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Time-Correlation Function for Macroscopic Observables in a Classical Gas

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The state of a gas is characterized by occupation numbers of cells in μ-space. The mean values and fluctuations of these numbers are studied with the help of a master equation. The results are discussed within the framework of the theory of random forces. An equation of motion of the time-correlation function (TCF) is derived and it is shown that the temporal development of the TCF can be described by a linearized Boltzmann equation.

KEY WORDS: Boltzmann equation; master equation; macroscopic observables; Markov assumption; coarse-graining; random forces; entropy; Onsager coefficients; light scattering.

1. INTRODUCTION

Within the framework of the theory of light scattering, it is necessary to investigate the time-correlation function (TCF) for certain observables. The purpose of this paper is to study the TCF for a set of macroscopic observables —in this case, occupation numbers of cells in μ-space—which characterize the coarse-grained state of a gas. V. Leeuwen and Yip[2] have derived a linearized Boltzmann equation as the equation of motion for the "fine" TCF. Their

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paper takes as its starting point an Ursell expansion of the time-displacement operator. Since we only deal with macroscopic observables, we choose another way. Our starting point is a master equation for the motion of a coarse-grained density in Γ-space.

In Section 2, we define the coarse-grained TCF. In order to derive an equation of motion for this TCF, it is necessary to have the equation of motion for the coarse-grained density. Furthermore, we must have equations for the mean occupation numbers and their correlations. From these equations, we immediately get the equation of motion for the TCF in equilibrium. This can be brought into the form of a linearized Boltzmann equation with the help of assumptions which are discussed later in Section 6. Before this more rigorous treatment, we discuss the results within the framework of the theory of random forces in Section 5. It is possible, for instance, to rederive in this way the equations of motion for the mean occupation numbers and their correlations. In Section 6, we discuss the assumptions mentioned above. We introduce a new coarse-grained probability P_ρ in Γ-space. The moments of this probability fulfill the same equations as the mean values do, which are defined in Section 4. By solving these equations, we see that indeed the linearized Boltzmann equation is a good approximation for describing the coarse-grained TCF.

The connection between the derivation in Ref. 2 and that given here will be investigated in greater detail in a succeeding paper.

2. DEFINITION OF THE COARSE-GRAINED TIME-CORRELATION FUNCTION (TCF)

We consider a set M of systems S with fixed energy E, volume V, and number of particles N. Each system can be described at any instant t by a point $P(S) = (\mathbf{q}_\nu(t), \mathbf{p}_\nu(t)) \in \Gamma$, where Γ is the Γ-space, or by the corresponding distribution function

$$f_P(\mathbf{r}, \mathbf{p}, t) = \sum \delta(\mathbf{r} - \mathbf{q}_\nu(t)) \qquad \delta(\mathbf{p} - \mathbf{p}_\nu(t)) = f_P(\mathbf{x}, t)$$

which is defined on the μ-space. We divide the μ-space into cells Z_i of equal volume $\Delta = \Delta\mathbf{r}\,\Delta\mathbf{p}$: $\mu = \bigcup Z_i$, where $Z_i \cap Z_j = \varnothing$ for $i \neq j$. Each f yields a set of occupation numbers $\{N_i\}$ defined by

$$\begin{aligned} N_i &= \int_\mu f(\mathbf{x}, t)\, \chi_i(\mathbf{x})\, d\mathbf{x} \\ \chi_i(\mathbf{x}) &= 1 \qquad \text{for} \quad \mathbf{x} \in Z_i \qquad (1) \\ &= 0 \qquad \text{otherwise} \end{aligned}$$

The set $\{N_i\}$ is the occupation number vector: $\{N_i\} = \mathfrak{N}$. Thus we have constructed a coarsening mapping A of the set of the distribution functions into the set of the occupation number vectors: $Af = \{N_i[f]\} = \mathfrak{N}[f]$.

Now, each $\mathfrak{N}$ corresponds to a domain $\mathfrak{B}[\mathfrak{N}] \subset \Gamma$, defined by

$$P \in \mathfrak{B}[\mathfrak{N}] \rightleftharpoons Af_P = \mathfrak{N} \tag{2}$$

The measure of $\mathfrak{B}[\mathfrak{N}]$ is

$$\mu[\mathfrak{N}] = N!\, \Delta^N \Big/ \prod N_i\,! \tag{3}$$

This is of course the well-known Boltzmann measure. Now we consider all systems S in M with $P(S) \in \mathfrak{B}[\mathfrak{N}]$ at $t = 0$. All systems will change their domains according to the Hamilton equations. Thus, after a time τ, some systems will be found in another domain $\mathfrak{B}[\mathfrak{M}]$. So we are led to the concept of a transition probability. We do not discuss here the difficulties involved. Let $P(\mathfrak{N} \mid \mathfrak{M}, \tau)$ be the probability of finding the vector $\mathfrak{M}$ after the time τ. Then we get the following expression for the probability of finding a system S which transforms during the time t from $\mathfrak{B}[\mathfrak{N}]$ into $\mathfrak{B}[\mathfrak{M}]$:

$$P(\mathfrak{N}, \mathfrak{M}, t) = P(\mathfrak{N}, 0)\, P(\mathfrak{N} \mid \mathfrak{M}, t) \tag{4}$$

Now we can define the TCF:

$$K_{ij}(t, \tau) = \sum_{\mathfrak{N}\mathfrak{M}} P(\mathfrak{N}, t)\, P(\mathfrak{N} \mid \mathfrak{M}, \tau)\, N_i M_j \tag{5}$$

If we want to calculate the TCF for an equilibrium ensemble M, we must know $P^{eq}[\mathfrak{N}]$ and $P(\mathfrak{N} \mid \mathfrak{M}, \tau)$. This can be done with the help of the master equation of Ludwig[1] In the next section, we give a short derivation of this equation.

3. EQUATION OF MOTION FOR THE TRANSITION PROBABILITY $P(\mathfrak{N} \mid \mathfrak{M}, \tau)$

The cells Z_i can be labeled by the coordinates of their centers. Each system is assumed to change only due to binary collisions and streaming. The length l of the space cell is choosen to be much larger than $\sigma^{1/2} = k$, where σ is the cross section. Therefore each collision occurs in a well-defined space cell. Each system which is scattered into a domain $\mathfrak{B}[\mathfrak{N}]$ during a time Δt is found immediately before in a domain $\mathfrak{B}[\mathfrak{N} + \eta_{ijkl}]$, with

$$(\mathfrak{N} + \eta_{ijkl})_r = N_r + \delta_{ir} + \delta_{jr} - \delta_{kr} - \delta_{lr}$$

δ_{ir} being the Kronecker symbol. Conservation of energy and momentum yields

$$\mathbf{v}_i^2 + \mathbf{v}_j^2 \cong \mathbf{v}_k^2 + \mathbf{v}_l^2, \qquad \mathbf{v}_i + \mathbf{v}_j \cong \mathbf{v}_k + \mathbf{v}_l$$

where $\mathbf{v} = m^{-1}\mathbf{p}$. Furthermore, we have $\mathbf{r}_i = \mathbf{r}_j = \mathbf{r}_k = \mathbf{r}_l$. In the same way, we describe a system scattered out immediately after the collision by a vector $\mathfrak{N} + \eta_{i'j'k'l'}$. Therefore we need to count only these collisions for calculation of the collision balance. We now ask for the probability $P(\mathfrak{N} + \eta_{ijkl} \mid \mathfrak{N}, \Delta t)$. The concept of probability only makes sense if the systems in $\mathfrak{B}[\mathfrak{N} + \eta_{ijkl}]$ can be regarded at any instant as distributed at random. This corresponds to the Markov assumption. Furthermore, we assume the validity of the *Stosszahlansatz* in the form given below. This *ansatz* yields the right number of collisions $(\mathbf{v}_i, \mathbf{v}_j) \to (\mathbf{v}_k, \mathbf{v}_l)$ in the mean, where the mean value is taken over a set of independent systems in $\mathfrak{B}[\mathfrak{N} + \eta_{ijkl}]$. This assumption is more general than the corresponding one for a single system. We now turn to the influence of the streaming processes. If there were no collisions, each system in $\mathfrak{B}[\mathfrak{N}]$ would move into $\mathfrak{B}[\mathfrak{N}']$ during Δt, where $\mathfrak{N}'$ is defined as follows:

$$\mathfrak{N}'(\mathbf{r}_i + \mathbf{v}_i \Delta t, \mathbf{v}_i) = (\mathfrak{N})(\mathbf{r}_i, \mathbf{v}_i) = N_i$$

These remarks are made in order to clarify the following formalism. The temporal change of $P(\mathfrak{N} \mid \mathfrak{M}, t)$ is described by

$$P(\mathfrak{N} \mid \mathfrak{M}', \Delta t) = (\mathfrak{N} \mid 1 \mid \mathfrak{M}) + \Delta t(\mathfrak{N} \mid Q \mid \mathfrak{M}) \tag{6}$$

with

$$(\mathfrak{N} \mid 1 \mid \mathfrak{M}) = \prod \delta M_i N_i = \delta(\mathfrak{M}, \mathfrak{N})$$

$$(\mathfrak{N} \mid Q \mid \mathfrak{M}) = \tfrac{1}{2} \sum{}' w(ij \mid kl)\, N_i N_j\, \delta(\mathfrak{N}, \mathfrak{M} - \eta_{klij}) + \sum w(ij \mid ij)\, \delta(\mathfrak{N}, \mathfrak{M})\, N_i N_j$$

The prime indicates that the sum excludes all terms with $(ij) = (kl)$. Further on, we need

$$P(\mathfrak{N} \mid \mathfrak{M}, t + t') = \sum_{\mathfrak{R}} P(\mathfrak{N} \mid \mathfrak{R}, t)\, P(\mathfrak{R} \mid \mathfrak{M}, t') \tag{7}$$

where $t, t' > 0$. From $\sum_{\mathfrak{M}} P(\mathfrak{N} \mid \mathfrak{M}, \Delta t) = 1$, we have

$$\sum_{\mathfrak{M}} (\mathfrak{N} \mid Q \mid \mathfrak{M}) = 0 \tag{8}$$

Therefore we get

$$(\mathfrak{N} \mid Q \mid \mathfrak{M}) = - \sum_{\mathfrak{N} \neq \mathfrak{M}} (\mathfrak{N} \mid Q \mid \mathfrak{M})$$

For $w(ij \mid kl)$, we get from the above remarks

$$w(ij \mid kl) = \sigma(ij \mid kl)(\Delta \mathbf{v}_k \, \Delta \mathbf{v}_l / \Delta \mathbf{r}) \, \delta(\mathbf{r}_i \, , \mathbf{r}_k) \, \delta(\mathbf{r}_j \, , \mathbf{r}_k) \, \delta(\mathbf{r}_l \, , \mathbf{r}_k). \tag{9}$$

$\sigma(ij \mid kl)$ is the usual differential cross section as it appears in the Boltzmann equation written down in the cell language:

$$\begin{aligned} &N(\mathbf{r}_i + \mathbf{v}_i \, \Delta t, \mathbf{v}_i \, , t + \Delta t) - N(\mathbf{r}_i \, , \mathbf{v}_i \, , t) \\ &\quad = \Delta t \, \Sigma'(\Delta \mathbf{v}_k \, \Delta \mathbf{v}_1 / \Delta \mathbf{r}) \, \sigma(ij \mid kl)(N_k N_l - N_j N_i) \end{aligned} \tag{10}$$

For hard spheres, for instance, we get

$$\sigma(ij \mid nm) = k^2 \, \delta(\mathbf{v}_m + \mathbf{v}_n \, , \mathbf{v}_i + \mathbf{v}_j) \, \delta(\mathbf{v}_n{}^2 + \mathbf{v}_m{}^2 \, , \mathbf{v}_i{}^2 + \mathbf{v}_j{}^2) \, c^{-5} \tag{11}$$

where c is the length of the velocity cell. Therefore $\Delta \mathbf{v} = c^3$. Now, $\sigma(ij \mid kl)$ is assumed to have the following symmetry properties:

$$\sigma(ij \mid kl) = \sigma(kl \mid ij) = \sigma ji \mid kl) \tag{12}$$

From (6)–(8), we have, after a short calculation,

$$\begin{aligned} &P(\mathfrak{N} \mid \mathfrak{M}', t + \Delta t) - P(\mathfrak{N} \mid \mathfrak{M}, t) \\ &\quad = \tfrac{1}{2} \Delta t \{ \textstyle\sum' w(ij \mid kl)(M_i + 1)(M_j + 1) \, P(\mathfrak{N} \mid \mathfrak{M} + \eta_{ijkl}) \\ &\quad\quad - \textstyle\sum' w(ij \mid kl) \, M_i M_j P(\mathfrak{N} \mid \mathfrak{M}, t) \} \end{aligned} \tag{13}$$

This is the master equation. For more exact derivations of this equation, see Schröter[3] and Förster[4]. It is possible to show the validity of an H-theorem by use of the functional

$$\mathfrak{H}[P(\mathfrak{N} \mid \mathfrak{M}, t)] = \sum_{\mathfrak{M}} \rho(\mathfrak{N} \mid \mathfrak{M}, t) \log \rho(\mathfrak{N} \mid \mathfrak{M}, t) \, \mu[\mathfrak{M}] \tag{14}$$

with $P(\mathfrak{N} \mid \mathfrak{M}, t) = \mu[\mathfrak{M}] \, \rho(\mathfrak{N} \mid \mathfrak{M}, t)$. This H-theorem yields[5]

$$\lim_{t \to \infty} P(\mathfrak{N} \mid \mathfrak{M}, t) = \mu[\mathfrak{M}] \, D, \qquad D = \text{const} \tag{15}$$

4. EQUATIONS OF MOTION FOR THE MEAN VALUES $\langle M_i \rangle$ AND $\langle M_i M_j \rangle$

We have

$$\begin{aligned} \langle M_i \rangle &= \textstyle\sum \rho(\mathfrak{N} \mid \mathfrak{M}, t) \, \mu[\mathfrak{M}] \, M_i \\ \langle M_i M_j \rangle &= \textstyle\sum \rho(\mathfrak{N} \mid \mathfrak{M}, t) \, \mu[\mathfrak{M}] \, M_i M_j \end{aligned}$$

We multiply (13) by M_i, M_iM_j. We define

$$\langle M_iM_j\rangle = \langle M_i\rangle\langle M_j\rangle + G_{ij} \tag{16}$$

With the symmetry properties of $w(ij \mid kl)$ [Eqs. (12)] and the properties of $\mu[\mathfrak{M}]$, we get, after summation,

$$\begin{aligned}
&[\langle M\rangle(\mathbf{r}_i + \mathbf{v}_i\,\Delta t, \mathbf{v}, t + \Delta t) - \langle M\rangle(\mathbf{r}_i, \mathbf{v}_i, t)](\Delta t)^{-1} \\
&\quad = D_i\langle M\rangle \qquad \text{(definition)} \\
&\quad = \textstyle\sum' w(nm \mid ij)[\langle M_n\rangle\langle M_m\rangle - \langle M_i\rangle\langle M_j\rangle] + \textstyle\sum' w(nm \mid ij)[G_{nm} - G_{ij}]
\end{aligned} \tag{17}$$

Whenever it is necessary, we write instead of $\langle M_i\rangle$ more accurately $\langle M\rangle(\mathbf{r}_i, \mathbf{v}_i)$. Equation (17) agrees with (10) except for the second term on the r.h.s. of (17), so that (17) is more general than the Boltzmann equation. Analogously, the assumptions

$$\langle M_iM_jM_k\rangle = \langle M_i\rangle\langle M_j\rangle\langle M_k\rangle + \langle M_i\rangle\,G_{jk} + \langle M_j\rangle\,G_{ik} + \langle M_k\rangle\,G_{ij} \tag{18}$$

yields the following equation for G_{ij}:

$$\begin{aligned}
&\tfrac{1}{2}\,\Delta t[G(\mathbf{r}_i + \mathbf{v}_i\,\Delta t, \mathbf{r}_j + \mathbf{v}_j\,\Delta t, \mathbf{v}_i, \mathbf{v}_j, t + \Delta t) - G_{ij}(t)] \\
&\quad = D_{ij}G \qquad \text{(definition)} \\
&\quad = \tfrac{1}{2}\textstyle\sum' w(mn \mid kl)(\delta_{ik} + \delta_{il} - \delta_{im} - \delta_{in})(\delta_{jk} + \delta_{jl} - \delta_{jm} - \delta_{jn}) \\
&\qquad \times (\langle M_m\rangle\langle M_n\rangle + G_{nm}) \\
&\qquad + [\textstyle\sum' w(mn \mid jl)(\langle M_m\rangle\,G_{ni} + \langle M_n\rangle\,G_{mi} \\
&\qquad - \langle M_j\rangle\,G_{li} - \langle M_l\rangle\,G_{ji}) + \{i \leftrightarrow j\}]
\end{aligned} \tag{19}$$

Equation (18) seems to be an *ad hoc* assumption, but its consequences in (19) can be clarified by a heuristic argument: we are only interested in the macroscopic properties of the system. Ludwig[1] has shown that this leads in a natural way to (19). We now introduce the following abbreviations:

$$\begin{aligned}
\textstyle\sum' w(mn \mid ij)(\langle M_k\rangle\langle M_l\rangle - \langle M_i\rangle\langle M_j\rangle) &= B_i[\langle\mathfrak{M}\rangle] \\
\textstyle\sum' w(mn \mid ij)(G_{mn} - G_{ij}) &= B_i[\mathfrak{G}] \\
\tfrac{1}{2}\textstyle\sum' w(mn \mid kl)(\delta_{ik} + \delta_{il} - \delta_{im} - \delta_{in})(\delta_{jk} + \delta_{jl} - \delta_{jm} - \delta_{jn})\langle M_m\rangle\langle M_n\rangle & \\
&= L_{ij}[\langle\mathfrak{M}\rangle] \\
\tfrac{1}{2}\textstyle\sum' w(mn \mid kl)(\delta_{ik} + \delta_{il} - \delta_{im} - \delta_{in})(\delta_{jk} + \delta_{jl} - \delta_{jm} - \delta_{jn})\,G_{mn} & \\
&= L_{ij}[\mathfrak{G}] \\
[\textstyle\sum' w(mn \mid jl)(\langle M_m\rangle\,G_{ni} + \langle M_n\rangle\,G_{mi} - \langle M_j\rangle\,G_{li} - \langle M_l\rangle\,G_{ji})] + [i \leftrightarrow j] & \\
&= H_{ij}[\langle\mathfrak{M}\rangle, \mathfrak{G}]
\end{aligned} \tag{20}$$

Thus we have for (16) and (19)

$$D_i\langle M\rangle = B_i[\langle\mathfrak{M}\rangle] + B_i[\mathfrak{G}]$$
$$D_{ij}G = L_{ij}[\langle\mathfrak{M}\rangle] + L_{ij}[\mathfrak{G}] + H_{ij}[\langle\mathfrak{M}\rangle, \mathfrak{G}] \tag{21}$$

In addition, we give some remarks on the order of magnitude of the cells. The *Stosszahlansatz* for a single system can be justified only for times $\Delta t \simeq t_f$, with $t_f = \lambda\langle v\rangle^{-1}$, λ being the mean free path. Therefore we choose

$$l \simeq \lambda \tag{22}$$

since smaller lengths yield finer properties, which cancel out by coarsening in time. Furthermore, the cells Z_i with $|v_i| \leqslant \langle v\rangle$ should contain many particles, because the occupation numbers N_i are macroscopic observables. For $\langle v\rangle$, we have $\langle v\rangle = (2kTm^{-1})^{1/2} = b^{-1/2}$. If we demand, for example, that

$$\langle(N_i - \langle N_i\rangle^{\text{eq}})^2\rangle(\langle N_i\rangle^{\text{eq}})^{-2} < \epsilon$$

we get

$$\epsilon^{-1} \leqslant \langle N_i\rangle^{\text{eq}} \simeq n(b\pi^{-1})^{3/2}\, \Delta\mathbf{r}\, \Delta\mathbf{v}$$

Therefore we have

$$(\Delta\mathbf{v})\, b^{3/2} \geqslant \pi^{3/2}[n(\Delta\mathbf{r})\, \epsilon]^{-1}$$

Let us choose, for instance,

$$n = 3 \times 10^{19} \quad \text{cm}^{-3}; \qquad l = 10^{-4} \quad \text{cm}; \qquad \epsilon = 10^{-3}$$

Then we get

$$c\langle v\rangle^{-1} \geqslant 1/20 \tag{23}$$

We now are able to write down the equation for the TCF in equilibrium. With (5) and (21), we get

$$(\Delta t)^{-1}\, [K(\mathbf{r}_i, \mathbf{v}_i, \mathbf{r}_j + \mathbf{v}_j\, \Delta t, \mathbf{v}_j, t + \Delta t) - K_{ij}(t)]$$
$$= \sum_{\mathfrak{M}} D\mu[\mathfrak{N}](B_j[\langle\mathfrak{M}\rangle] + B_j[\mathfrak{G}]) \tag{24}$$

Here, $\langle\mathfrak{M}\rangle(t)$, $\mathfrak{G}(t)$ are solutions of (21) with the initial conditions $\langle\mathfrak{M}\rangle(0) = \mathfrak{N}$, $\mathfrak{G}(0) = 0$. When $\mathfrak{G}$ is dropped and the remaining Boltzmann term is linearized with respect to equilibrium, the result is

$$D_jK_i = \sum{}' w(kl \mid jm)(\langle M_k\rangle^{\text{eq}}\, K_{il} + \langle M_l\rangle^{\text{eq}}\, K_{ik}$$
$$- \langle M_j\rangle^{\text{eq}}\, K_{im} - \langle M_m\rangle^{\text{eq}}\, K_{ij}) \tag{25}$$

where we have used the fact that $B_i[\langle\mathfrak{M}\rangle^{\text{eq}}] = 0$. We see at once that

$$R_{ij} = \sum_{\mathfrak{M},\mathfrak{N}} D\mu[\mathfrak{N}]\, P(\mathfrak{N} \mid \mathfrak{M}, t)(N_i - \langle N_i\rangle^{\text{eq}})(M_j - \langle M_j\rangle^{\text{eq}}) \tag{26}$$

fulfills (25), too, with the initial condition

$$\begin{aligned} R_{ij}(0) &= \sum D\mu[\mathfrak{N}](N_i - \langle N_i\rangle^{\text{eq}})(N_j - \langle N_j\rangle^{\text{eq}}) \\ &= N_i^{\text{eq}}\,\delta_{ij} \end{aligned} \tag{27}$$

This result agrees with Ref. 1. In a following section. we derive equations which enable us to test the validity of this equation.

5. RELATION TO THE THEORY OF RANDOM FORCES

We describe the motion of any system $S \in M$ by the following stochastic equation:

$$D_i M[S] = B_i[\mathfrak{M}[S]] + (\Delta t)^{-1} \int_0^{\Delta t} F_i(t + \tau)[S]\, d\tau \tag{28}$$

where $\mathfrak{M}[S]$ is the vector, which corresponds to S. Taking the mean value, we get

$$D_i\langle M\rangle = B_i[\langle\mathfrak{M}\rangle] + B_i[\mathfrak{G}] + (\Delta t)^{-1} \int_0^{\Delta t} \langle F_i(t + \tau)\rangle\, d\tau$$

Comparison with (21) yields

$$(\Delta t)^{-1} \int_0^{\Delta t} \langle F_i(t + \tau)\rangle\, d\tau = 0 \tag{29}$$

S corresponds to a random variable in $\mathfrak{B}[\mathfrak{M}]$. So, taking the mean value over all S can be performed in the following way:

$$\sum_S P(S)\, A(S) = \sum_{\mathfrak{M}} P(\mathfrak{M}) \sum_{S\in\mathfrak{B}[\mathfrak{M}]} P(S \mid \mathfrak{M})\, A(S)$$

where $A(S)$ is an observable depending on S and $P(S \mid \mathfrak{M})$ is the conditional probability. From the definition of $\mathfrak{G}$, we get

$$\begin{aligned} D_{ij}G = (\Delta t)^{-1}[&\langle M(\mathbf{r}_i + \mathbf{v}_i\,\Delta t, \mathbf{v}_i)\, M(\mathbf{r}_j + \mathbf{v}_j\,\Delta t, \mathbf{v}_j)\rangle(t + \Delta t) - \langle M_i M_j\rangle(t) \\ &- \langle M(\mathbf{r}_i + \mathbf{v}_i\,\Delta t, \mathbf{v}_i)\rangle(t + \Delta t)\langle M(\mathbf{r}_j + \mathbf{v}_j\,\Delta t, \mathbf{v}_j)\rangle(t + \Delta t) \\ &+ \langle M_i\rangle(t)\langle M_j\rangle(t)] \end{aligned} \tag{30}$$

Inserting (28) into (30) yields, after a short calculation,

$$\begin{aligned} D_{ij}G = {} & [\langle M_i B_j[\mathfrak{M}]\rangle(t) + (\Delta t)^{-1}\left\langle M_i \int_0^{\Delta t} F_j(t+\tau)\,d\tau\right\rangle - \langle M_i\rangle\langle B_j[\mathfrak{M}]\rangle \\ & + \tfrac{1}{2}\Delta t\,\langle B_i[\mathfrak{M}]\,B_j[\mathfrak{M}]\rangle - \tfrac{1}{2}\Delta t\langle B_i[\mathfrak{M}]\rangle\langle B_j[\mathfrak{M}]\rangle \\ & + \tfrac{1}{2}(\Delta t)^{-1}\left\langle \int_0^{\Delta t}\int_0^{\Delta t} F_i(t+\tau)\,F_j(t+\tau')\,d\tau\,d\tau'\right\rangle \\ & + \left\langle B_i[\mathfrak{M}]\int_0^{\Delta t} F_j(t+\tau)\,d\tau\right\rangle] + [i\leftrightarrow j] \end{aligned} \tag{31}$$

With (18) and (21), we get, after dropping terms $O(\Delta t)$, from (31),

$$\begin{aligned} D_{ij}G = {} & H_{ij}[\langle\mathfrak{M}\rangle, \mathfrak{G}] + \Big[(\Delta t)^{-1}\left\langle M_i \int_0^{\Delta t} F_j(t+\tau)\,d\tau\right\rangle \\ & + \left\langle B_i[\mathfrak{M}]\int_0^{\Delta t} F_j(t+\tau)\,d\tau\right\rangle \\ & + \tfrac{1}{2}(\Delta t)^{-1}\left\langle \iint_0^{\Delta t} F_i(t+\tau)\,F_j(t+\tau')\,d\tau\,d\tau'\right\rangle\Big] \\ & + [i\leftrightarrow j] \end{aligned} \tag{32}$$

From the Markov assumption, if follows that

$$\sum_{S\in\mathfrak{B}[\mathfrak{M}]} P(S\mid\mathfrak{M})\,A[S] = \tilde{A}[\mathfrak{M}]$$

is completely defined by $\mathfrak{M}$, because $P(S\mid\mathfrak{M})$ does not depend on the time t and the probability $P(\mathfrak{M}, t)$. Now let us suppose that

$$\sum_{S\in\mathfrak{B}[\mathfrak{M}]} P(S\mid\mathfrak{M})\,F_j[S] = \tilde{F}_j[\mathfrak{M}] \tag{33}$$

is different from zero. We consider an ensemble with $\mathfrak{G} = 0$ and $\langle\mathfrak{M}\rangle = \mathfrak{M}$ initially. Then we have

$$\begin{aligned} \left\langle \int_0^{\Delta t} F_j(\tau)\,d\tau\right\rangle &= \int_0^{\Delta t}\sum_{\mathfrak{M}} P(\mathfrak{M})\,\tilde{F}_j[\mathfrak{M}]\,d\tau \\ &= \int_0^{\Delta t}\tilde{F}_j[\mathfrak{M}]\,d\tau = 0 \end{aligned} \tag{34}$$

from (29), in contradiction to our supposition. Therefore we get from (32)

$$D_{ij}G = (\Delta t)^{-1}\iint_0^{\Delta t}\langle F_i(t+\tau)\,F_j(t+\tau')\rangle\,d\tau\,d\tau' + H_{ij}[\langle\mathfrak{M}\rangle, \mathfrak{G}] \tag{35}$$

Comparison with (21) then yields

$$(\Delta t)^{-1} \iint_0^{\Delta t} \langle F_i(t+\tau) F_j(t+\tau') \rangle \, d\tau \, d\tau' = L_{ij}[\langle \mathfrak{M} \rangle] + L_{ij}[\mathfrak{G}] \qquad (36)$$

Thus we are led to the following interpretation. If there were no random forces F_i, the equation

$$D_{ij}G = H_{ij}[\langle \mathfrak{M} \rangle, \mathfrak{G}]$$

would describe the development of correlations in the set M. If M is dispersionless ($\mathfrak{G} = 0$) initially, it remains dispersionless for all times. In (21), the term $L_{ij}[\langle \mathfrak{M} \rangle] + L_{ij}[\mathfrak{G}]$ therefore describes the creation of correlations due to the correlations of the random forces, while the term $H_{ij}[\langle \mathfrak{M} \rangle, \mathfrak{G}]$ describes the development of these correlations in time, when the random forces are "switched off."

We now define an "entropy" for each system $S \in M$ by

$$\mathfrak{S}[\mathfrak{N}] = -\sum N_k \log N_k \qquad (37)$$

This definition comes from

$$\log \mu[\mathfrak{N}] = \log(N! \, \Delta^N) - \log \prod N_i!$$

With Stirling's formula, we get

$$\mathfrak{S}[\mathfrak{N}] \simeq \log \mu[\mathfrak{N}] - \log(N! \, \Delta^N)$$

We consider small deviations from equilibrium and get, with $N_k = N_k^{\text{eq}} + M_k$ after expansion up to terms of second order,

$$\mathfrak{S}[\mathfrak{N}] = \mathfrak{S}[\mathfrak{N}^{\text{eq}}] + \tfrac{1}{2} \sum (\partial^2 \mathfrak{S} / \partial N_i \, \partial N_k)[\mathfrak{N}^{\text{eq}}] \, M_i M_k \qquad (38)$$

Here we used the conservation laws in the following form:

$$\sum_k M_k = 0, \qquad \sum_k \tfrac{1}{2} m v_k^2 M_k = 0$$

Then we get for the "forces" $X_j[\mathfrak{N}]$

$$X_j[\mathfrak{N}] = -\partial \mathfrak{S}[\mathfrak{N}] / \partial N_j = M_j (N_j^{\text{eq}})^{-1} \qquad (39)$$

By linearizing the equation of motion (28), we get

$$D_i N = D_i M = \sum{}' \, w(nm \mid kl) \, \delta_{ki} (N_n^{\text{eq}} M_m + N_m^{\text{eq}} M_n - N_k^{\text{eq}} M_l - N_l^{\text{eq}} M_k)$$
$$+ (\Delta t)^{-1} \int_0^{\Delta t} F_i(t+\tau) \, d\tau \qquad (40)$$

We now define

$$g_{ij} = \sum{}' w(nm \mid kl)\, \delta_{ki}(N_n^{\text{eq}}\delta_{mj} + N_m^{\text{eq}}\delta_{nj} - N_k^{\text{eq}}\delta_{lj} - N_l^{\text{eq}}\delta_{kj}) \tag{41}$$

Then we can write (40) in the following form:

$$D_i M = \sum g_{ij} M_j + (\Delta t)^{-1} \int_0^{\Delta t} F_i(t + \tau)\, d\tau \tag{42}$$

We put $g_{ij} N_j^{\text{eq}} = \gamma_{ij}$. Here, the γ_{ij} correspond to Onsager coefficients, as can be seen from the following relations[6]:

$$\partial^2 \Xi[\mathfrak{N}^{\text{eq}}]/\partial N_j\, \partial N_k = \beta_{jk}\,, \qquad \sum g_{ij}\beta_{jl}^{-1} = \gamma_{jl}$$

After a short calculation, we get

$$\begin{aligned}\gamma_{ij} &= \tfrac{1}{4} \sum{}' w(nm \mid kl)\, N_n^{\text{eq}} N_m^{\text{eq}} (\delta_{mj} + \delta_{nj} - \delta_{kj} - \delta_{lj})(\delta_{mi} + \delta_{ni} - \delta_{ki} - \delta_{li}) \\ &= \tfrac{1}{2} L_{ij}[\mathfrak{N}^{\text{eq}}]\end{aligned} \tag{43}$$

according to (19). Now, for systems which fulfill the stochastic equation

$$(d/dt)\, x_k = -\sum \gamma_{kl} X_l + F_k(t)$$

the following equation is valid:

$$F_{lm}(\omega) = 2\pi(\gamma_{ml} + \gamma_{lm})$$

where

$$\begin{aligned}F_{kl}(\tau) &= (1/2\pi)^2 \int \exp(-i\omega\tau)\, F_{kl}(\omega)\, d\omega \\ &= \langle F_k(t) F_l(t + \tau)\rangle^{\text{eq}}\end{aligned}$$

These relations can be found in the book of Landau and Lifschitz.[6] Thus we have

$$F_{kl}(\tau) = \delta(\tau)(\gamma_{kl} + \gamma_{lk}) \tag{44}$$

Comparison with (36) using (42) shows the validity of this equation for our case, too. Perhaps it is useful to see this in another way: At first, we get, with (42), (24), and (34), the following equation for the TCF, in agreement with (23):

$$R(\mathbf{r}_i, \mathbf{v}_i, \mathbf{r}_j + \mathbf{v}_j \Delta t, \mathbf{v}_j, t + \Delta t) - R_{ij}(t) = \Delta t \sum g_{js} R_{is}(t) \tag{45}$$

On the other hand, we get from (42)

$$\left\langle \left\{ [M(\mathbf{r}_i + \mathbf{v}_i\,\Delta t, \mathbf{v}_i, t + \Delta t) - M_i](\Delta t)^{-1} - \sum g_{is} M_s \right\} \right.$$
$$\left. \times \left\{ [M(\mathbf{r}_j + \mathbf{v}_j\,\Delta t, \mathbf{v}_j, t + \Delta t) - M_j](\Delta t)^{-1} - \sum g_{js} M_s \right\} \right\rangle^{\mathrm{eq}}$$
$$= (\Delta t)^{-2} \int_0^{\Delta t}\!\!\int \langle F_i(t + \tau)\, F_j(t + \tau')\rangle^{\mathrm{eq}}\, d\tau\, d\tau'$$

For calculation of the left-hand side, we can first replace the value t by 0. Then, we get with (45) and (24),

$$\sum_{s,t} g_{is} g_{jt} R_{st}(0) - 2 \sum_{s,t} g_{is} g_{jt} R_{st}(0)$$
$$- (\Delta t)^{-1} \left[\sum_s g_{js} R_{is}(0) - \sum_s g_{is} R_{js}(0)\right]$$
$$= (\Delta t)^{-2} \int_0^{\Delta t}\!\!\int \langle F_i(\tau)\, F_j(\tau')\rangle^{\mathrm{eq}}\, d\tau\, d\tau'$$

With $R_{nm}(0) = G^{\mathrm{eq}}_{nm} = N^n_{\mathrm{eq}}\,\delta_{nm}$ and dropping terms $O(\Delta t)$, we get

$$-(g_{ji} N_i^{\mathrm{eq}} + g_{ij} N_j^{\mathrm{eq}}) = (\Delta t)^{-1} \int_0^{\Delta t}\!\!\int \langle F_i(\tau)\, F_j(\tau')\rangle^{\mathrm{eq}}\, d\tau\, d\tau'$$

or

$$\gamma_{ij} + \gamma_{ji} = L_{ij}[\mathfrak{N}^{\mathrm{eq}}] = (\Delta t)^{-1} \int_0^{\Delta t}\!\!\int \langle F_i(\tau)\, F_j(\tau')\rangle\, d\tau\, d\tau'$$

This is the proof.

We conclude with the following remarks. We consider an equilibrium ensemble of systems which fulfill the stochastic equation (28). With the entropy (37), we get the forces (39).

Linearizing the equation of motion yields the Onsager coefficients (43). These give us, according to (43), the correlation of the random forces. Now, (20) can be rederived in the following way: If there were no random forces, we would have the following equation for $\mathfrak{G}$:

$$D_{ij} G = H_{ij}[\langle \mathfrak{N} \rangle, \mathfrak{G}]$$

The remaining term can be constructed in equilibrium:

$$\gamma_{ij} + \gamma_{ji} = L_{ij}[\mathfrak{N}^{\mathrm{eq}}]$$

Now we can replace $N_n^{eq} N_m^{eq}$ by $N_n^{eq} N_m^{eq} + G_{nm}^{eq}$ in (43) without changing the left-hand side. Replacing $\mathfrak{N}^{eq}$ and $\mathfrak{G}^{eq}$ by the time-dependent mean values $\langle \mathfrak{N} \rangle (t)$ and $\mathfrak{G}(t)$ then yields

$$D_{ij} G = H_{ij}[\langle \mathfrak{N} \rangle, \mathfrak{G}] + L_{ij}[\langle \mathfrak{N} \rangle, \mathfrak{G}]$$

which is (21). Perhaps it is possible to go on along this line in order to get equations for the correlations functions in nonequilibrium for more general cases. This would enable us to treat fluctuation phenomena in non equilibrium for these more general cases, too.

6. MORE RIGOROUS DERIVATION OF THE EQUATION OF MOTION FOR THE TCF

First, we define

$$\sum_{\mathfrak{N}} N_\rho P^{eq}(\mathfrak{N})\, P(\mathfrak{N} \mid \mathfrak{M}, t) = \hat{N}_\rho(\mathfrak{M}, t) \tag{46}$$

With $\sum \hat{N}_\rho(\mathfrak{M}, t) = \langle N_\rho \rangle^{eq}$, we can define a new coarse-grained probability in Γ-space by

$$(\langle N_\rho \rangle^{eq})^{-1}\, \hat{N}_\rho(\mathfrak{M}, t) = P_\rho(\mathfrak{M}, t) \tag{47}$$

Looking at the master equation (12), we see that the same equation is valid for P_ρ, too. The initial condition for P_ρ is

$$P_\rho(\mathfrak{M}, 0) = (\langle N_\rho \rangle^{eq})^{-1}\, P^{eq}(\mathfrak{M})\, M_\rho \tag{48}$$

Now we can translate all conclusions from the master equation for $P(\mathfrak{N} \mid \mathfrak{M}, t)$ to conclusions from the equation for P_ρ. For example, defining

$$\begin{aligned} M_{\rho i}(t) &= \sum P_\rho(\mathfrak{M}, t)\, M_i \\ G_{\rho ik}(t) &= \sum P_\rho(\mathfrak{M}, t)(M_i - M_{\rho i})(M_k - M_{\rho k}) \end{aligned} \tag{49}$$

we get for these functions, according to (21), the following equations of motion:

$$\begin{aligned} D_i M_\rho &= B_i[\mathfrak{M}_\rho] + B_i[\mathfrak{G}_\rho] \\ D_{ij} G_\rho &= L_{ij}[\mathfrak{M}_\rho] + L_{ij}[\mathfrak{G}_\rho] + H_{ij}[\mathfrak{M}_\rho, \mathfrak{G}_\rho] \end{aligned} \tag{50}$$

Now we get with (24) and

$$\sum_{\mathfrak{N}\mathfrak{M}} P^{eq}(\mathfrak{N})\, P(\mathfrak{N} \mid \mathfrak{M}, t)(M_i - \langle M_i \rangle^{eq}) = 0$$

the following equation:

$$R_{\rho i} = \langle N_\rho \rangle^{\text{eq}} M_{\rho i} - \langle N_\rho \rangle^{\text{eq}} \langle N_i \rangle^{\text{eq}} \tag{51}$$

Thus a knowledge of $\mathfrak{M}_\rho$ is equivalent to a knowledge of $\mathfrak{R}_\rho$. With (51) we get from (50)

$$D_i R_\rho = (\langle N_\rho \rangle^{\text{eq}})^{-1} B_i[\mathfrak{R}_\rho] + B_i^l[\mathfrak{R}_\rho] + \langle N_\rho \rangle^{\text{eq}} B_i[\mathfrak{G}_\rho] \tag{52}$$

where

$$\begin{aligned} B_i^l[\mathfrak{R}_\rho] = \sum{}' w(mn \mid kl)\, \delta_{ik}[\langle N_n \rangle^{\text{eq}} R_{\rho m} + \langle N_m \rangle^{\text{eq}} R_{\rho n} \\ - \langle N_k \rangle^{\text{eq}} R_{\rho l} + \langle N_l \rangle^{\text{eq}} R_{\rho k}] \end{aligned}$$

The initial conditions are:

$$\begin{aligned} R_{\rho i}(0) &= \langle N_\rho \rangle^{\text{eq}} \delta_{\rho i} \\ G_{\rho ik}(0) &= \langle N_i \rangle^{\text{eq}} \delta_{ij} - \delta_{ij}\delta_{\rho i} \end{aligned} \tag{53}$$

Now, it seems to be hopeless to look for an exact solution of (50). Therefore we confine ourselves to a proof of consistency. We assume that $B_i[\mathfrak{G}_\rho]$ and $L_{ij}[\mathfrak{G}_\rho]$ are negligibly small on the r.h.s. of (50). Thus Eqs. (50) decouple. Then we can see if the solutions fulfill our initial assumptions or not. We get

$$\begin{aligned} D_i M_\rho &= B_i[\mathfrak{M}_\rho] \\ D_{ij} G_\rho &= L_{ij}[\mathfrak{M}_\rho] + H_{ij}[\mathfrak{M}_\rho, \mathfrak{G}_\rho] \end{aligned} \tag{54}$$

From the initial conditions (53), we have

$$G_{\rho ik}(0) \cong M_{\rho i}(0)\, \delta_{ik}$$

Furthermore, we have

$$\lim_{t\to\infty} G_{\rho ik}(t) = \lim_{t\to\infty} M_{\rho i}(t)\, \delta_{ik}$$

Therefore we try the following *ansatz*:

$$G_{\rho ij} = M_{\rho i}\delta_{ij} + G'_{\rho ij} \tag{55}$$

Inserting (55) into (54) yields:

$$D_i M_\rho = B_i[\mathfrak{M}_\rho] \tag{56a}$$

$$D_{ij} G_\rho' = \psi_{ij}[\mathfrak{M}_\rho] + H_{ij}[\mathfrak{M}_\rho, \mathfrak{G}_\rho'] \tag{56b}$$

where:

$$\psi_{ij}[\mathfrak{M}_\rho] = \sum{}' w(mn \mid kl)(\delta_{ik}\,\delta_{jl} - \delta_{im}\,\delta_{jn})\, M_{\rho n} M_{\rho m}$$

The functional ψ has the following remarkable property:

$$\sum_j \psi_{ij}[\mathfrak{M}_\rho] = B_i[\mathfrak{M}_\rho] \tag{57}$$

Now, looking at the initial condition $M_{\rho i}(0) = \langle N_i\rangle^{\text{eq}} + \delta_{\rho i}$, we can linearize (56) with respect to total equilibrium: $M_{\rho i}(t) = \hat{M}_{\rho i}(t) + \langle N_i\rangle^{\text{eq}}$. Now, we have: $M_{\rho i}(t) = \langle N_i\rangle^{\text{eq}} + R_{\rho i}(\langle N_\rho\rangle^{\text{eq}-1}$. Thus we get

$$\hat{M}_{\rho i}(t) = R_{\rho i}(\langle N_\rho\rangle^{\text{eq}})^{-1}.$$

Therefore we have

$$\begin{aligned} D_i R_\rho &= B_i{}^l[\mathfrak{R}_\rho] \\ D_{ij} G_\rho' &= \psi_{ij}^l[\mathfrak{R}_\rho] + H_{ij}[\langle\mathfrak{R}\rangle^{\text{eq}}, \mathfrak{G}_\rho'] + H_{ij}[\mathfrak{R}_\rho(\langle N_\rho\rangle^{\text{eq}})^{-1}, \mathfrak{G}_\rho'] \end{aligned} \tag{58}$$

with

$$\begin{aligned} B_i{}^l[\mathfrak{R}_\rho] = \sum{}' w(mn \mid kl)\, \delta_{ki}(\langle N_m\rangle^{\text{eq}} R_{\rho n} + \langle N_n\rangle^{\text{eq}} R_{\rho m} \\ - \langle N_k\rangle^{\text{eq}} R_{\rho l} - \langle N_l\rangle^{\text{eq}} R_{\rho k}) \end{aligned}$$

and

$$\begin{aligned} \psi_{ij}^l = \sum{}' w(mn \mid kl)\, \delta_{ki}(\langle N_m\rangle^{\text{eq}} R_{\rho n} + \langle N_n\rangle^{\text{eq}} R_{\rho m} \\ - \langle N_k\rangle^{\text{eq}} R_{\rho l} - \langle N_l\rangle^{\text{eq}} R_{\rho k}) \end{aligned} \tag{59}$$

Now we introduce the following norm:

$$\| S \| = \operatorname*{Max}_{i,j} \mid S_{ij} \mid$$

We assume that $\| G_\rho' \| \ll \| G_\rho \|$; this is true initially and finally. So we are led to the farther assumption that the third term on the r.h.s. of (58) is negligibly small. Thus we get

$$D_i R_\rho = B_i{}^l[\mathfrak{R}_\rho] \tag{60a}$$

$$D_{ij} G_\rho' = \psi_{ij}^l[\mathfrak{R}_\rho](\langle N_\rho\rangle^{\text{eq}})^{-1} + H_{ij}[\langle\mathfrak{R}\rangle^{\text{eq}}, \mathfrak{G}_\rho'] \tag{60b}$$

(60a) is the linearized Boltzmann equation for the TCF. Now, (60b) is a linear inhomogeneous equation. The solution of this equation can be written as the sum of the solution of the inhomogeneous equation with the initial condition $\mathfrak{G}_\rho'(0) = 0$ and of the solution of the homogeneous equation with the initial condition $G'_{\rho ij}(0) = -2\delta_{\rho i}\,\delta_{\rho j}$. First, we consider the homogeneous equation

$$D_{ij}\tilde{G}_\rho = H_{ij}[\langle\mathfrak{N}\rangle^{\text{eq}}, \tilde{\mathfrak{G}}_\rho]$$

We can see that

$$\tilde{G}_{\rho ij} = -2R_{\rho i}R_{\rho j}(\langle N_\rho\rangle^{\text{eq}})^{-2} \tag{61}$$

is the solution of this equation. Our problem thus reduces to the problem of solving the inhomogeneous equation

$$D_{ij}G_\rho' = \psi^l_{ij}[\mathfrak{R}_\rho](\langle N_\rho\rangle^{\text{eq}})^{-1} + H_{ij}[\langle\mathfrak{N}\rangle^{\text{eq}}, \mathfrak{G}_\rho']$$

with the initial condition $G'_{\rho ij}(0) = 0$.

Before treating this problem, let us investigate some properties of $\psi^l_{ij}[\mathfrak{R}_\rho]$ and $R_{\rho ij}$. We choose the molecules to be hard spheres. We put

$$\mathbf{v}_i + \mathbf{v}_j = \mathbf{s}_{ij}\,, \qquad \mathbf{v}_i - \mathbf{v}_j = \mathbf{g}_{ij} \tag{62}$$

With (11), we get, after some calculation.

$$\begin{aligned}\psi^l_{ij} = \delta(\mathbf{r}_i\,, \mathbf{r}_j)(8l^3)^{-1}\,k^2\langle N_i\rangle^{\text{eq}}\,\langle N_j\rangle^{\text{eq}}\Big\{-4\pi(T_{\rho i} + T_{\rho j})\,g_{ij} \\ + \sum_{\mathbf{e}} c^2(g_{ij})^{-1}\,[T_\rho(\tfrac{1}{2}(\mathbf{s}_{ij} + g_{ij}\mathbf{e}) + T_\rho(\tfrac{1}{2}(\mathbf{s}_{ij} - g_{ij}\mathbf{e}))]\Big\}\end{aligned} \tag{63}$$

where $T_{\rho i} = R_{\rho i}(\langle N_i\rangle^{\text{eq}})^{-1}$. The sum runs over all unit vectors e. We have f terms in this sum, where $4\pi g_{ij}c = fc^3$. Therefore we get $f = 4\pi g_{ij}^2c^{-2}$. Now let us calculate $\psi^l_{ij}[\mathfrak{R}_\rho]$, when $\mathfrak{R}_\rho$ has the following form:

$$R_{\rho i} = A(\mathbf{r}_\rho\,, \mathbf{r}_i\,, \mathbf{v}_\rho\,, t)\,\delta(\mathbf{v}_\rho\,, \mathbf{v}_i)\langle N_i\rangle^{\text{eq}} \tag{64}$$

Then we get from (63)

$$\begin{aligned}\psi^l_{ij}[\mathfrak{R}_\rho] = \{&-4\pi g_{ij}[\delta(\mathbf{v}_\rho\,, \mathbf{v}_i) + \delta(\mathbf{v}_\rho\,, \mathbf{v}_j)] \\ &+ 2c^2g_{ij}^{-1}\delta((\mathbf{v}_\rho - \mathbf{v}_i\,, \mathbf{v}_\rho - \mathbf{v}_j), 0)\} \\ &\times k^2(8l^3)^{-1}\,\langle N_i\rangle^{\text{eq}}\,\langle N_j\rangle^{\text{eq}}\,\delta(\mathbf{r}_i\,, \mathbf{r}_j)\,A\end{aligned} \tag{65}$$

It should be noted that $g_{ij} = 0$ is forbidden by the exclusion condition [see (26)]. We now consider two different cases.

Case (a) $g_{ij} \cong c$.

Only in this case are the terms $\sim g_{ij}^{-1}2c^2$ on the r.h.s. of (65) of equal magnitude as the first terms. But the second term is different from zero only when $v_\rho \simeq c$.

Case (b) $g_{ij} \cong \langle v \rangle \gg c$.

In this case, the second term becomes negligibly small. Therefore we can drop the second term, thus obtaining

$$\psi_{ij}^{l}[\mathfrak{R}_\rho] = -\tfrac{1}{2}\pi k^2 l^{-3}\, \delta(\mathbf{r}_i\,,\mathbf{r}_j)\, A\langle N_i\rangle^{\text{eq}} \langle N_j\rangle^{\text{eq}}\, g_{ij}[\delta(\mathbf{v}_\rho\,,\mathbf{v}_i) + \delta(\mathbf{v}_\rho\,,\mathbf{v}_j)] \quad (66)$$

or

$$\psi_{ij}^{l}[\mathfrak{R}_\rho] = -\tfrac{1}{2}\pi k^2 l^{-3}\, \delta(\mathbf{r}_i\,,\mathbf{r}_j)[\langle N_i\rangle^{\text{eq}} R_{\rho j} + \langle N_j\rangle^{\text{eq}} R_{\rho i}] \quad (67)$$

This equation is valid whenever the positive term in $\psi_{ij}[\mathfrak{R}_\rho]$ is negligibly small. Now we get from (57) and (64):

$$\begin{aligned}\delta(\mathbf{v}_\rho\,,\mathbf{v}_i)\langle N_i\rangle^{\text{eq}}\, D_i A_\rho = {} & \tfrac{1}{2}\pi k^2 l^{-3} A_\rho \langle N_i\rangle^{\text{eq}} \textstyle\sum \delta(\mathbf{r}_i\,,\mathbf{r}_j)\langle N_j\rangle^{\text{eq}}\, g_{ij}\, \delta(\mathbf{v}_\rho\,,\mathbf{v}_i) \\ & - \tfrac{1}{2}\pi k^2 l^{-3} A_\rho \langle N_i\rangle^{\text{eq}}\langle N_\rho\rangle^{\text{eq}}\, g_{i\rho} \end{aligned} \quad (68)$$

(68) shows that (64) cannot be valid exactly; (68) is not self-consistent. But we are led to the following *ansatz*:

$$R_{\rho i} = A(\mathbf{r}_\rho\,,\mathbf{r}_i\,,\mathbf{v}_\rho\,,t)\, \delta(\mathbf{v}_\rho\,,\mathbf{v}_i)\langle N_i\rangle^{\text{eq}} + S_{\rho i} \quad (69)$$

with $S_{\rho i} = 0$ for $\mathbf{v}_\rho = \mathbf{v}_i$. Thus we get

$$\begin{aligned} & D_i S_\rho + \delta(\mathbf{v}_\rho\,,\mathbf{v}_i)\langle N_i\rangle^{\text{eq}}\, D_i A_\rho \\ & \quad = -\tfrac{1}{2}\pi k^2 l^{-3} A_{\rho i}\langle N_i\rangle^{\text{eq}} \textstyle\sum \delta(\mathbf{r}_i\,,\mathbf{r}_j)\langle N_j\rangle^{\text{eq}}\, g_{ij}\, \delta(\mathbf{v}_\rho\,,\mathbf{v}_i) \\ & \quad\quad - \tfrac{1}{2}\pi k^2 l^{-3} A_{\rho i}\langle N_i\rangle^{\text{eq}}\langle N_\rho\rangle^{\text{eq}}\, g_{i\rho} + B_i^{1}[\mathfrak{S}_\rho] \end{aligned} \quad (70)$$

Therefore we have

$$\begin{aligned} & \langle N_\rho\rangle^{\text{eq}}[A(\mathbf{r}_\rho\,,\mathbf{r}_i + \mathbf{v}_\rho \Delta t\,,\mathbf{v}_\rho\,,t + \Delta t) - A(\mathbf{r}_\rho\,,\mathbf{r}_i\,,\mathbf{v}_\rho\,,t)] \\ & \quad = -\tfrac{1}{2}\pi k^2 l^{-3}\, \Delta t\langle N_\rho\rangle^{\text{eq}}\, A(\mathbf{r}_\rho\,,\mathbf{r}_i\,,\mathbf{v}_\rho\,,t) \textstyle\sum \delta(\mathbf{r}_i\,,\mathbf{r}_j)\langle N_j\rangle^{\text{eq}}\, g_{\rho j} \\ & \quad\quad + \Delta t \textstyle\sum' w(mn \mid kl)\, \delta(\mathbf{r}_i\,,\mathbf{r}_k)\, \delta(\mathbf{v}_\rho\,,\mathbf{v}_k) \\ & \quad\quad \times [\langle N_m\rangle^{\text{eq}} S_{\rho n} + \langle N_n\rangle^{\text{eq}} S_{\rho m} - \langle N_k\rangle^{\text{eq}} S_{\rho l} - \langle N_l\rangle^{\text{eq}} S_{\rho k}] \end{aligned} \quad (71a)$$

$$D_i S_\rho = -\tfrac{1}{2}\pi k^2 l^{-3} A_{\rho i}\langle N_i\rangle^{\text{eq}}\langle N_\rho\rangle^{\text{eq}}\, g_{i\rho} + B_i^{l}[\mathfrak{S}_\rho] \quad (71b)$$

for $\mathbf{v}_i \neq \mathbf{v}_\rho$.

Now, in first approximation, we consider the second term on the right-hand side of (71a) as negligibly small. Therefore we get the following equation for A:

$$\begin{aligned} & (\Delta t)^{-1}[A(\mathbf{r}_\rho\,,\mathbf{r}_i + \mathbf{v}_\rho \Delta t\,,\mathbf{v}_\rho\,,t + \Delta t) - A(\mathbf{r}_\rho\,,\mathbf{r}_i\,,\mathbf{v}_\rho\,,t)] \\ & \quad = -\tfrac{1}{2}\pi k^2 l^{-3} A(\mathbf{r}_\rho\,,\mathbf{r}_i\,,\mathbf{v}_\rho\,,t)\langle n\rangle\, \gamma_\rho \end{aligned} \quad (72)$$

with $\langle n\rangle \gamma_\rho = \sum \delta(\mathbf{r}_i, \mathbf{r}_j)\langle N_j\rangle^{\text{eq}} g_{\rho j}$. Therefore we get from (72), using $A_{\rho i}(t=0) = \delta(\mathbf{r}_\rho, \mathbf{r}_i)$,

$$A(\mathbf{r}_\rho, \mathbf{r}_i, \mathbf{v}_\rho, t) = \exp(-\tfrac{1}{2}\pi k^2 l^{-3}\langle n\rangle \gamma_\rho t)\, \delta(\mathbf{r}_i - \mathbf{v}_\rho t, \mathbf{r}_\rho) \tag{73}$$

By introducing an iteration process, we now can solve (71b) and then check our approximation. For example, we get

$$D_i \mathring{S}_\rho = -\tfrac{1}{2}\pi k^2 l^{-3} A_{\rho i}\langle N_i\rangle^{\text{eq}}\langle N_\rho\rangle^{\text{eq}} g_{i\rho}$$

For convenience, we choose a new coordinate system $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ with $\mathbf{e}_3 = (\mathbf{v}_i - \mathbf{v}_\rho)\, g_{i\rho}^{-1}$, $(\mathbf{e}_1, \mathbf{e}_2) = (\mathbf{e}_2, \mathbf{e}_3) = (\mathbf{e}_1, \mathbf{e}_3) = 0$. With $\mathbf{r}_{i\rho} = \mathbf{r}_i - \mathbf{r}_\rho$, we get

$$\begin{aligned} \mathring{S}_{\rho i}(t) = &-\tfrac{1}{2}\pi k^2 l^{-3}\langle N_i\rangle^{\text{eq}}\langle N_\rho\rangle^{\text{eq}}\, \delta((\mathbf{r}_{i\rho}, \mathbf{e}_2), 0)\, \delta((\mathbf{r}_{i\rho}, \mathbf{e}_2), 0) \\ &\times \exp[\tfrac{1}{2}\pi k^2 l^{-3}\gamma_\rho g_{i\rho}^{-1}\langle n\rangle(\mathbf{r}_{i\rho} - \mathbf{v}_i t, \mathbf{e}_3)] \\ &\times \varphi(0 \leqslant -(\mathbf{r}_{i\rho} - \mathbf{v}_i t, \mathbf{e}_3) \leqslant g_{i\rho} t) \end{aligned} \tag{74}$$

where

$$\begin{aligned} \varphi(a \leqslant x \leqslant b) &= 1 \qquad \text{for} \quad a \leqslant x \leqslant b \\ &= 0 \qquad \text{otherwise} \end{aligned}$$

Equation (74) shows that the following expression is a good approximation for $R_{\rho i}$, at least for sufficiently short times:

$$R_{\rho i}(t) = \delta(\mathbf{v}_\rho, \mathbf{v}_i)\, \delta(\mathbf{r}_i - \mathbf{v}_\rho t, \mathbf{r}_\rho)\langle N_i\rangle^{\text{eq}} \exp(-\tfrac{1}{2}\pi k^2 l^{-3}\langle n\rangle \gamma_\rho t) \tag{75}$$

We now turn to our initial problem. First, we put

$$\langle N_\rho\rangle^{\text{eq}} G'_{\rho ij} = \Gamma'_{\rho ij} \tag{76}$$

By (67) and the form of the functional H_{ij} [Eq. (20)], we are led to the *ansatz*:

$$\begin{aligned} \Gamma'_{\rho ij} = {} & \delta((\mathbf{r}_{ij}, \mathbf{e}_1), 0)\, \delta((\mathbf{r}_{ij}, \mathbf{e}_2), 0)(\langle N_i\rangle^{\text{eq}} R_{\rho j} + \langle N_j\rangle^{\text{eq}} R_{\rho i}) \\ & \times F((\mathbf{r}_{ij}, \mathbf{e}_3), t, g_{ij}) \end{aligned} \tag{77}$$

For brevity, we write $(\mathbf{r}_{ij}, \mathbf{e}_k) = d_k$. From (68), we obtain

$$\begin{aligned} D_{ij}\Gamma_\rho' = {} & \delta(d_1, 0)\, \delta(d_2, 0)(\langle N_i\rangle^{\text{eq}} D_j R_\rho + \langle N_j\rangle^{\text{eq}} D_i R_\rho)\, F(d_3, t, g_{ij}) \\ & + \delta(d_1, 0)\, \delta(d_2, 0)(\Delta t)^{-1}(\langle N_i\rangle^{\text{eq}} R_{\rho j} + \langle N_j\rangle^{\text{eq}} R_{\rho i}) \\ & \times [F(d_3 + g_{ij}\Delta t, t + \Delta t, g_{ij}) - F(d_3, t, g_{ij})] \end{aligned}$$

For $H_{ij}[\Gamma_\rho']$, we obtain

$$H_{ij}[\Gamma_\rho'] = \{\sum' w(mn \mid jl)[(\langle N_n\rangle^{\mathrm{eq}} R_{\rho i} + \langle N_i\rangle^{\mathrm{eq}} R_{\rho n})\langle N_n\rangle^{\mathrm{eq}} \check{F}_{ni} + (\langle N_m\rangle^{\mathrm{eq}} R_{\rho i} + \langle N_i\rangle^{\mathrm{eq}} R_{\rho m})\langle N_m\rangle^{\mathrm{eq}} \check{F}_{mi} - (\langle N_l\rangle^{\mathrm{eq}} R_{\rho i} + \langle N_i\rangle^{\mathrm{eq}} R_{\rho l})\langle N_j\rangle^{\mathrm{eq}} \check{F}_{li} - (\langle N_j\rangle^{\mathrm{eq}} R_{\rho i} + \langle N_i\rangle^{\mathrm{eq}} R_{\rho j})\langle N_l\rangle^{\mathrm{eq}} \check{F}_{ji})\} + [i \leftrightarrow j] \tag{78}$$

where

$$\check{F}_{ni} = \delta((\mathbf{e}_1, \mathbf{r}_{ni}), 0)\, \delta((\mathbf{e}_2, \mathbf{r}_{ni}), 0)\, F((\mathbf{g}_{ni}, \mathbf{r}_{ni})\, g_{ni}^{-1}, t, g_{ni})$$

From the Kronecker delta in $w(mn \mid jl)$, we have $\mathbf{r}_n = \mathbf{r}_j$. We can see that

$$\check{F}_{ni} = 0, \qquad \text{if} \quad g_{ni} \nparallel r_{ij} \tag{79}$$

Now, $R_{\rho n}$ contains a Kronecker delta $\delta(\mathbf{v}_\rho, \mathbf{v}_n)$. Therefore the second column of terms in (78) yields

$$T_2 = \langle N_i\rangle^{\mathrm{eq}} B_j'[\mathfrak{R}_\rho]\, \check{F}_{\rho i} + [i \leftrightarrow j]$$

On the other hand, we get

$$T_1 = \sum' w(mn \mid jl)\langle N_j\rangle^{\mathrm{eq}}\langle N_l\rangle^{\mathrm{eq}} R_{\rho i}(\check{F}_{ni} + \check{F}_{mi} - \check{F}_{li} - \check{F}_{ji}) + [i \leftrightarrow j]$$

Now, (79) shows that

$$\sum' w(mn \mid jl)\langle N_j\rangle^{\mathrm{eq}}\langle N_l\rangle^{\mathrm{eq}}(\check{F}_{ni} + \check{F}_{mi} - \check{F}_{li})$$

can be neglected. Therefore we get for T_1

$$T_1 = -\check{F}_{ji} R_{\rho i} \tfrac{1}{2}\pi k^2 l^{-3} \langle N_j\rangle^{\mathrm{eq}} \langle n\rangle\, \gamma_j + [i \leftrightarrow j] \tag{80}$$

Thus we get the following equation for F:

$$DF = -\tfrac{1}{2}\pi k^2 l^{-3}\, \delta(d_3, 0)\, g_{ij} - \tfrac{1}{2}\pi k^2 l^{-3} \langle n\rangle\, \gamma_j F \tag{81}$$

The solution of (81) is

$$F(d_3, g_{ij}, t) = -\tfrac{1}{2}\pi(k/l)^2 \exp[-d_3(g_{ij} l^3)^{-1} \gamma_j \langle n\rangle \tfrac{1}{2}\pi]\, \varphi(0 \leqslant d_3 \leqslant g_{ij} t)$$

Therefore we have finally

$$\Gamma'_{\rho ij}(t) = -\tfrac{1}{2}\pi(k/l)^2 \exp(-\tfrac{1}{2}\pi k^2 l^{-3} r_{ij} \langle n\rangle\, \gamma_j g_{ij}^{-1})\, \varphi(0 \leqslant r_{ij} \leqslant g_{ij} t) \times \delta(r_1, 0)\, \delta(r_2, 0)(\langle N_i\rangle^{\mathrm{eq}} R_{\rho j} + \langle N_j\rangle^{\mathrm{eq}} R_{\rho i}) \tag{82}$$

with $r_1 = (\mathbf{r}_{ij}, \mathbf{e}_1)$, $\mathbf{r}_2 = (\mathbf{r}_{ij}, \mathbf{e}_2)$. The local values ($\mathbf{r}_i \gtrsim \mathbf{r}_j$) become after the time $\Delta\tau$

$$\Gamma'^{\text{loc}}_{\rho ij} = -(k/l)^2 \tfrac{1}{2}\pi(\langle N_i\rangle^{\text{eq}} R_{\rho j} + \langle N_j\rangle^{\text{eq}} R_{\rho i}) \tag{83}$$

Thus we have the following result: As long as (75) is valid, (60) has the following solution:

$$\begin{aligned} G'_{\rho ij} &= -2R_{\rho i}R_{\rho j}(\langle N_\rho\rangle^{\text{eq}})^{-2} \\ &\quad - \tfrac{1}{2}\pi(k/l)^2 \exp(-r_{ij}\tfrac{1}{2}\pi g_{ij}^{-1}k^2l^{-3}\langle n\rangle\, \gamma_j)\, \varphi(0 < r_{ij} < g_{ij}t) \\ &\quad \times \delta(r_1, 0)\, \delta(r_2, 0)(\langle N_i\rangle^{\text{eq}} R_{\rho j} + \langle N_j\rangle^{\text{eq}} R_{\rho i})(\langle N_\rho\rangle^{\text{eq}})^{-1} \end{aligned} \tag{84}$$

The first term remains valid for all times, while the validity of the second one will break down, but its order of magnitude will not increase.

After inserting (83) and (61) into $B_i[\Gamma_\rho]$, we see that indeed these terms are negligibly small, the first being

$$T_1 = -(k/l)^2 \tfrac{1}{2}\pi B_i^l[\mathfrak{R}_\rho]$$

and the second one

$$\begin{aligned} T_2 &= -2 \textstyle\sum' w(mn \mid ij)(\langle N_\rho\rangle^{\text{eq}})^{-1}(R_{\rho m}R_{\rho n} - R_{\rho i}R_{\rho j}) \\ &= -2(\langle N_\rho\rangle^{\text{eq}})^{-1} B_i[\mathfrak{R}_\rho] \end{aligned} \tag{85}$$

T_2 was dropped initially by our linearization; furthermore, as long as $R_{\rho i} \sim \delta(\mathbf{v}_\rho, \mathbf{v}_i)$, $B_i[\mathfrak{R}_\rho]$ vanishes exactly because of the exclusion condition. T_1 is negligibly small because $(k/l)^2$ is the ratio of the cross section to the square of the mean free path, and this ratio is, according to our initial assumption negligibly small. In a similar way, we can see that $L_{ij}[\mathfrak{G}_\rho]$ is indeed negligibly small on the r.h.s. of (50).

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