \rangle \text{ etc.}\end{gathered} \tag{2.8}$$

where the averages on the right-hand side are defined by Eq. (2.6). Here $f(1t, 1't')$ is the probability density to find a particle in the phase $x_1$ at time $t$ and a particle (the same or another) in the phase $x_1'$ at time $t'$ and similarly for $f(12t, 1't')$, etc. One verifies easily from (2.1), (2.5), and (2.8) that

$$f(1t, 2t) = f(12t) + \delta(1 - 2) f(1t) \tag{2.9}$$

A hierarchy of equations for $f(1t, 1't')$, etc., can be obtained in similar way as for $f(1t)$, etc., before. As shown in Appendix A, one finds for $t > t'$

$$\left[\frac{\partial}{\partial t} + L_0(1)\right] f(1t, 1't') = \int d2\, \bar{T}_-(12) f(12t, 1't') \tag{2.10}$$

$$\left[\frac{\partial}{\partial t} + L_0(12) - \bar{T}_-(12)\right] f(12t, 1't') = \int d3 (1 + P_{12}) \bar{T}_-(13) f(123t, 1't') \text{etc.}$$

In this same fashion hierarchies can be derived for multitime distribution functions in general.

In connection with the weakening of correlations between groups of particles with increasing spatial separation and also for the discussion of

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[4] This hierarchy is valid only for $t > 0$. It is interesting to observe that for $t < 0$, one obtains a "backward" hierarchy with $\bar{T}_-$ replaced by $-\bar{T}_+$ as follows from Appendix A. In the low-density approximation, discussed in Section 3, the first equation of the backward hierarchy reduces to the "backward" or "anti"-Boltzmann equation discussed by Cohen and Berlin.$^{(28)}$

correlations between fluctuations it is convenient to introduce a set of cluster functions: the correlation functions.

The one-, two-, multitime correlation functions are defined in a way analogous to the Ursell functions in equilibrium statistical mechanics:

$$\begin{aligned} f(12t) &= f(1t)f(2t) + g(12t) \\ f(123t) &= f(1t)f(2t)f(3t) + f(1t)g(23t) + f(2t)g(13t) \\ &\quad + f(3t)g(12t) + g(123t) \text{ etc.} \end{aligned} \tag{2.11}$$

for the one-time correlation functions $g(12t)$, $g(123t)$, etc., and by

$$\begin{aligned} f(1t,1't') &= f(1t)f(1't') + C(1t,1't') \\ f(12t,1't') &= f(1t)f(2t)f(1't') + f(1t)C(2t,1't') + f(2t)C(1t,1't') \\ &\quad + f(1't')g(12t) + C(12t,1't') \text{ etc.} \end{aligned} \tag{2.12}$$

for the two-time correlation functions $C(1t,1't')$, $C(12t,1't')$, etc.

The $g$ and $C$ functions will have a cluster property, i.e., decrease for separated configurations of the particles they depend on if the separation between the particles exceeds a correlation length. These functions also determine the correlations between microscopic density fluctuations. For, if one introduces $\delta\psi(1t) = \psi(1t) - \langle\psi(1t)\rangle = \psi(1t) - f(1t)$ as the density fluctuation at the point $x_1$ in $\mu$ space, then its unequal time correlation function is given by

$$\langle\delta\psi(1t)\delta\psi(1't')\rangle = f(1t,1't') - f(1t)f(1't') = C(1t,1't') \tag{2.13}$$

while the equal time correlation function is given by

$$\langle\delta\psi(1t)\delta\psi(2t)\rangle = C(1t,2t) = \delta(1-2)f(1t) + g(12t) \tag{2.14}$$

as follows from (2.9) and (2.12).

A hierarchy for these correlation functions follows directly from (2.10) -(2.12):

$$\left[\frac{\partial}{\partial t} + L_0(1)\right] f(1t) = \int d2\,\bar{T}_-(12)\left[f(1t)f(2t) + g(12t)\right] \tag{2.15a}$$

$$\begin{aligned} \left[\frac{\partial}{\partial t} + L_0(12) - \bar{T}_-(12)\right] g(12t) &= \bar{T}_-(12)f(1t)f(2t) \\ &\quad + \int d3\,(1+P_{12})\bar{T}_-(13)\left[(1+P_{13})\right. \\ &\quad \times \left. f(3t)g(12t) + g(123t)\right] \text{ etc.} \end{aligned} \tag{2.15b}$$

for the one-time correlation functions and

$$\left[\frac{\partial}{\partial t}+L_0(1)\right]C(1t,1't')=\int d2\,\bar{T}_-(12)(1+P_{12})f(2t)C(1t,1't')$$
$$+\int d2\,\bar{T}_-(12)C(12t,1't')\text{ etc.}\qquad(2.16)$$

for the two-time correlation functions for $t > t'$.

We note that each term in Eq. (2.15) or (2.16) is connected in the sense that all particle labels in each term are interconnected by $\bar{T}$ operators, $g$ or $C$ functions.

## 3. LOW-DENSITY RESULTS

In this section we want to derive kinetic equations for the correlation functions for fluctuations in $\mu$ space at equal and unequal times in a dilute gas in or outside thermal equilibrium. We are interested here in particular in correlations of fluctuations at relative distances large compared to the hard-sphere diameter $\sigma$ but not necessarily large compared to the mean free path. Our starting point is the hierarchies of equations for the distribution and correlation functions derived in the previous section. Each hierarchy forms a set of coupled equations, where the right-hand side of each equation in the hierarchy contains a distribution or correlation function that involves one more particle than appears on the left-hand side of the equation. In order to obtain a set of closed equations for the distribution or correlation functions the hierarchy equations have to be decoupled. Thereto the same methods can be applied that have been used before to obtain closed kinetic equations for nonequilibrium distribution functions and equilibrium time correlation functions.

For a smooth potential many methods are available to achieve this. Although these methods could and many have been applied to the case of interest here, they are unfortunately rather complicated. However, for the special case of hard spheres a simple, straightforward method exists to derive kinetic equations. This method was introduced by Ernst and Dorfman(13) for the study of the two-time hierarchy in equilibrium, and will be applied here to the hierarchies (2.15) and (2.16), derived in the previous section, in order to illustrate how these equations can be solved.

The main idea is that kinetic equations for the correlation functions can be derived correct to increasing orders in the density by neglecting correlation functions involving an increasing number of particles. First, in Eq. (2.15a) the ansatz is made, which will be verified later, that $\bar{T}_-(12)$ $g(12t)$ is of higher order in the density than $\bar{T}_-(12)f(1t)f(2t)$ and that, similarly, in Eq. (2.15b), $\overline{T}_-(13)g(123t)$ is of higher order in the density than $\overline{T}_-(13)f(3t)g(12t)$ for all phases 2. For a kinetic equation to lowest order in the density $\overline{T}_-(12)g(12t)$ and $\overline{T}_-(12)g(123t)$ can therefore be neglected in Eq. (2.15). In addition, since we are only interested in distances $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2| \gg \sigma$, we can make a further simplification by replacing $\overline{T}_-(12)$ by a point $T$ operator defined by

$$\hat{T}(12) = \delta(\mathbf{r}_{12})T_0(12) = \delta(\mathbf{r}_{12})\sigma^2\int_{\mathbf{v}_{12}\cdot\hat{\sigma}>0} d\hat{\sigma}\,|\mathbf{v}_{12}\cdot\hat{\sigma}|\left[b_{\hat{\sigma}} - 1\right] \tag{3.1}$$

$\hat{T}(12)$ follows from $\overline{T}_-(12)$ by ignoring the $\sigma\hat{\sigma}$ in the delta functions on the right-hand side of Eq. (2.4a), which implies that we neglect the difference in position between the two colliding particles.

Using the above in Eq. (2.15a) leads immediately to the nonlinear Boltzmann equation for $f(1t)$:

$$\left[\frac{\partial}{\partial t} + L_0(1)\right]f(1t) = \int d2\,\hat{T}(12)f(1t)f(2t) \tag{3.2}$$

while Eq. (2.15b) yields the following equation for the equal time correlation function $g(12t)$:

$$\left[\frac{\partial}{\partial t} + L(1t) + L(2t)\right]g(12t) = \hat{T}(12)f(1t)f(2t) \tag{3.3}$$

where $(i = 1, 2)$

$$L(it) = L_0(i) - \Lambda(it) \tag{3.4a}$$

with

$$\Lambda(it) = \int d3\,\hat{T}(i3)(1 + P_{i3})f(3t) \tag{3.4b}$$

Using (2.14), (3.2), and (3.3), the following equation for $C(1t, 2t)$ can be obtained valid for $r_{12} \gg \sigma$:

$$\left[\frac{\partial}{\partial t} + L(1t) + L(2t)\right]C(1t, 2t) = \Gamma(12t) \tag{3.5a}$$

with

$$\begin{aligned}\Gamma(12t) = {} & -\left[\Lambda(1t) + \Lambda(2t)\right]\delta(1-2)f(1t) \\ & + \delta(1-2)\int d3\,\hat{T}(13)f(1t)f(3t) + \hat{T}(12)f(1t)f(2t)\end{aligned} \tag{3.5b}$$

which is our main result for the correlations between equal time fluctuations in a dilute nonequilibrium gas. Both in Eq. (3.3) and in Eq. (3.5) the $f(it)$ $(i = 1, 2)$ have to be found from Eq. (3.2). In thermal equilibrium, when $f_{\text{eq}}(i)$ is the Maxwellian velocity distribution function, the last two terms on the right-hand side in Eq. (3.5b) vanish, i.e.,

$$\Gamma_{\text{eq}}(12) = -\left[\Lambda_{\text{eq}}(1) + \Lambda_{\text{eq}}(2)\right]\delta(1-2)f_{\text{eq}}(1) \tag{3.6}$$

and ($i = 1,2$):

$$\Lambda_{\mathrm{eq}}(i) = \int d3\,\hat{T}(i3)(1 + P_{i3})f_{\mathrm{eq}}(3) \tag{3.7}$$

We emphasize that the contribution of $g(12t)$ to $C(12t)$ [cf. Eq. (2.14)] has been kept in Eq. (3.5) and is in general *not* of higher order in the density as one might think.$^{(14)}$ For, the space and time derivatives of $\delta(1-2)f(1t)$ and $g(12t)$ are of the same order in the density for linear deviations from equilibrium as follows immediately from the last two terms on the right-hand side of Eq. (3.5b). For later use we also note that the solution of Eq. (3.3) for $g(12t)$ can easily be found for the special case of a stationary nonequilibrium state. In that case $f_{\mathrm{ss}}(1)$ is independent of $t$ and can be found using the Chapman–Enskog procedure in Eq. (3.2), while the stationary pair correlation function $g_{\mathrm{ss}}(12)$ follows from (3.3) to be$^{(14)}$

$$g_{\mathrm{ss}}(12) = \left[L_{\mathrm{ss}}(1) + L_{\mathrm{ss}}(2)\right]^{-1}\hat{T}(12)f_{\mathrm{ss}}(1)f_{\mathrm{ss}}(2) \tag{3.8}$$

where $L_{\mathrm{ss}}(i)$ ($i = 1,2$) is given by Eq. (3.4) with $f(3t)$ replaced by $f_{\mathrm{ss}}(3)$.

Using (3.8) for $g_{\mathrm{ss}}(12)$ in Eq. (2.15a) in the case of a stationary state or the corresponding expression for $g(12t)$ in the general nonequilibrium case, one can verify the ansatz made above for the solution of the hierarchy (2.15).

Finally, we determine the low-density equations for the correlation function $C(1t, 1't')$ describing unequal time fluctuations for distances large compared to $\sigma$. This equation is obtained from Eq. (2.16) by replacing $\bar{T}_-(12)$ by $\hat{T}(12)$ and in the spirit of the above-mentioned solution method, neglecting $C(12t, 1't')$ on the right-hand side. For $t > t'$ one obtains then the equation

$$\left[\frac{\partial}{\partial t} + L(1t)\right]C(1t, 1't') = 0 \tag{3.9}$$

This equation for the unequal time correlation function $C(1t, 1't')$ can be solved with the equal time correlation function $C(1t, 1't)$, given by Eq. (2.14), as initial value. We determine the solution of Eq. (3.9) for the special case of a stationary nonequilibrium state where $C(1t+\tau, 2t) = C_{\mathrm{ss}}(12\tau)$. Using the Laplace transform of Eq. (3.9) combined with (3.8) and (2.14), one obtains for $\tau > 0$

$$\hat{C}_{\mathrm{ss}}(12z) = \left[z + L_{\mathrm{ss}}(1)\right]^{-1}\left[\delta(1-2)f_{\mathrm{ss}}(1) + \left\{L_{\mathrm{ss}}(1) + L_{\mathrm{ss}}(2)\right\}^{-1}\hat{T}(12)f_{\mathrm{ss}}(1)f_{\mathrm{ss}}(2)\right] \tag{3.10}$$

where $z$ is the Laplace transform variable.

One can generalize systematically the low-density results obtained above to higher densities, as has been done for distribution functions and time correlation functions in equilibrium. Thus in particular contributions due to three-body collisions, rings, etc., to $C(1t,2t)$ and $C(1t,1't')$ could be obtained. We will not do so, since the main purpose of this paper is to illustrate that the methods used before to derive kinetic equations for nonequilibrium distribution functions and equilibrium time correlation functions can be extended straightforwardly to equilibrium or nonequilibrium multitime correlation functions.

We now compare the results obtained in this and the previous section on the basis of kinetic equations with those obtained in the literature. In doing so, one should bear in mind that our equations obtained for hard-sphere potentials can be generalized to smooth potentials by replacing(1) the operator $\hat{T}(12)$ in (3.1) with

$$\hat{T}(12) = \delta(\mathbf{r}_{12})T_0(\mathbf{v}_1\mathbf{v}_2) = \delta(\mathbf{r}_{12})\int d\Omega\, I(g,\chi)(b_\Omega - 1) \tag{3.11}$$

where $g = |\mathbf{v}_1 - \mathbf{v}_2|$, $I(g,\chi)$ is the differential scattering cross section, $d\Omega = \sin\chi\, d\chi\, d\phi$ with $\chi$ the scattering angle in the binary collision between the particles 1 and 2, and $\phi$ the azimuthal angle of the plane in which the scattering takes place. The operator $b_\Omega$ acts only on the velocities $\mathbf{v}_i$ such that $b_\Omega \mathbf{v}_i = \mathbf{v}_i'$ $(i = 1,2)$, where the primed velocities are the velocities of the particles after the binary collision. For the special case of hard spheres $I(g,\chi)$ is constant and independent of $g$.

Equal time correlation functions $g(12t)$ and $C(1t,2t)$ for smooth potentials have been discussed by many authors.(15–19) Explicit equations equivalent to our equations (3.3)–(3.5)[5] have been derived by Kogan(17) on the basis of Bogolubov's functional method, by Blatt *et al.*(16) and Kritz *et al.*(58) using a hierarchy method essentially equivalent to that of Refs. 9 and 10, and by Ronis *et al.*(19),[6] using a binary collision expansion. The results given by Morita *et al.*, (18) obtained on the basis of the BBGKY hierarchy by a scaling method, differ from ours, however.[7]

An interesting feature of Eq. (3.3) or (3.5) for the nonequilibrium equal time pair function $g(12t)$ or $C(1t,2t)$ in a dilute gas is that its solution has a long range in certain directions, where it behaves as $1/r_{12}$. This was already noticed by Ludwig(20) in 1962, but has been appreciated and fully investigated only recently by Onuki,(21) Ronis *et al.*,(22,19) Kirkpatrick *et al.*,(14,23) and Tremblay, Siggia, and Arai.(24) The asymptotic behavior of the pair correlation function is not $1/r_{12}$ but will have a different form that falls off

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[5] In Refs. 16 and 17 the right-hand side of Eq. (3.3) is replaced by the low-density limit of $\theta(12)[f(1t)f(2t) + g(12t)]$, where $\theta(12) = m^{-1}(\partial/\partial\mathbf{v}_1 - \partial/\partial\mathbf{v}_2)\cdot\partial\phi(r_{12})/\partial\mathbf{r}_{12}$ and $\phi(r_{12})$ is the intermolecular pair potential. In the limit of hard spheres and low densities this leads to the right-hand side of our Eq. (3.3).

[6] In Ref. 19 $g_{ss}(12)$ of Eq. (3.8) is given to linear order in the deviations from equilibrium, in which case the $L_{ss}(i)$ $(i = 1,2)$ can be replaced by its equilibrium expression.

[7] In Ref. 18 an inconsistent expression $\Gamma(12t)$ is obtained since the term $\hat{T}(12)f(1t)f(2t)$, which is of the same order as the other terms in Eq. (3.5b), is missing.

faster than $1/r_{12}$ and involves the gradients in the local temperature or velocity of the system. It can be obtained using the method of Ernst *et al.*(25) developed for the case of a shear flow. The directions and the strength of these long-range correlations depend on the gradients in the system.

For the two-time correlation function $C(1t, 1't')$ most authors derive results for thermal equilibrium.(7,26,27,10,6) They obtain Eq. (3.9) with $L(1t)$ replaced by $L_{\mathrm{eq}}(1) = L_0(1) - \Lambda_{\mathrm{eq}}(1)$, defined in Eqs. (2.3) and (3.7), and solve it with the first term on the right-hand side of Eq. (2.14) as an initial condition, where $f(1t)$ is replaced by $f_{\mathrm{eq}}(1)$. Tolmachev(7) applied Bogolubov's functional method, Van Leeuwen and Yip(26) a diagrammatic method combined with the binary collision expansion, and Chappell(27) as well as Saleeby and Lewis(10) a hierarchy method(35,9,10) to solve the two-time hierarchy for a smooth potential. Their results agree with those obtained here. Van Beijeren *et al.*(6) give a rigorous derivation of Eq. (3.9) for hard spheres for times smaller than the mean free time in the so-called Grad limit, using Lanford's method of deriving the Boltzmann equation.(29) Spohn(30) has recently generalized these results to the case of a hard-sphere gas not in thermal equilibrium and his results agree with ours, as will be shown in Appendix D.

The two-time correlation function for the nonequilibrium case has been considered in Refs. 9, 12, and 31. Hinton(9) uses the hierarchy method for a smooth potential to derive an equation for $C(1t, 1't')$ equivalent to (3.9). However, he solves this equation with only the first term on the right-hand side of Eq. (2.14) as an initial condition for $C(1t, 2t)$. The neglect of $g(12t)$ in (2.14) leads to unphysical results in the case of a gas not in equilibrium, as has been discussed in Refs. 1 and 14. Gantsevich *et al.*(31) develop a kinetic method to obtain unequal time fluctuation correlations between electrons in a semiconductor in a stationary state. When applied to dilute gases their method leads to our Eqs. (3.3)–(3.9) for that case. It is not possible to compare our results with those of Tsuge and Sagara(12) because these authors do not derive a closed equation[8] for the unequal time correlation function $C(1t, 1't')$, nor do they indicate how to obtain the equal time correlation function, which is needed as an initial value for such an equation.

The hierarchy method used here to obtain results for the one- and two-time correlation functions can easily be specialized to the case of a test particle in a dilute gas or generalized to the case of multitime correlation

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[8] In deriving an equation for $C(1t, 1't')$ valid for low densities, Tsugé and Sagara do not neglect the full $C(12t, 1't')$ as we do, but keep the contributions to $C(12t, 1't')$ for which the particle at the field point 1′ is identical to either the particle at 1 or at 2. This is inconsistent since both contributions are higher-order density corrections to Eq. (3.9).

functions. The test particle case is discussed in Appendix B, while results for the three-time correlation function are obtained in Appendix C.

Fluctuations of a test particle have been considered by many authors for plasmas(32,33) as well as for dilute gases in equilibrium(26,34,27,10,6,7) or not in equilibrium.(9,12) Our results agree with those obtained in Refs. 6, 9, 10, 26, and 27. The difference between these results and those of Ref. 34 has been explained in Ref. 9. The difference with Ref. 12 is discussed in Appendix A.

Our result for the three-time correlation function reduces for the case of thermal equilibrium to that derived by Dufty(35) on the basis of a different method.

## 4. MASTER HIERARCHY

Fluctuations in a dilute gas not in equilibrium have been studied frequently on the basis of a master equation.(36) We restrict ourselves here to the case of a spatially homogeneous system(37–39) in a volume $\Omega$ but the considerations can be generalized to spatially inhomogeneous systems as well.(20,21,40–42) We are interested in particular in the analogy between the hierarchy method discussed in Section 2 and the master equation studied in this section. For this purpose we develop here a master hierarchy starting from the master equation in velocity space, just as we derived hierarchies in Section 2, from what was essentially the Liouville equation.

Following Siegert(43) we divide the velocity space of a single particle in a number of discrete cells labeled by a Greek index $\alpha$, $\beta$, . . . . If $N_\alpha$ is the number of particles in cell $\alpha$, then the basic quantity we consider is the conditional probability $P(\mathbf{N}t\,|\,\mathbf{N}'t')$ for finding the set of occupation numbers $\mathbf{N} = (N_\alpha, N_\beta, \ldots)$ of the cells at time $t$, given the set of occupation numbers $\mathbf{N}' = (N'_\alpha, N'_\beta, \ldots)$ at time $t'$. $P(\mathbf{N}t\,|\,\mathbf{N}'t')$ satisfies for $t > t'$ a master equation of the form

$$\frac{\partial P(\mathbf{N}t\,|\,\mathbf{N}'t')}{\partial t} = \frac{1}{2\Omega} \sum_{\alpha\beta\gamma\delta} w_{\alpha\beta\gamma\delta}\left[E_\alpha^{-1}E_\beta^{-1}E_\gamma E_\delta - 1\right] N_\gamma N_\delta P(\mathbf{N}t\,|\,\mathbf{N}'t') \tag{4.1}$$

Here $(1/2\Omega) w_{\alpha\beta\gamma\delta} N_\gamma N_\delta$ is the transition probability per unit time for a binary collision between particles with initial velocities $(v_\gamma, v_\delta)$ in cells $\gamma$ and $\delta$ and final velocities $(v_\alpha, v_\beta)$ in cells $\alpha$ and $\beta$. $w_{\alpha\beta\gamma\delta}$ is symmetric for the interchange of the indices $\alpha$ and $\beta$, the indices $\gamma$ and $\delta$, and satisfies microscopic reversibility, i.e., $w_{\alpha\beta\gamma\delta}$ is also symmetric in the pairs of indices $\alpha\beta$ and $\gamma\delta$. The step operator $E$ is defined by $E_\alpha f(N_\alpha) = f(N_\alpha + 1)$ and satisfies the relation

$$\sum_{N=0}^{\infty} g(N) E f(N) = \sum_{N=0}^{\infty} f(N) E^{-1} g(N) \tag{4.2}$$

for any functions $f$ and $g$, if either $g(0) = 0$ or $f(-1) = 0$, conditions that are always fulfilled in our applications.

For a given initial condition $P(\mathbf{N}',0)$, the one-time probability distribution to have the set of occupation numbers $\mathbf{N}$ at time $t$ is then

$$P(\mathbf{N}t) = P(\mathbf{N}t\,|\,\mathbf{N}'0)P(\mathbf{N}'0) \tag{4.3}$$

while the two-time probability distribution function for $\mathbf{N}$ at $t$ and $\mathbf{N}'$ at $t'$ is

$$P(\mathbf{N}t,\mathbf{N}'t') = P(\mathbf{N}t\,|\,\mathbf{N}'t')P(\mathbf{N}'t') \tag{4.4}$$

Since the master equation describes a Markov process, $P(\mathbf{N}t\,|\,\mathbf{N}'t')$ suffices to calculate all multitime probability distributions.

In order to exhibit the analogy with the hierarchy method we derive here first from the master equation hierarchy equations for the moments of $P(\mathbf{N}t)$: the one-time distribution functions $\langle N_\mu(t)\rangle$, $\langle N_\mu(t)N_\nu(t)\rangle$, etc., which correspond to the one-time distribution functions $f(1t)$, $f(12t)$, etc., of Section 2, as well as for the moments of $P(\mathbf{N}t,\mathbf{N}'t')$: the two-time distribution functions $\langle N_\mu(t)N_\nu(t')\rangle$, $\langle N_\mu(t)N_\nu(t)N_\lambda(t')\rangle$, etc., that correspond to the two-time distribution functions $f(1t,1't')$, $f(12t,1't')$, etc., of Section 2.

To derive the master hierarchy for the one-time distribution functions, we multiply Eq. (4.1) by $N_{\mu_1}$, $N_{\mu_1}N_{\mu_2}, \ldots$ and sum over all $\mathbf{N}$ to obtain in general for the $s$-cell distribution function the equation

$$\begin{aligned}&\frac{d}{dt}\langle N_{\mu_1}N_{\mu_2}\ldots N_{\mu_s}\rangle\\ &\quad= \frac{1}{2\Omega}\sum_{\alpha\beta\gamma\delta} w_{\alpha\beta\gamma\delta}\langle N_\gamma N_\delta\big[E_\delta^{-1}E_\gamma^{-1}E_\alpha E_\beta - 1\big]N_{\mu_1}N_{\mu_2}\ldots N_{\mu_{s+1}}\rangle\end{aligned} \tag{4.5}$$

In obtaining this equation, we have used Eq. (4.2) so that on the right-hand side of Eq. (4.5) the function $P(\mathbf{N}t\,|\,\mathbf{N}'t')$ is understood to be to the left of the $E$ operators. Using the relations

$$\begin{aligned}E_\gamma^{-1}E_\delta^{-1}E_\alpha E_\beta N_\mu &= N_\mu + \Delta_\mu\\ E_\gamma^{-1}E_\delta^{-1}E_\alpha E_\beta N_{\mu_1}N_{\mu_2} &= N_{\mu_1}N_{\mu_2} + N_{\mu_1}\Delta_{\mu_2} + N_{\mu_2}\Delta_{\mu_1} + \Delta_{\mu_1}\Delta_{\mu_2}\end{aligned} \tag{4.6a}$$

with

$$\Delta_\mu = \delta_{\alpha\mu} + \delta_{\beta\mu} - \delta_{\gamma\mu} - \delta_{\delta\mu} \tag{4.6b}$$

which follow directly from the definition of the $E$ operators, the right-hand side of Eq. (4.5) can be further evaluated to yield the following hierarchy for the one-time distribution functions(43,38–41):

$$\begin{aligned}\frac{d}{dt}\langle N_\mu(t)\rangle &= \frac{1}{2\Omega}\sum_{\alpha\beta\gamma\delta} w_{\alpha\beta\gamma\delta}\Delta_\mu\langle N_\gamma(t)N_\delta(t)\rangle\\ \frac{d}{dt}\langle N_\mu(t)N_\nu(t)\rangle &= \frac{1}{2\Omega}\sum_{\alpha\beta\gamma\delta} w_{\alpha\beta\gamma\delta}(1 + P_{\mu\nu})\Delta_\mu\langle N_\gamma(t)N_\delta(t)N_\nu(t)\rangle\\ &\quad+ \frac{1}{2\Omega}\sum_{\alpha\beta\gamma\delta} w_{\alpha\beta\gamma\delta}\Delta_\mu\Delta_\nu\langle N_\gamma(t)N_\delta(t)\rangle, \text{ etc.}\end{aligned} \tag{4.7}$$

The hierarchy for the two-time distribution functions $\langle N_\mu(t)N_\rho(t')\rangle$, etc., can be obtained in a similar fashion using (4.4) and (4.1). The result is identical to (4.7) except that the one-time distribution functions $\langle N_\mu(t)\ldots\rangle$, etc., should be replaced by corresponding two-time distribution functions $\langle N_\mu(t)\ldots N_\rho(t')\rangle$, etc., containing the additional $N_\rho(t')$. These distribution functions have been considered by Malek-Mansour *et al.*(41) for the case of thermal equilibrium.

As in Section 2 we can introduce correlation functions $\langle\cdots\rangle_c$, or cumulants as they are usually called in this context, instead of the distribution functions $\langle\cdots\rangle$. They are defined by

$$\begin{aligned}\langle N_\alpha N_\beta\rangle &= \langle N_\alpha\rangle\langle N_\beta\rangle + \langle N_\alpha N_\beta\rangle_c\\ \langle N_\alpha N_\beta N_\gamma\rangle &= \langle N_\alpha\rangle\langle N_\beta\rangle\langle N_\gamma\rangle + \langle N_\alpha\rangle\langle N_\beta N_\gamma\rangle_c\\ &\quad + \langle N_\beta\rangle\langle N_\alpha N_\gamma\rangle_c + \langle N_\gamma\rangle\langle N_\alpha N_\beta\rangle_c\\ &\quad + \langle N_\alpha N_\beta N_\gamma\rangle_c, \text{ etc.}\end{aligned} \tag{4.8}$$

for the one-time correlation functions and similarly for multitime correlation functions. As in Section 2, the two lowest multitime correlation functions are simply related to the correlation functions of time-dependent fluctuations:

$$\begin{aligned}\langle\delta N_\alpha(t)\delta N_\beta(t')\rangle &= \langle N_\alpha(t)N_\beta(t')\rangle_c\\ \langle\delta N_\alpha(t)\delta N_\beta(t')\delta N_\gamma(t'')\rangle &= \langle N_\alpha(t)N_\beta(t')N_\gamma(t'')\rangle_c\end{aligned} \tag{4.9}$$

where $\delta N_\alpha(t) = N_\alpha(t) - \langle N_\alpha(t)\rangle$ is the fluctuation of the number of particles $N_\alpha(t)$ in cell $\alpha$ at time $t$. The time arguments in (4.9) may be equal or different.

Using (4.8) and (4.9) in (4.7), the following hierarchy for the equal time correlation functions, analogous to (2.15) is obtained:

$$\frac{d}{dt}\langle N_\mu(t)\rangle = \frac{1}{2\Omega}\sum_{\alpha\beta\gamma\delta} w_{\alpha\beta\gamma\delta}\Delta_\mu\big[\langle N_\gamma(t)\rangle\langle N_\delta(t)\rangle + \langle\delta N_\gamma(t)\delta N_\delta(t)\rangle\big] \tag{4.10a}$$

$$\begin{aligned}&\frac{d}{dt}\langle\delta N_\mu(t)\delta N_\nu(t)\rangle\\ &\quad = \frac{1}{2\Omega}\sum_{\alpha\beta\gamma\delta} w_{\alpha\beta\gamma\delta}(1 + P_{\mu\nu})\Delta_\mu\big[(1 + P_{\gamma\delta})\langle N_\gamma(t)\rangle\langle\delta N_\delta(t)\delta N_\nu(t)\rangle\\ &\qquad + \langle\delta N_\gamma(t)\delta N_\delta(t)\delta N_\nu(t)\rangle\big]\\ &\qquad + \frac{1}{2\Omega}\sum_{\alpha\beta\gamma\delta} w_{\alpha\beta\gamma\delta}\Delta_\mu\Delta_\nu\big[\langle N_\gamma(t)\rangle\langle N_\delta(t)\rangle + \langle\delta N_\gamma(t)\delta N_\delta(t) >\big], \text{ etc.}\end{aligned} \tag{4.10b}$$

In a similar manner one finds for the two-time correlation functions the hierarchy

$$\begin{aligned}\frac{d}{dt}\langle\delta N_\mu(t)\delta N_\nu(t')\rangle &= \frac{1}{2\Omega}\sum_{\alpha\beta\gamma\delta} w_{\alpha\beta\gamma\delta}\Delta_\mu(1+P_{\gamma\delta})\langle N_\gamma(t)\rangle\langle\delta N_\delta(t)\delta N_\nu(t')\rangle \\ &+ \frac{1}{2\Omega}\sum_{\alpha\beta\gamma\delta} w_{\alpha\beta\gamma\delta}\Delta_\mu\langle\delta N_\gamma(t)\delta N_\delta(t)\delta N_\nu(t')\rangle, \text{ etc.} \qquad (4.11)\end{aligned}$$

Like the hierarchies (2.15) and (2.16) in Section 2, the hierarchies (4.10) and (4.11) consist of sets of coupled equations and in order to solve them, they have to be decoupled. This can be done on the basis of the observation that each cell in velocity space contains a large number of particles, so that it seems reasonable to assume that $\langle\delta N_\mu(t)\delta N_\nu(t')\rangle_c$ as well as all the higher correlations $\langle\cdots\rangle_c$ are proportional to the volume $\Omega$ of the system.(44,38) Then the terms on the right-hand side of the hierarchies (4.10) and (4.11) can be ordered in powers of $\Omega$ and the equations can be decoupled and solved by using an expansion in powers of $\Omega^{-1}$.(40,44–46) For the one-time correlation functions one obtains to leading order in $\Omega$ for $\varphi_\mu(t) = \langle N_\mu(t)\rangle/\Omega$ the equation

$$\frac{d}{dt}\varphi_\mu(t) = \frac{1}{2}\sum_{\alpha\beta\gamma\delta} w_{\alpha\beta\gamma\delta}\Delta_\mu\varphi_\gamma(t)\varphi_\delta(t) \qquad (4.12a)$$

or with Eq. (4.6b)

$$\begin{aligned}\frac{d}{dt}\varphi_\alpha(t) &= \sum_{\beta\gamma\delta} w_{\alpha\beta\gamma\delta}(\varphi_\gamma\varphi_\delta - \varphi_\alpha\varphi_\beta) \\ &= \sum_\beta T_0(v_\alpha v_\beta)\varphi_\alpha\varphi_\beta \qquad (4.12b)\end{aligned}$$

where the binary collision operator $T_0(v_\alpha v_\beta)$ is defined for an arbitrary function $h(v_\alpha v_\beta)$ by

$$T_0(v_\alpha v_\beta)h(v_\alpha v_\beta) = \sum_{\gamma\delta} w_{\alpha\beta\gamma\delta}\left[h(v_\gamma v_\delta) - h(v_\alpha v_\beta)\right] \qquad (4.13)$$

Equation (4.12) is the nonlinear Boltzmann equation in discrete velocity space in the spatially homogeneous case and the analogue of Eq. (3.2)

Similarly an equation for the one-time correlation $C_{\mu\nu}(t,t)$ can be obtained from Eq. (4.10b) by collecting the terms of leading order in $\Omega$, i.e.,

$$\begin{aligned}\left[\frac{d}{dt} + L_\mu(t) + L_\nu(t)\right]C_{\mu\nu}(t,t) &= \frac{1}{2}\sum_{\alpha\beta\gamma\delta} w_{\alpha\beta\gamma\delta}\Delta_\mu\Delta_\nu\varphi_\gamma(t)\varphi_\delta(t) \\ &= \Gamma_{\mu\nu}(t) \qquad (4.14)\end{aligned}$$

Here we have defined in general

$$C_{\mu\nu}(t,t') = \frac{1}{\Omega}\langle\delta N_\mu(t)\delta N_\nu(t')\rangle$$

and $L_\mu(t)$ is the Boltzmann collision operator, linearized around the solution $\varphi_\mu(t)$ of Eq. (4.12) and defined for an arbitrary function $h_\mu$ by

$$L_\mu h_\mu = \frac{1}{2}\sum_{\alpha\beta\gamma\delta} w_{\alpha\beta\gamma\delta}\Delta_\mu\left[\varphi_\gamma h_\delta + \varphi_\delta h_\gamma\right]$$

$$= \sum_\nu T_0(v_\mu v_\nu)(1 + P_{\mu\nu})\varphi_\nu h_\mu \tag{4.15}$$

The equations (4.12) and (4.14) describe together the equal time fluctuations in the occupation numbers of the velocity cells in the spatially homogeneous case and are the analogs of the equations (3.2) and (3.5), respectively.

For the unequal time correlation function $C_{\mu\nu}(t,t')$ one obtains in a similar fashion from Eq. (4.11) to leading order in $\Omega$ the equation for $t > t'$:

$$\left[\frac{d}{dt} + L_\mu(t)\right]C_{\mu\nu}(t,t') = 0 \tag{4.16}$$

which is to be solved with the initial condition $C_{\mu\nu}(t,t)$, in complete analogy with Eq. (3.9).

We note the formal analogy between the classification in terms of the volume $\Omega$ of the master hierarchies (4.10) and (4.11) in this section and the classification in terms of the density $n$ of the hierarchies (2.15) and (2.16) in Section 2. For, in this section we neglected the equal time correlation function $\langle\delta N_\gamma \delta N_\delta\rangle$ in the Eqs. (4.10a) since it is of relative order $\Omega^{-1}$ compared to $\langle N_\gamma\rangle\langle N_\delta\rangle$, while we neglected the correlation function $g(12t)$ in Eq. (2.15a) since it was of relative order $n$ compared to $f(1t)f(2t)$. Similarly in Eqs. (4.10b) and (4.11) the equal or unequal time correlation functions $\langle\delta N_\gamma \delta N_\delta \delta N_\nu\rangle$ were ignored since they were of relative order $\Omega^{-1}$ compared to $\langle N_\gamma\rangle\langle\delta N_\delta \delta N_\nu\rangle$, while in Eq. (2.15b) $g(123t)$ was ignored, since it was of relative order $n$ compared to $f(3t)g(12t)$.

We now compare the results derived in this section on the basis of a master equation for fluctuation correlation functions with those obtained in the literature. As easly as 1962 Ludwig$^{(20)}$ discussed equal time fluctuations in $\mu$ space for a dilute gas not in equilibrium. His considerations were based on a master equation for the probability distribution of occupation numbers of cells in $\mu$ space. Onuki$^{(21)}$ derived from the Klimontovich hierarchy a master equation in continuous $\mu$ space variables instead of discrete labels $\alpha$ and from this the equal time hierarchy (2.15) with binary collision operators for a smooth- rather than a hard-sphere potential [cf. (3.11)]. Unequal time correlations of $\mu$ space fluctuations in thermal equilibrium were derived by Seeberg,$^{(40)}$ Malek-Mansour *et al.*,$^{(41)}$ and van den Broeck and Brenig.$^{(42)}$ Their methods are essentially $\mu$ space versions of what was presented here in velocity space.

Equal time correlations of fluctuations in cells in velocity space have been studied for a dilute gas in equilibrium or nonequilibrium by Van Kampen(37) and Kac and Logan.(38,39) By scaling the fluctuations $\delta N_\alpha$ with $\Omega^{-1/2}$ a Fokker–Planck equation is derived from the master equation in leading order in $\Omega^{-1}$, from which equal time correlations of fluctuations can be calculated. As shown in Appendix D, the results obtained in the literature are all equivalent to those derived here except for Ref. 39, where the expression corresponding to $\Gamma_{\mu\nu}(t)$ agrees in the nonequilibrium case with ours only for $\mu \neq \nu$.[9]

## 5. THE FLUCTUATING BOLTZMANN EQUATION

Kinetic and hydrodynamic equations with fluctuating terms, analogous in form to the Langevin equation,(47) have been derived by many authors.(48–55,9,31,38,39,14) They have been used to describe fluctuations around the average behavior of the system inside or outside thermal equilibrium. We will sketch here how a fluctuating Boltzmann equation of the Langevin type can be obtained and used to derive equal and unequal time fluctuation correlations in $\mu$ space. In the case of thermal equilibrium, fluctuations are assumed to be described by the macroscopic regression equation, i.e., the Boltzmann equation linearized around thermal equilibrium with a random force added. The force is defined by giving its statistical properties.(49,50,56) Away from equilibrium the macroscopic regression equation for the average state of the system is the nonlinear Boltzmann equation (3.2). The fluctuations[10] $\delta\psi(1t) = \psi(1t) - f(1t)$ around this average state are described by a Boltzmann equation linearized around the solution $f(1t)$ of (3.2) with a random force $\tilde{S}(1t)$ added.(48,9,53,21,14) In general one has then

$$\frac{\partial \delta\psi(1t)}{\partial t} + L(1t)\delta\psi(1t) = \tilde{S}(1t) \tag{5.1}$$

where $L(1t)$ is defined by Eq. (3.4). The random force $\tilde{S}(1t)$ is determined by its correlations, which in turn are assumed to be completely determined

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[9] Our expression (4.14) contains the term $\delta_{\mu\nu}\sum_{\alpha\beta\gamma} w_{\mu\alpha\beta\gamma}(\varphi_\alpha\varphi_\mu + \varphi_\beta\varphi_\gamma)$, which is missing in Kac and Logan,(39) so that their result does not reduce to the proper equilibrium expression.(38,49,50)

[10] The fluctuations $\delta\psi(1t)$ have to be interpreted in a coarse-grained sense, where the short-wavelength Fourier components of the microscopic $\delta\psi(1t)$, defined in Section 2, are neglected. As a consequence, the averaging $\langle \cdots \rangle^{(0)}$ in Eq. (5.2) is over the short-wavelength Fourier components of $\delta\psi(1t)$.

by[11]

$$\langle \tilde{S}(1t)\rangle^{(0)} = 0 \tag{5.2a}$$

and

$$\langle \tilde{S}(1t)\tilde{S}(2t')\rangle^{(0)} = \Gamma(12t)\delta(t-t') \tag{5.2b}$$

i.e., $\tilde{S}(1t)$ is assumed to be Gaussian white noise. The average $\langle \cdots \rangle^{(0)}$ in (5.2) is a phase space average constrained by a fixed initial value $\psi(10)$.[12] Once $\Gamma(12t)$ is known, one can calculate the pair and all higher correlation functions of $\delta\psi(1t)$ at equal or different times.(47) We will illustrate this first and later determine the actual form of $\Gamma(12t)$. Thus we formally solve Eq. (5.1), leading to

$$\delta\psi(1t) = G_1(t,0)\delta\psi(10) + \int_0^t d\tau\, G_1(t,\tau)\tilde{S}(1\tau) \tag{5.3}$$

where the Green's function $G_1(t,t')$ satisfies for $t > t'$ the equation

$$\frac{\partial}{\partial t} G_1(t,t') = L(1t)G_1(t,t') \tag{5.4}$$

with the initial condition $G_1(t,t) = 1$. $C(1t,2t')$ defined in Eq. (2.13) can then be found with Eqs. (5.3) and (5.2). In order to use (5.2) one has to perform the average $\langle \cdots \rangle$ in two steps: first an average $\langle \cdots \rangle^{(0)}$ at fixed $\psi(10)$ and then an average over $\psi(10)$. For comparison of the results obtained with this Langevin–Boltzmann method with those derived on the basis of the hierarchy method in Section 2, we differentiate the resulting $C(1t,2t')$ with respect to time, yielding for equal times $t' = t$,

$$\left[\frac{\partial}{\partial t} + L(1t) + L(2t)\right]C(1t,2t) = \Gamma(12t) \tag{5.5}$$

and for unequal times $t' \neq t$,

$$\left[\frac{\partial}{\partial t} + L(1t)\right]C(1t,2t') = 0 \tag{5.6}$$

where the initial condition for Eq. (5.6) is given by the solution of Eq. (5.5).

An expression for $\Gamma(12t)$ is not given by the theory but has to be found from elsewhere. In equilibrium the fluctuation–dissipation theorem has been used(49,50,56) to yield Eq. (3.6). Outside equilibrium an explicit expression for $\Gamma(12)$ has been obtained on the basis of phenomenological argu-

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[11] If one is only interested in $C(1t,2t')$ one can relax the conditions (5.2) on $\tilde{S}(1t)$ considerably, as has been by Lax,(57) Akcasu,(46) and Kirkpatrick *et al.*(14): $\tilde{S}(1t)$ need not be Gaussian and the restricted averages $\langle \cdots \rangle^{(0)}$ in (5.2) can be replaced by the full average $\langle \cdots \rangle$ over the initial ensemble provided one assumes in addition that $\langle \psi(10)\tilde{S}(1t)\rangle = 0$ for $t > 0$.

[12] See footnote 10 above.

ments(48,53),[13] or by simply employing Eq. (5.5) as a definition of $\Gamma(12t)$ and calculating the equal time correlation function $C(1t, 2t)$ on the left-hand side of this equation by one of the methods discussed in Sections 3 and 4.

This last procedure has been described in Refs. 36 and 38–40, using the master or Fokker–Planck equation; in Refs. 9, 31, and 14, using kinetic methods and in Ref. 21 using the Klimontovich hierarchy. Kirkpatrick *et al.*(14) employed the equal time hierarchy discussed in Section 3, and the fluctuating Boltzmann equation is used only to express the unequal time correlation function $C(1t, 2t')$ in terms of the equal time correlation function $C(1t, 2t)$ by means of Eq. (5.6).

The explicit expressions for $\Gamma(12t)$ found in the literature vary widely in appearance; we will discuss their equivalence in Appendix D. We note that many more assumptions had to be made in this Langevin method than in the hierarchy or master equation method. In the hierarchy or master equation method all properties of the fluctuations were contained in those of the correlation functions and only assumptions concerning these average quantities were needed. In the Langevin method, on the other hand, additional assumptions are necessary concerning the statistical properties of the fluctuating force, i.e., $\tilde{S}(1t)$ is a random-Gaussian process with correlation strength $\Gamma(12t)$. In fact, in nonequilibrium the correlation of the fluctuating force or equivalently $\Gamma(12t)$ is not determined within the theory, but is usually(9,14,21,31,36,38–40) simply defined through the left-hand side of Eq. (5.5). Of course, any extension of this approach to higher densities will involve even more assumptions.

Apart from these rather *ad hoc* ways of obtaining Langevin-type equations for $\mu$ space fluctuations, Mori(51) has introduced a projection operator method through which equations of motion for microscopic densities such as $\psi(1t)$ in Eq. (2.1) can be cast in the form of a Langevin-type equation. The correlation function for the random force in this equation is given by a formal expression. This method has been applied to fluctuations in $\mu$ space by Mori and many others(52, 54,59,60) but only for equilibrium fluctuations an explicit expression for $\Gamma(12t)$ has been given for the case of a dilute gas with which we can compare our result (3.5b).

## APPENDIX A

The time evolution of the $\psi$ functions in the case of hard spheres is generated by pseudo-streaming operators.(2) These are defined for forward

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[13] Kadomtsev(48) gave already in 1957 Eq. (5.1) for a nonequilibrium gas, where the correlation strength for the random force was given by $\Gamma(12t) = -[\Lambda(1t) + \Lambda(2t)]\delta(1-2)f(1t)$. This result is only correct for the case of thermal equilibrium, as can be seen from Eqs. (3.5) and (3.6).

and backward streaming in time by

$$\psi(1t) = \exp\left[t\mathcal{L}_+(X^N)\right]\psi(1,0) \qquad (t > 0) \tag{A.1a}$$

and

$$\psi(1t) = \exp\left[t\mathcal{L}_-(X^N)\right]\psi(1,0) \qquad (t < 0) \tag{A.1b}$$

respectively, and similarly for $\psi(12t)$, etc. The pseudo-Liouville-operators $\mathcal{L}_\pm$ are given by

$$\mathcal{L}_\pm(X^N) = \sum_{i=1}^{N} L_0(x_i) \pm \frac{1}{2}\sum_{i\neq j}^{N}\sum T_\pm(X_iX_j) \tag{A.2}$$

with binary collision operators

$$T_\pm(X_1X_2) = \sigma^2\int d\hat{\sigma}\,|\mathbf{V}_{12}\cdot\hat{\sigma}|\,\theta(\mp\mathbf{V}_{12}\cdot\hat{\sigma})\,\delta(\mathbf{R}_{12}-\sigma\hat{\sigma})(b_{\hat{\sigma}}-1) \tag{A.3}$$

Here $\theta(x)$ is the unit step function and capital variables refer to $\Gamma$-space variables. The operators $\exp(t\mathcal{L}_\pm)$ generate the physical trajectories in $\Gamma$ space either in the forward or backward direction starting from physical initial positions, in which hard spheres are not overlapping. These streaming operators also generate unphysical trajectories for unphysical, i.e., overlapping, initial conditions. However, we need only to consider here the following type of averages with $t$, $t'$, $t'' > 0$:

$$\begin{aligned} f(1t) = \langle\psi(1t)\rangle = \sum_N \int dX_1 \cdots dX_N\, D(X_1 \cdots X_N, 0) \\ \times \exp\left[t\mathcal{L}_+(X^N)\right]\psi(1,0) \end{aligned} \tag{A.4}$$

$$\begin{aligned} f(1t, 1't') &= \langle\psi(1t)\psi(1't')\rangle \\ &= \int dX_1 \cdots dX_N D(X_1 \cdots X_N, 0) \\ &\quad \times \exp\left[t'\mathcal{L}_\pm(X^N)\right]\psi(1',0)\exp\left[(t-t')\mathcal{L}_\pm(X^N)\right]\psi(1,0) \end{aligned} \tag{A.5}$$

$$\begin{aligned} f(1t, 1't', 1''t'') &= \langle\psi(1t)\psi(1't')\psi(1''t'')\rangle \\ &= \int dX_1 \cdots dX_N D(X_1 \cdots X_N, 0)\exp\left[t''\mathcal{L}_\pm(X^N)\right]\psi(1'',0) \\ &\quad \times \exp\left[(t'-t'')\mathcal{L}_\pm(X^N)\right]\psi(1',0) \\ &\quad \times \exp\left[(t-t')\mathcal{L}_\pm(X^N)\right]\psi(1,0) \text{ etc.} \end{aligned} \tag{A.6}$$

The + or − sign on $\mathcal{L}_\pm$ has to be chosen, depending on whether the sign of the preceding time difference is positive or negative, respectively.

Therefore, inside these averages (A.4)–(A.6) the unphysical overlapping initial configurations have a vanishing weight $D(X^N, 0)$, so that only physical trajectories occur inside the averages.

In order to derive the equations of motion for the distribution functions defined in (A.4)–(A.6) we start from the equation

$$\frac{\partial\psi(1\tau)}{\partial\tau} = \mathcal{L}_{\pm}(X^N)\exp\left[\tau\mathcal{L}_{\pm}(X^N)\right]\psi(1,0) \qquad \text{(A.7a)}$$

$$= -L_0(1)\psi(1\tau) \pm \int d2\,\bar{T}_{\mp}(12)\psi(12\tau) \qquad \text{(A.7b)}$$

where the upper and lower signs refer to $\tau > 0$ or $\tau < 0$, respectively. This equation can be derived using that due to the presence of $\delta$-functions in the definition (2.1), the operators $L_0$ and $T_{\pm}$ can be made to act on the field variables $x_1x_2, \ldots,$ instead of on the $\Gamma$-space variables $X_1X_2, \ldots,$ so that

$$T_{\pm}(X_iX_j)\delta(X_i - x_1)\delta(X_j - x_2) = \bar{T}_{\mp}(x_1x_2)\delta(X_i - x_1)\delta(X_j - x_2) \qquad \text{(A.8)}$$

This is equivalent to taking the Hermitian adjoint, $(T_{\pm})^{\dagger} = \bar{T}_{\mp}$, as shown in Ref. 2. In (A.8)

$$\bar{T}_{\mp}(x_1x_2) \equiv \bar{T}_{\mp}(12)$$
$$= \sigma^2\int d\hat{\sigma}\,|\mathbf{v}_{12}\cdot\hat{\sigma}|\theta(\pm\mathbf{v}_{12}\cdot\hat{\sigma})\{\delta(\mathbf{r}_{12} - \sigma\hat{\sigma})b_{\hat{\sigma}} - \delta(\mathbf{r}_{12} + \sigma\hat{\sigma})\} \qquad \text{(A.9)}$$

The equation of motion (A.7b) is the first of a hierarchy with $\tau = t$, i.e.,

$$\left[\frac{\partial}{\partial t} + \mathcal{L}_0(1)\right]\psi(1t) = \pm\int d2\,\bar{T}_{\mp}(12)\psi(12t) \qquad \text{(A.10)}$$

$$\left[\frac{\partial}{\partial t} + \mathcal{L}_0(12) \mp \bar{T}_{\mp}(12)\right]\psi(12t) = \pm\int d3(1 + P_{12})\bar{T}_{\mp}(13)\psi(123t), \text{ etc.}$$

where the upper and lower signs refer to $t > 0$ and $t < 0$, respectively. For $t > 0$ we obtain the Klimontovich hierarchy (2.2) for the special case of hard spheres. To derive the equations of motion for the two-time distribution functions (2.8), we use Eq. (A.7a) with $\tau = t - t'$ in (A.5) with the result:

$$\left[\frac{\partial}{\partial t} + L_0(1)\right]f(1t, 1't') = \pm\int d2\,\bar{T}_{\mp}(12)f(12t, 1't')$$

$$\left[\frac{\partial}{\partial t} + L_0(12) \mp T_{\mp}(12)\right]f(12t, 1't') \qquad \text{(A.11)}$$

$$= \pm\int d3\,(1 + P_{12})T_{\mp}(13)f(123, 1't'), \text{ etc.}$$

where the upper and lower signs refer to $t > t'$ or $t' < t$, respectively. In Section 2, Eq. (2.10) we have quoted only the result for $t > t'$. The hierarchy for the three-time distribution functions follows from (A.6) and

(A.7a) with $\tau = t - t'$ and has exactly the same form as (A.11), only $f(1 \ldots t, 1't')$ is replaced by $f(1 \ldots t, 1't', 1''t'')$.

## APPENDIX B: FLUCTUATIONS OF A TAGGED PARTICLE

The hierarchy method discussed in Sections 2 and 3 can be directly extended to self-correlations or the two-time distribution functions $f_s(1t, 1't')$, $f_s(12t, 1't')$, etc., of a tagged particle in a gas. These self-distribution functions are defined by

$$\begin{aligned} f_s(1t, 1't') &= \Big\langle \sum_{i=1}^{N} \delta(X_i(t') - x_1')\delta(X_i(t) - x_1)\Big\rangle \\ f_s(12t, 1't') &= \Big\langle \sum_{i \neq j}^{N} \delta(X_i(t') - x_1')\delta(X_i(t) - x_1)\delta(X_j(t) - x_2)\Big\rangle, \text{ etc.} \end{aligned} \tag{B.1}$$

The hierarchy for the functions $f_s(1t, 1't')$, etc., reads for $t > t'$ [cf. Eq. (2.10)]:

$$\left[\frac{\partial}{\partial t} + L_0(1)\right] f_s(1t, 1't') = \int d2\, \bar{T}_-(12) f_s(12t, 1't'), \text{ etc.} \tag{B.2}$$

We can introduce correlation functions by the relations [cf. Eq. (2.12)]:

$$\begin{aligned} f_s(1t, 1't') &= C_s(1t, 1't') \\ f_s(12t, 1't') &= f(2t) C_s(1t, 1't') + C_s(12t, 1't'), \text{ etc.} \end{aligned} \tag{B.3}$$

For distances $r_{12} \gg \sigma$ the binary collision operator $\bar{T}_-$ can be replaced by the point operator $\hat{T}$ and for low densities $C_s(12t, 1't')$ can be neglected on the right-hand side of Eq. (B.2), so that one obtains the following equation for $C_s(1t, 2t')$:

$$\left[\frac{\partial}{\partial t} + L_s(1t)\right] C_s(1t, 2t') = 0 \tag{B.4}$$

where

$$\begin{aligned} L_s(1t) &= L_0(1) - \Lambda_s(1t) \\ \Lambda_s(1t) &= \int d3\, \hat{T}(13) f(3t) \end{aligned} \tag{B.5}$$

The equation (A.4) has to be solved with the initial condition

$$C_s(1t, 2t) = \delta(1 - 2) f(1t) \tag{B.6}$$

For fluctuations of a tagged particle in a gas in equilibrium $f(1t)$ is given by the Maxwellian velocity distribution function.

The results (B.4)–(B.6) agree with those obtained in Refs. 9, 34, and 27[14] for the nonequilibrium case.

## APPENDIX C: THREE-TIME CORRELATION FUNCTIONS

As an example of how the hierarchy method can be used to compute multitime correlation functions, we will sketch here how the three-time correlation function $C(1t, 2t', 3t'')$ can be obtained for a low-density gas not in equilibrium.

As derived in Appendix A, we have for the three-time distribution function $f(1t, 2t', 3t'')$ the equation ($t > t' > t''$):

$$\left[\frac{\partial}{\partial t} + L_0(1)\right] f(1t, 2t', 3t'') = \int d4\,\overline{T}_-(14) f(14t, 2t', 3t'') \tag{C.1}$$

Introducing cluster functions by the expansion [cf. Eq. (2.12)]

$$\begin{aligned} f(1t, 2t', 3t'') = {} & f(1t) f(2t') f(3t'') + f(1t) C(2t', 3t'') \\ & + f(2t') C(1t, 3t'') + f(3t'') C(1t, 2t') \\ & + C(1t, 2t', 3t'') \end{aligned} \tag{C.2}$$

and similarly for $f(14t, 2t', 3t'')$ (where in addition to $C$ functions, a $g(14t)$ function appears), one obtains the following equation for the three-time correlation function $C(1t, 2t', 3t'') = \langle \delta\psi(1t)\delta\psi(2t')\delta\psi(3t'')\rangle$:

$$\begin{aligned} \left[\frac{\partial}{\partial t} + L(1, t)\right] C(1t, 2t', 3t'') = {} & \int d4\,\overline{T}_-(14)(1 + P_{14}) C(1t, 2t') C(4t, 3t'') \\ & + \int d4\,\overline{T}_-(14) C(14t, 2t', 3t'') \end{aligned} \tag{C.3}$$

where $L(1, t)$ has been defined in Eq. (3.4). In Eq. (C.3) only connected terms appear, as discussed below Eq. (2.16).

We now solve this equation for $C(1t, 2t', 3t'')$ in the low-density approximation and for relative distances $r_{12}$, $r_{13}$, and $r_{23}$ large compared to $\sigma$. As before, we drop the last term on the right-hand side of Eq. (C.3) and replace $\overline{T}_-$ operators by $\hat{T}$ operators. Equation (C.3) can then be solved for $C(1t, 2t', 3t'')$ in terms of the initial value $C(1t, 2t, 3t'')$, which still has to be determined. Generalizing thereto equations like (2.12) and (2.14) to three-time distribution and correlation functions, one has

$$C(1t, 2t, 3t'') = \delta(1 - 2) C(2t, 3t'') + C(12t, 3t'') \tag{C.4}$$

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[14] In Ref. 12 the equation for $C_s(1t, 1't')$, which corresponds to (B.4), contains $L(1t)$ as given by Eq. (3.4) instead of $L_s(1t)$. This would imply that $f_s(12t, 1't')$ in Eq. (B.3) contains an additional term $f(1t)C_s(2t, 1't')$ on the right-hand side, which is not consistent with the cluster property of $C_s(12t, 1't')$.

We can now compute $C(12t,3t''))$ in (C.4) as a function of $t$ or $t''$. For a comparison with the results obtained by Dufty$^{(35)}$ we will use $t''$. Thus we need to consider the equation of motion for $f(12t,3t'')$ as a function of $t''$. Since $t'' < t$ we have to apply the "backward" hierarchies derived in Appendix A, the first equation of which reads [cf. Eq. (A.11)]

$$\left[\partial_{t''} + L_0(3)\right] f(12t,3t'') = -\int d4\,\bar{T}_+(34) f(12t,34t'') \qquad \text{(C.5)}$$

By expanding $f(12t,3t''), f(12t,34t'') \ldots$, in the appropriate Ursell functions, neglecting the correlation function $C(12t,34t'')$, and replacing $\bar{T}_+(ij)$ by $\hat{T}(ij)$,[15] we obtain

$$\{\partial_{t''} + L^-(3t'')\} C(12t,3t'') = -\int d4\,\hat{T}(34)(1+P_{34}) C(1t,3t'') C(2t,4t'') \qquad \text{(C.6)}$$

where [cf. (3.4)]

$$L^-(3t'') = L_0(3) + \int d4\,\hat{T}(34)(1+P_{34}) f(4t'') \qquad \text{(C.7)}$$

This equation has to be solved with the initial value:

$$C(12t'',3t'') = \delta(1-3)\,g(23t'') + \delta(2-3)\,g(13t'') + g(123t'') \qquad \text{(C.8)}$$

We emphasize that like in the discussion of Eq. (3.5) before, in general $g(123t'')$ has to be kept in Eq. (C.8). To complete the calculation one has to compute $g(123t'')$ from the third hierarchy equation, which can be done in a straightforward manner and leads to an expression for $g(123t'')$ in terms of $f(it)$ and $g(ijt)$ $(i,j = 1,2,3)$. We will not give the result here, since it is rather lengthy. In the special case of thermal equilibrium, the equal time correlation functions $g(12)$ and $g(123)$ vanish in the low-density limit for spatial separations of interest here, so that $C(12t'',3t'') = 0$. Then formal integration of Eq. (C.6) with the initial condition $C(12t'',3t'') = 0$ yields an expression for $C(1t,2t,3t'')$ which can serve in turn as an initial value for the low-density approximation of Eq. (C.3). After a formal integration of this equation an expression for $C(1t,2t',3t'')$ in equilibrium is obtained which agrees with that derived before by Dufty [cf. his Eq. (3.10)].$^{(35)}$

## APPENDIX D: COMPARISON OF EXPRESSIONS FOR $\Gamma(12t)$

For the inhomogeneous term $\Gamma(12t)$ in Eq. (3.5) four different expressions occur in the literature. In this Appendix we will show that they are all

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[15] After one replaces both $\delta$ functions in (A.9) by $\delta(\mathbf{r}_{12})$, $\bar{T}_\pm(12)$ reduces to $\hat{T}(12)$ defined in (3.1). In $\hat{T}(12)$ there is no difference between forward and backward any more, since the integrand is an even function of $\hat{\sigma}$.

identical. With slight modifications these expressions are the following:

1. $$\Gamma_1(12t) = -\left[\Lambda(1t) + \Lambda(2t)\right]\delta(1-2)f(1t) + \delta(1-2)\int d3\,\hat{T}(13)f(1t)f(3t) + \hat{T}(12)f(1t)f(2t) \tag{D.1}$$

was obtained as Eq. (3.5b) in this paper as well as by Kirkpatrick *et al.*(14);

2. $$\begin{aligned}\Gamma_2(12t) = \delta(\mathbf{r}_1 - \mathbf{r}_2)\Big\{ &\int d\mathbf{v}_1' \int d\mathbf{v}_2'\, W(\mathbf{v}_1\mathbf{v}_2 \,|\, \mathbf{v}_1'\mathbf{v}_2')\left[f(1't)f(2't) + f(1t)(2t)\right] \\ &+ \delta(\mathbf{v}_1 - \mathbf{v}_2)\int d\mathbf{v}_3 \int d\mathbf{v}_1' \int d\mathbf{v}_3'\, W(\mathbf{v}_1\mathbf{v}_3 \,|\, \mathbf{v}_1'\mathbf{v}_3')\left[f(1't)f(3't) + f(1t)f(3t)\right] \\ &- \int d\mathbf{v}_3 \int d\mathbf{v}_1' \int d\mathbf{v}_3'(1 + P_{12})\,W(\mathbf{v}_1\mathbf{v}_3 \,|\, \mathbf{v}_1'\mathbf{v}_3')(1 + P_{13})f(1't)f(3't)\delta(\mathbf{v}_1' - \mathbf{v}_2)\Big\}\end{aligned} \tag{D.2}$$

was obtained by Ludwig(20),[16] and Logan and Kac(38,39),[17];

3. $$\Gamma_3(12t) = \frac{1}{2}\int d\bar{1}\int d\bar{2}\int d1'\int d2'\,A(\bar{1}\bar{2} \,|\, 1'2')f(1't)f(2't)\Delta(x_1)\Delta(x_2) \tag{D.3}$$

was obtained by Seeberg,(40),[18] Onuki,(21),[18] van Kampen,(37) and Spohn(30);

4. $$\Gamma_4(12t) = -\delta(\mathbf{r}_1 - \mathbf{r}_2)\int d\mathbf{v}_3 \int d\mathbf{v}_1' \int d\mathbf{v}_3'\, W(\mathbf{v}_1\mathbf{v}_3 \,|\, \mathbf{v}_1'\mathbf{v}_3') \times \left[f(1't)f(3't) + f(1t)f(3t)\right]\Delta(\mathbf{v}_2) \tag{D.4}$$

was obtained by Keizer(53) and van den Broeck and Brenig.(42),[17] In these expressions $W(\mathbf{v}_1\mathbf{v}_2 \,|\, \mathbf{v}_1'\mathbf{v}_2')$ is the transition probability per unit time for a binary collision with initial velocities $(\mathbf{v}_1\mathbf{v}_2)$ and final velocities $(\mathbf{v}_1'\mathbf{v}_2')$; it is symmetric for the interchange of $\mathbf{v}_1$ and $\mathbf{v}_2$, $\mathbf{v}_1'$ and $\mathbf{v}_2'$, satisfies microscopic reversibility and is related through Eq. (4.13) to the binary collision operator $T_0(\mathbf{v}_1\mathbf{v}_2)$, introduced in Eq. (3.11). Furthermore,

$$A(12 \,|\, 1'2') = \delta(\mathbf{r}_1 - \mathbf{r}_2)\delta(\mathbf{r}_1' - \mathbf{r}_2')\delta(\mathbf{r}_1 - \mathbf{r}_2')W(\mathbf{v}_1\mathbf{v}_2 \,|\, \mathbf{v}_1'\mathbf{v}_2') \tag{D.5}$$

[16] Ludwig has $f(ijt)$ instead of $f(it)f(jt)$. In view of Eq. (2.11), $f(ijt)$ contains $g(ijt)$, which for $\mathbf{r}_i = \mathbf{r}_j = \mathbf{r}_1$ is of higher order in the density than $f(it)f(jt)$ and should therefore be dropped.

[17] van Kampen as well as Kac and Logan discuss fluctuations in discrete velocity space. For our comparison we change to continuous variables and consider therefore $\Gamma(\mathbf{v}_1\mathbf{v}_2t) = (1/V)\cdot\int d\mathbf{r}_1\int d\mathbf{r}_2\,\Gamma(12t)$. As noted already in Section 4, the term containing $\delta(\mathbf{v}_1 - \mathbf{v}_2)$ in (D.2) is missing in the expression of Kac and Logan, so that their expression for $\Gamma(12t)$ does not reduce to the proper equilibrium value (3.6).

[18] $f(ijt)$ occurs instead of $f(it)$, $f(jt)$ (see footnote 15 above).

and

$$\Delta(x_i) = \delta(x_1' - x_i) + \delta(x_2' - x_i) - \delta(\mathbf{x}_1 - x_i) - \delta(\mathbf{x}_2 - x_i) \qquad (\text{D.6})$$

and similarly for $\Delta(\mathbf{v}_i)$. All $f(it) = f(\mathbf{r}_1\mathbf{v}_i t)$ are taken at the same position $\mathbf{r}_1$.

We now show the identity of the four expressions for $\Gamma(12t)$. Using Eqs. (3.1), (3.11), (4.13), and (D.5) which yield

$$\hat{T}(12)h(12) = \int d1' \int d2' A(12 \mid 1'2')[h(1'2') - h(12)] \qquad (\text{D.7})$$

for an arbitrary function $h(12)$, as well as Eq. (3.4b), one obtains from (D.1)

$$\begin{aligned}\Gamma_2'(12t) = &\int d1' \int d2' A(12 \mid 1'3')[f(1')f(3') + f(1)f(3)] \\ &+ \int d3 \int d1' \int d3' A(13 \mid 1'3')[f(1')f(3') + f(1)f(3)]\delta(12) \\ &- \int d3 \int d1' \int d3' A(13 \mid 1'3') f(1')f(3')[\delta(1'2) + \delta(3'2)] \\ &- \int d3 \int d2' \int d3' A(23 \mid 2'3') f(2')f(3')[\delta(12') + \delta(13')] \qquad (\text{D.8})\end{aligned}$$

Notice that the plus signs in the first two lines on the right-hand side of Eq. (D.8) originate not only from the last two terms on the right-hand side of Eq. (D.1) but also in part from the preceding terms. Carrying out the integrations over the position coordinates $\mathbf{r}_1'$, $\mathbf{r}_2'$, $\mathbf{r}_3'$, and $\mathbf{r}_3$ leads directly to $\Gamma_2(12t)$ of Eq. (D.2). In order to derive $\Gamma_3(12t)$ we proceed as follows. We apply $\int d\bar{1} \int d\bar{2}\, \delta(\bar{1}1)\delta(\bar{2}2)$ to the first line of (D.8); $\int d\bar{1}\, \delta(\bar{1}1)$ to the second and third line of (D.8) and relabel $3, 3'$ as $2, 2'$, respectively; $\int d\bar{1}\, \delta(2\bar{1})$ to the fourth line of (D.8) and relabel 2, 3, 2′, 3′ as $\bar{1}$, $\bar{2}$, 1′, 2′, respectively. Symmetrizing the resulting expression in primed and unprimed variables, in $\bar{1}$ and $\bar{2}$ and in 1′ and 2′, and using that $A(\bar{1}\bar{2} \mid 1'2') = A(1'2' \mid \bar{1}\bar{2})$, one obtains

$$\begin{aligned}\Gamma_{3'}(12t) = \frac{1}{4} &\int d\bar{1} \int d\bar{2} \int d1' \int d2' A(\bar{1}\bar{2} \mid 1'2')[f(1't)f(2't) + f(\bar{1}t)f(\bar{2}t)] \\ &\times \Delta(x_1)\Delta(x_2) \qquad (\text{D.9})\end{aligned}$$

which is identical to $\Gamma_3(12t)$ as given by Eq. (D.3).

Finally $\Gamma_4(12t)$ is obtained using that symmetries of the integrand on the right-hand side of (D.9) allow the replacement of $\Delta(x_1)\Delta(x_2)$ by $-4\delta(\bar{1}1)\Delta(x_2)$ so that $\Gamma_3(12t)$ can be written in the form

$$\Gamma_{4'}(12t) = -\int d3 \int d1' \int d3' A(13 \mid 1'3')[f(1't)f(3't) + f(1t)f(3t)]\Delta(x_2) \qquad (\text{D.10})$$

which reduces directly to $\Gamma_4(12t)$ as given by Eq. (D.4).

## ACKNOWLEDGMENTS

The authors are much indebted to Mr. T. Kirkpatrick for many helpful discussions, in particular, in connection with Appendix C. One of us (M. H.. E.) wants to thank the Rockefeller University for its hospitality during March 1980 when this paper was finished.

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