Matrix continued-fraction representation of the dynamical self-structure factor $S_s(q,\omega)$

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(Received 16 July 1986)

A new approach is presented for determining the dynamical self-structure factor $S_s(q,\omega)$ for a multicomponent dilute gas mixture. The starting point is the three-dimensional linear inhomogeneous Boltzmann equation with a Maxwell interaction potential. It is shown that the dynamical self-structure factor can be expressed analytically in terms of a continued fraction of infinite but sparse matrices. Although other methods and approximation schemes for calculating $S_s(q,\omega)$ via the Boltzmann equation have been suggested so far, the method and the results presented here are new in the following sense. First, to our knowledge there does not exist an analytical solution of the Boltzmann equation covering the entire (q,ω) range for $S_s(q,\omega)$ and yielding in particular the correct dynamical self-structure factor $S_s(q,\omega)$ for both the hydrodynamical limit $(q\rightarrow 0)$ and the free-gas limit $(q\rightarrow\infty)$. Second, at least the example considered in this paper shows most clearly that the commonly suggested expansion of $S_s(q,\omega)$ in a continued fraction of scalars cannot be regarded as a useful expansion method.

I. INTRODUCTION

When describing the motion of a tagged particle in a dilute gas mixture the linear inhomogeneous Boltzmann equation is a proper starting point.[1-3] In the context of the theory of stochastic processes the linear Boltzmann equation can be viewed as a particular master equation where the transition probability is given by Boltzmann's *Stosszahlansatz*.[4-6] Although the Boltzmann equation has been known for more than a hundred years there are still a lot of predominately mathematical problems concerning this equation. In general, these difficulties arise due to the complexity of the transition probability $\omega(\mathbf{v}\rightarrow\mathbf{v}')$ which, in order to make the Boltzmann equation amenable to an analytical solution, is often replaced by a much simpler kernel.

Regardless of the special structure of the transition probability $\omega(\mathbf{v}\rightarrow\mathbf{v}')$ one can formally transform the Boltzmann equation into a partial differential equation of infinite order. This expansion is called the Kramers-Moyal expansion.[7] However, this equation is not easier to deal with than the Boltzmann equation itself, unless one breaks off the infinite series after a suitable number of terms. Assuming that the third and all higher moments of the transition probability are negligible and that the first moment is proportional to the velocity and the second moment is a constant, one arrives at the Fokker-Planck equation of Klein-Kramers type which originally was used to describe chemical reactions.[8] It is evident that with these approximations the influence of the interaction potential on the distribution function $h(\mathbf{r},\mathbf{v},t)$ has been dropped. Although, compared to the Boltzmann equation, the Klein-Kramers equation looks rather simple, there are still quite interesting problems concerning this equation. The problem of reducing the Klein-Kramers equation to the Smoluchowski equation under the influence of an external force and also transforming the boundary conditions for the reduced distribution function $h(\mathbf{r},t)$ correctly, should be mentioned here.[9,10] In order to take a realistic interaction potential between the colliding particles into account, an approximation scheme, which originally was developed to solve master equations,[11-13] was applied to expand the Boltzmann transport equation for inverse repulsive power laws in powers of the mass ratio of the colliding particles.[14]

However, an analytical solution for both the homogeneous and the inhomogeneous Boltzmann equation for nontrivial kernels $\omega(\mathbf{v}\rightarrow\mathbf{v}')$ is only available in very few cases. The most important nontrivial examples are the one-dimensional inhomogeneous Boltzmann equations for a system of identical hard rods[15] and the three-dimensional homogeneous Boltzmann equation for a gas mixture of particles interacting via a Maxwell (r^{-4}) potential.[16] Although the eigenfunctions of the transition probability $\omega(\mathbf{v}\rightarrow\mathbf{v}')$ are explicitly known for a Maxwell potential, they are of limited use for getting an analytical solution of the $\mathbf{q}$-dependent or inhomogeneous Boltzmann equation. These eigenfunctions only allow an expansion of the distribution function $h(\mathbf{q},\mathbf{v},t)$ in powers of q and, in general, restrict the solution to small values of q. In order to bypass this problem model equations have been suggested which, roughly speaking, replace the kernel $\omega(\mathbf{v}\rightarrow\mathbf{v}')$ by a finite number of its eigenfunctions.[17] This idea has also been applied to other interaction potentials like the hard-sphere interaction potential yielding a good approximation to the Boltzmann equation for both small and large q.[18-20]

In this paper we restrict ourselves to the inhomogeneous Boltzmann equation for a gas mixture interacting via a Maxwell potential. It is not our objective to find a general solution of this equation. Rather we once more restrict ourselves to the solution of the Boltzmann equation for one particular initial condition, which enables us to calculate the dynamical self-structure factor $S_s(q,\omega)$. As

the central result of our paper, it will turn out that the dynamical self-structure factor $S_s(q,\omega)$ can most naturally be represented by a continued fraction of infinite matrices [see Eq. (3.15)]. In the theory of memory function equations an expansion of $S_s(q,\omega)$ in a continued fraction of scalars is sometimes suggested.[21] At least the example considered in this paper shows most clearly that the expansion of $S_s(q,\omega)$ in a continued fraction of scalars is not the adequate representation for the self-structure factor, whereas the expansion in a continued fraction of matrices seems more natural and straightforward.

The paper is organized as follows. In Sec. II we make use of the well-known eigenfunctions of the transition probability for Maxwell molecules in order to derive a hierarchy of equations for certain averages $\tilde{c}_{k,l}(q,s)$ [see Eq. (2.10)]. The function $\tilde{c}_{0,0}(q,s)$ is then closely related to $S_s(q,\omega)$. This hierarchy of equations, the solution of which plays the central role in this paper, was already obtained by Wang Chang and Uhlenbeck about 40 years ago.[16] In Sec. III we solve this hierarchy of equations in a new and very simple way. Furthermore, we show that the dynamical self-structure factor can be represented by a continued fraction of infinite matrices. In Sec. IV we derive a memory function equation for the intermediate scattering function $F_s(q,t)$ and present an explicit expression for the memory function itself. Finally we show that our expression for $S_s(q,\omega)$ yields both the correct hydrodynamic and the correct free-gas limit.

II. BOLTZMANN EQUATION FOR MAXWELL MOLECULES

Let us consider a dilute gas mixture of particles with masses $m_A, m_B, \ldots$ and number densities $n_A, n_B, \ldots$, etc. Our starting point is the Fourier transform of the linear Boltzmann equation for the tagged particle A,

$$\frac{\partial}{\partial t}\tilde{h}(\mathbf{q},\mathbf{v},t) - i\mathbf{q}\cdot\mathbf{v}\tilde{h}(\mathbf{q},\mathbf{v},t) = -P_A(v)\tilde{h}(\mathbf{q},\mathbf{v},t) + \int \omega_A(\mathbf{v}_1\to\mathbf{v})\tilde{h}(\mathbf{q},\mathbf{v}_1,t)d^3v_1 , \tag{2.1a}$$

where

$$P_A(v) = \sum_\beta P_{A\beta}(v) = \sum_\beta \int \omega_{A\beta}(\mathbf{v}\to\mathbf{v}')d^3v' \tag{2.1b}$$

and

$$\omega_A(\mathbf{v}_1\to\mathbf{v}) = \sum_\beta \omega_{A\beta}(\mathbf{v}_1\to\mathbf{v}) , \tag{2.1c}$$

and $\omega_{AB}(\mathbf{v}_1\to\mathbf{v})$ is the probability to change its velocity from $\mathbf{v}_1$ to $\mathbf{v}$ due to a collision with a B particle. As already mentioned above it is not our objective to solve Eqs. (2.1) for a general initial condition. Since we are interested in the dynamical self-structure factor $S_s(q,\omega)$ alone, we are only looking for a solution of Eqs. (2.1) subject to the particular initial condition

$$\tilde{h}(\mathbf{q},\mathbf{v},t=0) = f_A(v) = \frac{1}{\pi^{3/2}v_{T_A}^3}e^{v^2/v_{T_A}^2} \tag{2.2a}$$

with

$$v_{T_A}^2 = \frac{2kT}{m_A} . \tag{2.2b}$$

Then, by definition, the dynamical self-structure factor $S_s(q,\omega)$ is given by

$$S_s(q,\omega) = \frac{2}{\pi}\mathrm{Re}Q(q,i\omega) , \tag{2.3a}$$

where we have introduced an auxiliary function $Q(q,s)$

$$Q(q,s) = \int_0^\infty e^{-st}F_s(q,t)dt , \tag{2.3b}$$

which is the Laplace transform of the intermediate scattering function $F_s(q,t)$

$$F_s(q,t) = \int d^3v\,\tilde{h}(\mathbf{q},\mathbf{v},t) . \tag{2.3c}$$

Next we use the fact that for any repulsive interaction potential the transition probability $\omega(\mathbf{v}_1\to\mathbf{v})$ is only a function of the tagged particle speeds v_1, v and the angle between $\mathbf{v}_1$ and $\mathbf{v}$. Expanding both the distribution function $\tilde{h}(\mathbf{q},\mathbf{v},t)$ and the transition probability $\omega_A(\mathbf{v}_1\to\mathbf{v})$ into Legendre polynomials

$$\tilde{h}(\mathbf{q},\mathbf{v},t) = \sum_{l=0}^\infty P_l(\eta)\tilde{h}_l(q,v,t) , \tag{2.4a}$$

$$\omega_A(\mathbf{v}_1\to\mathbf{v}) = \frac{1}{4\pi v^2}\sum_{l=0}^\infty (2l+1)P_l(\xi)\omega_{A,l}(v_1\to v) , \tag{2.4b}$$

with

$$\eta = \frac{\mathbf{q}\cdot\mathbf{v}}{qv}, \quad \xi = \frac{\mathbf{v}_1\cdot\mathbf{v}}{v_1 v} , \tag{2.4c}$$

and inserting these expressions into Eqs. (2.1), one obtains[16] the following infinite hierarchy of integro-differential equations for the expansion coefficients $\tilde{h}_l(q,v,t)$:

$$\frac{\partial}{\partial t}\tilde{h}_l - iqv\left[\frac{l}{2l-1}\tilde{h}_{l-1} + \frac{l+1}{2l+3}\tilde{h}_{l+1}\right] = -P_A(v)\tilde{h}_l(q,v,t) + \int_0^\infty dv_1 \frac{v_1^2}{v^2}\omega_{A,l}(v_1\to v)\tilde{h}_l(q,v_1,t) \tag{2.5a}$$

with

$$\tilde{h}_l(q,v,0) = \delta_{l,0}f_A(v) \quad \text{for } l=0,1,2,\ldots . \tag{2.5b}$$

A further simplification can be obtained by confining ourselves to a Maxwell interaction potential for which the eigenfunctions and eigenvalues of the kernel $\omega_{A,l}(v_1\to v)$ are known explicitly

$$\int_0^\infty \omega_{AB,l}(v_1\to v)\psi_{k,l}\left[\frac{v}{v_{T_A}}\right]dv = \lambda_{k,l}^{AB}\psi_{k,l}\left[\frac{v_1}{v_{T_A}}\right] . \tag{2.6}$$

The eigenfunctions $\psi_{k,l}$, which are related to the Sonine polynomials $S_{l+1/2}^k$ via

$$\psi_{k,l}(x)=x^l S^k_{l+1/2}(x^2)\ , \tag{2.7}$$

obey the following orthogonality relation:

$$\int f_A(v)\psi_{k,l}\left[\frac{v}{v_{T_A}}\right]\psi_{s,l}\left[\frac{v}{v_{T_A}}\right]d^3v=A_{k,l}\delta_{k,s}\ , \tag{2.8}$$

where $A_{k,l}$ are normalization constants. Furthermore, the following recursion relations will be useful:[16]

$$x\psi_{k,l}(x)=-(k+1)\psi_{k+1,l-1}(x)+(k+l+\tfrac{1}{2})\psi_{k,l-1}(x)\ , \tag{2.9a}$$

$$x\psi_{k,l}(x)=\psi_{k,l+1}(x)-\psi_{k-1,l+1}(x)\ . \tag{2.9b}$$

Explicit expressions for the eigenvalues $\lambda^{AB}_{k,l}$ can be found in Ref. 16. Introducing coefficients $\tilde{c}_{k,l}$

$$\tilde{c}_{k,l}(q,s)=\int_0^\infty dt\, e^{-st}\int d^3v\,\tilde{h}_l(q,v,t)\psi_{k,l}\left[\frac{v}{v_{T_A}}\right]\ , \tag{2.10}$$

and making use of Eqs. (2.6)—(2.9), we can easily transform Eq. (2.5) to the following hierarchy of equations:

$$(s+\mu_{k,l})\tilde{c}_{k,l}-\delta_{k,0}\delta_{l,0}=i\tilde{q}\left[\frac{l}{2l-1}[-(k+1)\tilde{c}_{k+1,l-1}+(k+l+\tfrac{1}{2})\tilde{c}_{k,l-1}]+\frac{l+1}{2l+3}(\tilde{c}_{k,l+1}-\tilde{c}_{k-1,l+1})\right]\ , \tag{2.11}$$

where

$$\tilde{c}_{k,l}=0\ \text{ for } k<0\ \text{ or } l<0 \tag{2.12}$$

and

$$\mu_{k,l}=\sum_\beta(\lambda^{A\beta}_{0,0}-\lambda^{A\beta}_{k,l})\ , \tag{2.13a}$$

$$\tilde{q}=qv_{T_A}\ . \tag{2.13b}$$

Finally, comparing Eq. (2.10) and Eqs. (2.3b) and (2.3c) one easily proves the following relation:

$$Q(q,s)=\tilde{c}_{0,0}(\tilde{q},s)\ , \tag{2.14}$$

which allows the determination of $S_s(q,\omega)$ once that Eq. (2.11) has been solved. However, at a first glance it is not obvious how to compute $\tilde{c}_{0,0}$ by means of Eq. (2.11), since it is an infinite hierarchy of algebraic equations for the determination of the coefficients $\tilde{c}_{k,l}$. Wang Chang and Uhlenbeck,[16] who already derived Eq. (2.11) about 40 years ago, failed in finding its general solution. Nevertheless, they suggested an approximation scheme by rearranging the elements $\tilde{c}_{k,l}$ according to certain *ad hoc* rules and then rewriting Eq. (2.11) as an infinite system of algebraic equations. Truncating this system of equations after a suitable number of terms then defines the nth approximation of the coefficients $\tilde{c}_{k,l}$. Regardless of the fact that no analytic solution is obtained, their approximation scheme has the disadvantage that in order to take all eigenvalues $\mu_{k,l}$ up to an index n into account one has to solve, roughly speaking, a system of $n^2\times n^2$ algebraic equations. In Sec. III we will show how one can bypass this problem to obtain an analytic solution for $\tilde{c}_{0,0}$.

III. MATRIX CONTINUED-FRACTION REPRESENTATION OF $Q(q,s)$

Before discussing Eq. (2.11) in detail we perform the following transformation:

$$c_{k,l}=\tilde{c}_{k,l}\frac{k!}{l!}\frac{\Gamma(l+\frac{1}{2})\Gamma(\frac{3}{2})}{\Gamma(k+l+\frac{3}{2})\Gamma(\frac{1}{2})}\ , \tag{3.1}$$

which leaves $Q(q,s)$ unaltered

$$Q(q,s)=\tilde{c}_{0,0}(\tilde{q},s)=c_{0,0}(\tilde{q},s)\ . \tag{3.2}$$

Instead of Eq. (2.11) we then have

$$(s+\mu_{k,l})c_{k,l}-\delta_{k,0}\delta_{l,0}=\frac{i\tilde{q}}{2}\left[-c_{k+1,l-1}+c_{k,l-1}+\frac{4(l+1)^2}{(2l+1)(2l+3)}[(k+l+\tfrac{3}{2})c_{k,l+1}-kc_{k-1,l+1}]\right]\ . \tag{3.3}$$

Next we introduce the infinite vectors

$$\mathbf{c}_l=(c_{0,l},c_{1,l},c_{2,l},\ldots)^T\ , \tag{3.4a}$$

$$\mathbf{f}=\frac{1}{s}\mathbf{e}_1\ , \tag{3.4b}$$

$$\mathbf{e}_1=(1,0,0,\ldots)^T\ , \tag{3.4c}$$

and the infinite band matrices

$$M_l=-\frac{i\tilde{q}}{2}\begin{pmatrix}\alpha_{0,l+1} & -\alpha_{0,l+1} & 0 & 0 & \cdots\\ 0 & \alpha_{1,l+1} & -\alpha_{1,l+1} & 0 & \cdots\\ 0 & 0 & \alpha_{2,l+1} & -\alpha_{2,l+1} & \cdots\\ \cdots & \cdots & \cdots & \cdots & \cdots\end{pmatrix}\ , \tag{3.5a}$$

and

$$N_l=i\tilde{q}\frac{2(l+1)^2}{(2l+1)(2l+3)}\begin{bmatrix}\beta_{0,l} & 0 & 0 & \cdots\\ -\alpha_{1,l} & \beta_{1,l} & 0 & \cdots\\ 0 & -2\alpha_{2,l} & \beta_{2,l} & \cdots\\ 0 & 0 & -3\alpha_{3,l} & \cdots\\ \cdots & \cdots & \cdots & \cdots\end{bmatrix}, \tag{3.5b}$$

where

$$\alpha_{k,l}=\frac{1}{s+\mu_{k,l}}, \tag{3.5c}$$

$$\beta_{k,l}=\frac{k+l+\frac{3}{2}}{s+\mu_{k,l}}. \tag{3.5d}$$

With these quantities we are able to write Eq. (3.3) in a more compact and transparent form

$$\mathbf{c}_0=N_0\mathbf{c}_1+\mathbf{f}, \tag{3.6a}$$

$$\mathbf{c}_l=-M_{l-1}\mathbf{c}_{l-1}+N_l\mathbf{c}_{l+1},\quad l=1,2,\ldots. \tag{3.6b}$$

Let us briefly comment upon Eq. (3.6). It could be regarded as a recursion relation for the vectors $\mathbf{c}_l$, once that the initial condition $\mathbf{c}_0$ is given. But it is exactly the vector $\mathbf{c}_0$ (or strictly speaking its first element $c_{0,0}$) we want to know. In order to resolve this problem we have to impose an additional condition on Eq. (3.6). We therefore require that the elements of the vector $\mathbf{c}_l$ vanish for $l\to\infty$, i.e.,

$$\lim_{l\to\infty}\mathbf{c}_l=0. \tag{3.7}$$

Before we justify this statement let us study its consequences. Assuming Eq. (3.7) to be valid, we need the following *definition* to solve Eqs. (3.6): the lth approximant of the vectors $\mathbf{c}_k$, denoted by $\mathbf{c}_k^{(l)}$, is the solution of Eqs. (3.6) under the condition that $\mathbf{c}_s=0$ for $s=l+1,l+2,\ldots$. With this definition the vectors $\mathbf{c}_k^{(l)}$ can be determined from the following set of equations:

$$\mathbf{c}_l^{(l)}=-M_{l-1}\mathbf{c}_{l-1}^{(l)}, \tag{3.8a}$$

$$\mathbf{c}_k^{(l)}=-M_{k-1}\mathbf{c}_{k-1}^{(l)}+N_k\mathbf{c}_{k+1}^{(l)},\quad k=1,\ldots,l-1 \tag{3.8b}$$

$$\mathbf{c}_0^{(l)}=N_0\mathbf{c}_1^{(l)}+\mathbf{f}. \tag{3.8c}$$

This two-step recursion relation can be reduced to a one-step recursion relation by the *ansatz*

$$\mathbf{c}_k^{(l)}=-A_k^{(l-k)}M_{k-1}\mathbf{c}_{k-1}^{(l)},\quad k=l,l-1,\ldots,1. \tag{3.9}$$

Inserting Eq. (3.9) into Eqs. (3.8) one easily verifies the following relations:

$$A_l^{(0)}=1,\quad l=0,1,\ldots, \tag{3.10a}$$

$$A_k^{(l+1)}=[1+N_kA_{k+1}^{(l)}M_k]^{-1}, \tag{3.10b}$$

which, by means of Eq. (3.8c), yields for the lth approximant of $\mathbf{c}_0$

$$\mathbf{c}_0^{(l)}=A_0^{(l)}\mathbf{f}. \tag{3.11}$$

Finally, assuming that the limit

$$\lim_{l\to\infty}A_k^{(l)}=:A_k \tag{3.12}$$

exists (where the notation $a=:b$ means b is defined by a), we can summarize the above results in the following *lemma*: the solution of Eqs. (3.6) subject to the condition $\lim_{l\to\infty}\mathbf{c}_l=0$ is given by

$$\mathbf{c}_0=A_0\mathbf{f}, \tag{3.13}$$

where A_0 is an infinite matrix continued fraction which is most easily defined in terms of the recursion relation

$$A_k=[1+N_kA_{k+1}M_k]^{-1},\quad k=0,1,2,\ldots. \tag{3.14}$$

The other coefficients $\mathbf{c}_k$ ($k=1,2,\ldots$)—which are of no interest here—can then be obtained successively via Eq. (3.6b). Since the function $Q(q,s)$ is given by the first element of the vector $\mathbf{c}_0$ [cf. Eq. (3.2)], we obtain

$$Q(q,s)=\frac{1}{s}\mathbf{e}_1^TA_0\mathbf{e}_1. \tag{3.15}$$

Introducing the q-independent matrices $\tilde{M}_l$ and $\tilde{N}_l$ via

$$M_l=-i\tilde{q}\tilde{M}_l, \tag{3.16a}$$

$$N_l=i\tilde{q}\tilde{N}_l, \tag{3.16b}$$

we can write the q dependence of $Q(q,s)$ in terms of the infinite matrix continued fraction A_0

$$A_k=[1+\tilde{q}^2\tilde{N}_kA_{k+1}\tilde{M}_k]^{-1},\quad k=0,1,2,\ldots \tag{3.17}$$

or explicitly

$$A_0=[1+\tilde{q}^2\tilde{N}_0[1+\tilde{q}^2\tilde{N}_1[\ ]^{-1}\tilde{M}_1]^{-1}\tilde{M}_0]^{-1}. \tag{3.18}$$

This is the central result of our paper. We have shown that the dynamical self-structure factor $S_s(q,\omega)$, which is related to $Q(q,s)$ by Eq. (2.3a), can be expressed in terms of an infinite matrix continued fraction. In Sec. IV we will study the limiting properties of $Q(q,s)$ and $S_s(q,\omega)$, respectively, and show that both the hydrodynamical limit ($q\to0$) and the free-gas limit ($q\to\infty$) are correctly described by Eq. (3.15). Before doing this we still have to clarify one question: In deriving Eq. (3.15) we explicitly assumed Eq. (3.7) to be valid. This, however, is not obvious and requires further justification. In Appendix B we formally expand the matrix continued fraction A_0 in a power series of q, which, via Eq. (3.15), is a formal Taylor-series expansion of $Q(q,s)$. On the other hand,

without using Eq. (3.7), we can directly start from Eqs. (3.3) and (3.6) and expand the vector $\mathbf{c}_0$ in a power series in q. When considering only the first element of the vector $\mathbf{c}_0$ one obtains a power-series expansion of $Q(q,s)$. This approach is outlined in Appendix A. It should be stressed once again, that the Taylor-series expansion of $Q(q,s)$, as derived in Appendix A, is a direct consequence of the Boltzmann equation and does not make use of Eq. (3.7). We therefore call it the Boltzmann moment expansion of $Q(q,s)$. If we compare the results of Appendix A and Appendix B, we find that both the Boltzmann moment expansion of $Q(q,s)$ [cf. Eq. (A22)] and the power-series expansion of $Q(q,s)$, which is obtained by expanding the infinite matrix continued fraction A_0 in powers of q, are identical. This can be regarded as an *a posteriori* justification of Eq. (3.7).

It should be mentioned that at least for the free-gas limit the Boltzmann moment expansion of $Q(q,s)$ can be shown to be a totally divergent series. In the free-gas limit the collisions between the tagged particle and the bath particles become negligible and therefore the Van Hove self-correlation function $F_s(q,t)$ is determined by free streaming only. In this limit the solution of Eq. (2.1a) is given by

$$F_s(q,t)=\exp[-(\tilde{q}t/2)^2] . \tag{3.19}$$

Expansion $F_s(q,t)$ in a Taylor series in q and taking the Laplace transform term by term one finds

$$Q(q,s)=\frac{1}{s}\sum_{n=0}^{\infty}(-1)^n\tilde{q}^{2n}\frac{1}{(2s)^{2n}}\frac{(2n)!}{n!} , \tag{3.20}$$

which is totally divergent series. The arguments above show that even if the expansion coefficients $(\mathbf{e}_1^T a_{0,n}\mathbf{e}_1)$ of $Q(q,s)$ [see Eq. (A22)] could be found explicitly, they were of limited use for calculating $S_s(q,\omega)$ for the entire (q,ω) range, since the power series diverges in the free-gas limit.

We finally want to comment on the convergence of the infinite matrix continued fraction A_0. Although we are not able to give a rigorous mathematical proof, the numerical studies of Sec. IV suggest the convergence of A_0. Furthermore, the numerical calculation of $S_s(q,\omega)$ for the entire (q,ω) range, which shall be presented in a subsequent paper,[22] leaves no doubt as to the convergence of A_0. Accepting these numerical studies as a proof for the convergence of the infinite matrix continued fraction [Eq. (3.18)], we claim to have found the analytical solution of the Boltzmann equation for the dynamical self-structure factor $S_s(q,\omega)$.

IV. LIMITING PROPERTIES OF THE DYNAMICAL SELF-STRUCTURE FACTOR $S_s(q,\omega)$

For the following considerations it is convenient to scale $Q(q,s)$ and $S_s(q,\omega)$ to the self-diffusion coefficient D_A of species A. For Maxwell molecules D_A can be calculated analytically yielding[1]

$$D_A=\tfrac{1}{3}\int_0^{\infty}\langle\mathbf{v}(0)\mathbf{v}(t)\rangle_A dt=\frac{v_{T_A}^2}{2\mu_{0,1}} . \tag{4.1}$$

Next we introduce the dimensionless quantities s^*, $\mu_{k,l}^*$, and q^* via the following relations:

$$s^*=\frac{s}{\mu_{0,1}}=\frac{2D_A}{v_{T_A}^2}s , \tag{4.2a}$$

$$\mu_{k,l}^*=\frac{\mu_{k,l}}{\mu_{0,1}}=\frac{2D_A}{v_{T_A}^2}\mu_{k,l} , \tag{4.2b}$$

$$q^*=\frac{\tilde{q}}{\mu_{0,1}}=\frac{2D_A}{v_{T_A}}q . \tag{4.2c}$$

Inserting these expressions into Eqs. (3.15) and (3.17) yields the following dimensionless quantity $Q^*(q^*,s^*)$:

$$Q(q,s)=\frac{2D_A}{v_{T_A}^2}Q^*(q^*,s^*) , \tag{4.3a}$$

where

$$Q^*(q^*,s^*)=\frac{1}{s^*}\mathbf{e}_1^T A_0^*\mathbf{e}_1 \tag{4.3b}$$

and

$$A_l^*=[1+q^{*2}N_l^*A_{l+1}^*M_l^*]^{-1},\quad l=0,1,2,\ldots . \tag{4.3c}$$

The dimensionless infinite matrices N_l^* and M_l^* are given by

$$N_l^*=\frac{2(l+1)^2}{(2l+1)(2l+3)}\times\begin{bmatrix}\beta_{0,l}^* & 0 & 0 & \cdots\\ -\alpha_{1,l}^* & \beta_{1,l}^* & 0 & \cdots\\ 0 & -2\alpha_{2,l}^* & \beta_{2,l}^* & \cdots\\ 0 & 0 & -2\alpha_{3,l}^* & \cdots\\ \cdots & \cdots & \cdots & \cdots\end{bmatrix} \tag{4.4a}$$

and

$$M_l^*=\frac{1}{2}\begin{bmatrix}\alpha_{0,l+1}^* & -\alpha_{0,l+1}^* & 0 & 0 & \cdots\\ 0 & \alpha_{1,l+1}^* & -\alpha_{1,l+1}^* & 0 & \cdots\\ 0 & 0 & \alpha_{2,l+1}^* & -\alpha_{2,l+1}^* & \cdots\\ \cdots & \cdots & \cdots & \cdots & \cdots\end{bmatrix} , \tag{4.4b}$$

where

$$\alpha_{k,l}^*=\frac{1}{s^*+\mu_{k,l}^*} , \tag{4.4c}$$

$$\beta_{k,l}^*=\frac{k+l+\frac{3}{2}}{s^*+\mu_{k,l}^*} . \tag{4.4d}$$

In order to scale the dynamical self-structure factor $S_s(q,\omega)$ properly we make the variable transformation

$$\omega=v_{T_A}qx=\mu_{0,1}q^*x , \tag{4.5a}$$

$$S_s(q,\omega)d\omega=R(q^*,x)dx . \tag{4.5b}$$

With the aid of Eq. (2.3a) and Eq. (4.3a) we readily find

$$R(q^*,x)=\frac{2}{\pi}q^*\,\mathrm{Re}Q^*(q^*,ixq^*)\ . \tag{4.6}$$

There are two reasons for scaling ω with q according to Eq. (4.5). first, the normalization condition remains unaltered for the dimensionless quantity $R(q^*,x)$

$$\int_0^\infty S_s(q,\omega)d\omega=\int_0^\infty R(q^*,x)dx=1\ . \tag{4.7}$$

Second, for large q the so defined quantity $R(q^*,x)$ can be obtained directly from the Boltzmann equation [cf. Eq. (2.1)] as a power-series expansion in q^{-1} yielding in the limit $q^*\to\infty$ (free-gas limit) the well-known Gaussian distribution function[21]

$$\lim_{q^*\to\infty} R(q^*,x)=\frac{2}{\sqrt{\pi}}e^{-x^2}\ . \tag{4.8}$$

After these preliminary remarks we are now in the position to study both the hydrodynamical limit ($q\to 0$) and the free-gas limit ($q\to\infty$) of the dynamical self-structure factor.

Let us start with the *free-gas limit.* In this case the distribution function is determined by free streaming alone, and the influence of the collision operator becomes negligible. In order to derive Eq. (4.8) from our general result [Eqs. (4.3)] we first consider the limit $q^*\to\infty$ of the expression $q^*Q^*(q^*,s^*q^*)$ for real s^*. Replacing s^* by q^*s^* in the arguments of $\alpha^*_{k,l}$ and $\beta^*_{k,l}$, respectively, we see that in the limit of large q^* the matrices $q^*N_l^*$ and $q^*M_l^*$ becomes independent of the eigenvalues $\mu^*_{k,l}$

$$\lim_{q^*\to\infty} q^*\alpha^*_{k,l}(s^*q^*)=\frac{1}{s^*} \tag{4.9a}$$

and

$$\lim_{q^*\to\infty} q^*\beta^*_{k,l}(s^*q^*)=\frac{1}{s^*}(k+l+\tfrac{3}{2})\ . \tag{4.9b}$$

If we now insert Eqs. (4.9) into Eqs. (4.3) we readily find

$$\lim_{q^*\to\infty} q^*Q^*(q^*,q^*s^*)=\frac{1}{s^*}\mathbf{e}_1^T A_0^{\mathrm{FG}}\mathbf{e}_1=:T_{\mathrm{CF}}(s^*) \tag{4.10a}$$

with

$$A_l^{\mathrm{FG}}=\left[1+\frac{1}{s^{*2}}N_l^{\mathrm{FG}}A_{l+1}^{\mathrm{FG}}M_l^{\mathrm{FG}}\right]^{-1}\quad\text{for } l=0,1,2,\ldots\ . \tag{4.10b}$$

In Eq. (4.10b) we have introduced the free-gas limits of the matrices N_l^* and M_l^*, respectively, which, denoted by the superscript FG, are given by

$$N_l^{\mathrm{FG}}=\frac{2(l+1)^2}{(2l+1)(2l+3)}\begin{pmatrix} l+\frac{3}{2} & 0 & 0 & \cdots \\ -1 & l+\frac{5}{2} & 0 & \cdots \\ 0 & -2 & l+\frac{7}{2} & \cdots \\ 0 & 0 & -3 & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{pmatrix} \tag{4.11a}$$

and

$$M_l^{\mathrm{FG}}=M^{\mathrm{FG}}=\frac{1}{2}\begin{pmatrix} 1 & -1 & 0 & 0 & \cdots \\ 0 & 1 & -1 & 0 & \cdots \\ 0 & 0 & 1 & -1 & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix}\ . \tag{4.11b}$$

Next we want to show that Eqs. (4.10), which were obtained as the free-gas limit of our general solution [cf. Eqs. (4.3)] are identical to the solution of the free streaming term of the Boltzmann equation. In other words, we want to show that the above limit is identical to the following expression:

$$\lim_{q^*\to\infty} q^*Q^*(q^*,q^*s^*)=\sqrt{\pi}e^{s^{*2}}\left[1-\frac{2}{\sqrt{\pi}}\mathrm{erf}(s^*)\right]$$
$$=:T_{\mathrm{ex}}(s^*)\ . \tag{4.12}$$

The statement can be proved easily, provided the infinite matrix continued fraction [Eq. (4.10b)] converges. One only has to keep in mind that the above limits [Eqs. (4.10) and Eqs. (4.11)] can formally be obtained by putting in our general expression [Eq. (4.3)] all eigenvalues $\mu^*_{k,l}=0$ and $q^*=1$. On the other hand, putting all eigenvalues $\mu^*_{k,l}=0$ implies that the transition probability $\omega(\mathbf{v}\to\mathbf{v}')$ vanishes. One therefore can neglect the collision term in the Boltzmann equation and solve Eq. (2.1a) for the free-streaming term alone. The solution of this simple equation then yields exactly the right-hand side of Eq. (4.12). Note, when putting $s^*=ix$ in Eq. (4.12) and using the definition of $R(q^*,x)$ [Eq. (4.6)] one immediately obtains the free-gas limit given in Eq. (4.8). However, the above arguments only hold if the infinite matrix continued fraction converges. Since we are not able to give a mathematical proof for this convergence, we confine ourselves to a numerical comparison of Eqs. (4.10) and Eq. (4.12). In Table I we compare the exact result $T_{\mathrm{ex}}(s^*)$ with the

TABLE I. Comparison of the exact value $T_{\mathrm{ex}}(s^*)$ [see Eq. (4.12)] and its approximation by the truncated infinite matrix continued fraction $T_{\mathrm{CF}}(s^*)$ [see Eq. (4.10a)] for different values of s^*. N denotes the dimension of the matrices considered and L the length of the matrix continued fraction.

s^*	$T_{\mathrm{ex}}(s^*)$	$T_{\mathrm{CF}}(s^*)$	N	L
0.2	1.433 95	1.432 78	8	100
0.4	1.188 94	1.188 03	6	100
0.6	1.006 41	1.006 23	6	50
0.8	0.866 91	0.866 66	4	50
1.0	0.757 87	0.757 57	3	20
1.2	0.670 94	0.670 82	3	20
1.4	0.600 41	0.600 36	3	20
1.6	0.542 29	0.542 27	3	20
1.8	0.493 74	0.493 73	3	20
2.0	0.452 68	0.452 67	3	20

truncated matrix continued fraction $T_{CF}(s^*)$ for different values values of s^*. In addition, to get a better feeling for the convergence of the matrix continued fraction, both the size N of the matrices N_l^{FG} and M^{FG} and the length L of the continued fraction are presented in Table I. As expected, it turns out that the larger the values of s^* the faster is the convergence of the matrix continued fraction. In Table II we study the convergence of the infinite matrix continued fraction $T_{CF}(s^*)$. Keeping s^* fixed we compute the truncated continued fraction $T_{CF}(s^*)$ [see Eq. (4.10b)] for different values of N and L. The examples considered show that the infinite continued fraction ($L=\infty$) of infinite matrices ($N=\infty$) can be replaced by a finite continued fraction ($L\leq 100$) of finite matrices ($N\leq 10$) in order to achieve an accuracy of at least four digits. In our opinion the above results clearly indicate that $T_{CF}(s^*)$ [Eq. (4.10a)] is a convergent representation of the exact result [Eq. (4.12)]. Moreover, since—from a numerical point of view—the free-gas limit can be considered as our worst case the above results also suggest a convergence of our general expression for $Q^*(q^*,s^*)$ [Eq. (4.3)]. However, the actual numerical evaluation of $S_s(q,\omega)$ [via Eq. (3.18)] for the entire (q,ω) range shall be presented in a subsequent paper.[22]

Finally, let us turn to the *hydrodynamic limit of* $S_s(q,\omega)$. The hydrodynamic limit ($q\to 0$) can be easily studied by introducing a memory function equation for the intermediate scattering function $F_s(q,t)$ [see Eq. (2.3c)]

$$\frac{\partial}{\partial t}F_s(q,t)=-q^2\int_0^t D(q,t-\tau)F_s(q,\tau)d\tau \tag{4.13a}$$

with

$$F_s(q,0)=1\ . \tag{4.13b}$$

Taking the Laplace transform of Eq. (4.13a) the function $Q(q,s)$ can be expressed in terms of the Laplace transform $\hat{D}(q,s)$ of the memory function $D(q,t)$

$$Q(q,s)=\frac{1}{s}\left[1+q^2\frac{\hat{D}(q,s)}{s}\right]^{-1}\ . \tag{4.14}$$

The hydrodynamic limit of $Q(q,s)$ is then obtained by replacing in Eq. (4.14) $\hat{D}(q,s)$ by the diffusion coefficient D_A

$$D_A=\lim_{q\to 0}\lim_{s\to 0}\hat{D}(q,s)\ . \tag{4.15}$$

In this case $Q(q,s)$ reduces to a solution of the diffusion equation which justifies the term "hydrodynamic limit." It should be noted that by introducing the memory function equation [Eq. (4.13a)] as a generalization of the diffusion equation for large values of q one, in general, has only shifted the problem of finding a solution for $F_s(q,t)$

TABLE II. Variation of the truncated infinite matrix continued fraction $T_{CF}(s^*)$ [see Eq. (4.10a)] with N and L for (a) $s^*=0.2$, (b) $s^*=0.6$, and (c) $s^*=1.0$. N denotes the dimension of the matrices considered and L the length of the matrix continued fraction.

L \ N	2	3	4	6	8	10
			(a) $s^*=0.2$ $T_{ex}(s^*)=1.433\,95$			
2	2.739 43	2.645 96	2.592 15	2.535 54	2.508 07	2.492 88
5	0.904 56	0.973 24	1.018 99	1.080 19	1.119 19	1.145 32
10	1.746 62	1.747 29	1.726 11	1.676 13	1.634 79	1.603 49
15	1.200 41	1.227 78	1.246 22	1.276 34	1.301 01	1.321 30
20	1.515 84	1.543 83	1.551 00	1.546 21	1.533 99	1.521 08
50	1.404 73	1.428 79	1.436 91	1.444 18	1.447 83	1.449 14
100	1.389 65	1.414 36	1.423 77	1.430 61	1.432 78	1.433 70
			(b) $s^*=0.6$ $T_{ex}(s^*)=1.006\,41$			
2	1.105 10	1.098 41	1.095 36	1.093 11	1.092 47	1.092 26
5	0.978 30	0.989 00	0.993 26	0.996 66	0.997 83	0.998 28
10	1.001 89	1.007 10	1.007 86	1.007 56	1.007 19	1.006 97
15	0.997 28	1.003 25	1.004 87	1.005 81	1.006 10	1.006 23
20	0.998 38	1.004 29	1.005 76	1.006 39	1.006 46	1.006 46
50	0.998 16	1.004 06	1.005 55	1.006 23	1.006 36	1.006 39
100	0.998 16	1.004 06	1.005 55	1.006 23	1.006 36	1.006 39
			(c) $s^*=1.0$ $T_{ex}(s^*)=0.757\,87$			
2	0.773 07	0.773 27	0.773 24	0.773 20	0.773 19	0.773 19
5	0.755 16	0.756 79	0.757 14	0.757 29	0.757 32	0.757 33
10	0.756 23	0.757 61	0.757 83	0.757 88	0.757 88	0.757 88
15	0.756 17	0.757 56	0.757 79	0.757 86	0.757 87	0.757 87
20	0.756 17	0.757 57	0.757 80	0.757 87	0.757 87	0.757 87
50	0.756 17	0.757 57	0.757 80	0.757 86	0.757 87	0.757 87
100	0.756 17	0.757 57	0.757 80	0.757 86	0.757 87	0.757 87

to the problem of finding a closed equation for the memory function $D(q,t)$. However, our description of $F_s(q,t)$ on the footing of the Boltzmann equation for Maxwell molecules provides a nontrivial example for an analytic determination of the memory function $D(q,t)$. With the aid of Eq. (3.15) and Eq. (3.17) we can write $Q(q,s)$ in the following form:

$$Q(q,s)=\frac{1}{s}\mathbf{e}_1^T(1+\tilde{q}^2\tilde{N}_0A_1\tilde{M}_0)^{-1}\mathbf{e}_1 . \tag{4.16}$$

In analogy to Eq. (4.14) we can define a memory matrix $\hat{D}(\tilde{q},s)$

$$\hat{D}(\tilde{q},s)=sv_{T_A}^2\tilde{N}_0A_1\tilde{M}_0 , \tag{4.17}$$

where the infinite matrix A_1 is explicitly given by Eq. (3.17). It is convenient to scale $\hat{D}(\tilde{q},s)$ according to Eq. (4.2)

$$\hat{D}(\tilde{q},s)=D_AD^*(q^*,s^*) , \tag{4.18}$$

where the dimensionless memory matrix $D^*(q^*,s^*)$ is given by

$$D^*(q^*,s^*)=2s^*N_0^*A_1^*M_0^* \tag{4.19a}$$

with

$$A_l^*=[1+q^{*2}N_l^*A_{l+1}^*M_l^*]^{-1} \quad \text{for } l=1,2,3,\ldots . \tag{4.19b}$$

Keeping in mind that $\mu_{k,l}^*>0$ for $(k,l)\neq(0,0)$ and $\mu_{0,0}^*=0$ we readily find the following relation:

$$\lim_{q^*\to 0}\lim_{s^*\to 0}A_1^*=1 , \tag{4.20}$$

which implies for the hydrodynamic limit of the memory matrix $D^*(q^*,s^*)$

$$D_{\text{hyd}}^*=\lim_{q^*\to 0}\lim_{s^*\to 0}D^*(q^*,s^*)=\begin{pmatrix}1&-1&0&\cdots\\0&0&0&\cdots\\\cdots&\cdots&\cdots&\cdots\end{pmatrix} . \tag{4.21}$$

According to Eq. (4.16) we are now able to express the hydrodynamic limit of $Q^*(q^*,s^*)$ in terms of D_{hyd}^*

$$Q_{\text{hyd}}^*(q^*,s^*)=\frac{1}{s^*}\mathbf{e}_1^T\left[1+\frac{q^{*2}}{2s^*}D_{\text{hyd}}^*\right]^{-1}\mathbf{e}_1 . \tag{4.22}$$

Due to the special structure of the infinite matrix D_{hyd}^* we can easily invert the matrix $(1+\alpha D_{\text{hyd}}^*)$ yielding

$$(1+\alpha D_{\text{hyd}}^*)^{-1}=\begin{pmatrix}\frac{1}{1+\alpha}&\frac{\alpha}{1+\alpha}&0&\cdots\\0&1&0&\cdots\\0&0&1&\cdots\\\cdots&\cdots&\cdots&\cdots\end{pmatrix} , \tag{4.23}$$

and

$$Q_{\text{hyd}}^*(q^*,s^*)=\frac{1}{s^*+q^{*2}/2} . \tag{4.24}$$

Combining Eq. (4.24) and Eq. (4.6) one obtains the well-known Lorentz distribution for the hydrodynamic limit of $R(q^*,x)$

$$R_{\text{hyd}}(q^*,x)=\frac{2}{\pi}\frac{q^*/2}{(q^*/2)^2+x^2} . \tag{4.25}$$

Recalling Eqs. (4.5) we can easily express the dynamical self-structure factor $S_s(q,\omega)$ by means of the scaled function $R(q^*,x)$. On summarizing the above results, we can claim to have found an explicit solution of the Boltzmann equation for $Q(q,s)$ yielding both the correct hydrodynamic limit and the correct free-gas limit. In a subsequent paper[22] a detailed numerical analysis for the entire (q,ω) range of $S_s(q,\omega)$ shall be presented.

Finally, we briefly want to comment upon the question why we did not try to expand $Q(q,s)$ in a continued fraction of the following form

$$Q(q,s)=\frac{1}{s}\cfrac{1}{1+\cfrac{\alpha_0q^2}{1+\cfrac{\alpha_1q^2}{1+\cdots}}} , \tag{4.26}$$

where the α_n are scalars. It is exactly this expression which is commonly suggested by memory function techniques.[21] At a first glance this idea seems reasonable, for the Boltzmann equation allows an expansion of $Q(q,s)$ in powers of q (see Appendix A). One could then imagine to transform this series to the above continued fraction of scalars. However, this idea has to be abandoned for two reasons. First, as can be seen from Eq. (A22), it is rather difficult to find the generating law for the expansion coefficients of the power series of $Q(q,s)$. In Eq. (A23) we formally expressed each coefficient as one particular matrix element of products of infinite matrices. When actually evaluating the first few coefficients $(\mathbf{e}_1^Ta_{0,n}\mathbf{e}_1)$ one is easily convinced that a generating law is unlikely to be found. Second, only for a rather restricted class of power series one can find their convergent representation in terms of a continued fraction.[23] In our case we failed to find the generating law for the expansion coefficients α_n of the continued fraction. To put it differently we have actually calculated the coefficients α_n up to $n=2$. It turned out that the α_n's become rapidly involved with n increasing and a generating law or the explicit dependence of α_n on n could not be found. However, making use of the special generating law for the matrices $\alpha_{0,n}$ [see Eq. (A23)], we could, quite naturally, transform the power series expansion of $Q(q,s)$ to a convergent infinite matrix continued fraction.

In subsequent papers we shall apply this method to calculate the dynamical structure factor $S(q,\omega)$, starting from the Boltzmann equation for Maxwell molecules. Again, an analytic expression for $S(q,\omega)$ covering the entire (q,ω) range will be presented.[22] Furthermore, we shall consider a one-dimensional model where the above expansion of $Q(q,s)$ in terms of a scalar continued fraction is indeed valid.[24]

V. DISCUSSION

Starting from the inhomogeneous Boltzmann equation for Maxwell molecules we have derived an explicit expression for the dynamical self-structure factor $S_s(q,\omega)$ in terms of an infinite matrix continued fraction. In contrast to the kinetic model approach,[17] which is commonly regarded as an effective method for extracting time-correlation functions from kinetic equations, we did not alter or approximate the collision kernel in order to determine $S_s(q,\omega)$. Rather we presented an analytical solution for $S_s(q,\omega)$ taking into account the entire collision kernel and therefore all eigenvalues of the self-part of the Maxwell collision operator. We have shown that the expansion of the infinite matrix continued fraction in powers of q is identical with the Boltzmann moment expansion of $Q(q,s)$. The representation of $Q(q,s)$ in terms of an infinite matrix continued fraction was checked numerically for the case of a free gas, where the solution of the Boltzmann equation is known explicitly and where, in addition, the Boltzmann moment expansion does not converge. It turned out that in order to get a reasonable accuracy (up to four digits) the infinite continued fraction ($L=\infty$) of infinite matrices ($N=\infty$) can be replaced by a finite continued fraction ($L\leq 100$) of finite matrices ($N\leq 10$).

The advantage or special feature of our infinite matrix continued fraction representation of $Q(q,s)$ relative to the kinetic model approach[17] can be seen from the following two arguments. First, whenever one is looking for certain limiting properties of $Q(q,s)$, one approximates an *exact* expression [Eq. (3.15)]. This has been demonstrated in Sec. IV for both the hydrodynamic limit ($q\to 0$) and the free-gas limit ($q\to\infty$), where we arrived at exact expressions [see Eq. (4.10b) and Eq. (4.24)] in either case, using no approximations but the respective limiting processes. In contrast, kinetic models successively approximate the collision kernel. The starting point for any calculation is a model equation—not the exact Boltzmann equation—and therefore any limiting process, like the hydrodynamic limit or the free-gas limit yields approximate results only. Second, from a mathematical point of view our result is very simple. In actual computations one only has to invert rather small matrices and running a short iteration procedure in order to get highly accurate results.

For the sake of transparency we confined this paper to a mathematical analysis for $S_s(q,\omega)$. In a subsequent paper[22] we shall present a detailed numerical analysis of $S_s(q,\omega)$ for the entire (q,ω) range including a calculation of the linewidth. Furthermore, we shall present a detailed numerical analysis of the dynamical structure factor $S(q,\omega)$, which in the low-density limit is given by essentially the same infinite matrix continued fraction as $S_s(q,\omega)$. One only has to replace the eigenvalues by those of the full collision operator.[22] It will turn out that in the hydrodynamic limit our infinite matrix continued fraction reduces exactly to the well-known Landau-Placzeck[21] formula with the respective thermodynamic coefficients of the dilute Maxwell gas. Since, from a mathematical point of view, there is no difference between $S_s(q,\omega)$ and $S(q,\omega)$, when using the Boltzmann equation as a starting point, we presented the mathematical tools for calculating $S_s(q,\omega)$ in this paper and postpone a detailed numerical analysis to a subsequent paper.[22]

ACKNOWLEDGMENT

The author is grateful to Mr. M. Posch for stimulating discussions on this and related topics and for computing the tables.

APPENDIX A

Here we want to derive the formal Taylor-series expansion for $Q(q,s)$ in powers of q. According to Eq. (2.14) $Q(q,s)$ is given by the first element of the vector $\mathbf{c}_0$. So we can concentrate on a Taylor-series expansion of the vector $\mathbf{c}_l$ in powers of q.. With the aid of the matrices $\tilde{N}_l$ and $\tilde{M}_l$ [see Eqs. (3.5) and (3.16)] we can write [cf Eq. (3.6)]

$$\mathbf{c}_l = i\mathbf{q}(\tilde{M}_{l-1}\mathbf{c}_{l-1}+\tilde{N}_l\mathbf{c}_{l+1}),\quad l=1,2,\ldots \tag{A1}$$

$$\mathbf{c}_0 = i\tilde{q}\tilde{N}_0\mathbf{c}_1+\frac{1}{s}\mathbf{e}_1 . \tag{A2}$$

Since for $q\to 0$ the Boltzmann equilibrium distribution function is the only solution of Eq. (2.1a) subject to the initial condition [(2.1b)], we obtain [cf. Eqs. (2.8) and (2.10)]

$$\mathbf{c}_0(q=0,s)=\frac{1}{s}\mathbf{e}_1 , \tag{A3}$$

$$\mathbf{c}_l(q=0,s)=0 \quad \text{for } l\geq 1 . \tag{A4}$$

Next let us expand the function $\mathbf{c}_l$ in a Taylor series in $\tilde{q}$

$$\mathbf{c}_l=\sum_{n=0}^{\infty}(i\tilde{q})^n\mathbf{c}_l^{(n)} . \tag{A5}$$

Inserting Eq. (A5) into Eqs. (A1) and (A2) and comparing equal powers in $\tilde{q}$ yields the following relations for the expansion coefficients $\mathbf{c}_l^{(n)}$:

$$\mathbf{c}_l^{(n)}=\tilde{M}_{l-1}\mathbf{c}_{l-1}^{(n-1)}+\tilde{N}_l\mathbf{c}_{l+1}^{(n-1)},\quad n=1,2,\ldots,\ L=0,1,\ldots \tag{A6}$$

$$\mathbf{c}_l^{(0)}=\frac{1}{s}\delta_{l,0}\mathbf{e}_1,\quad l=0,1,\ldots \tag{A7}$$

where, by definition,

$$\mathbf{c}_l^{(n)}\equiv 0 \quad \text{for } l<0 . \tag{A8}$$

Equations (A6)—(A8) can be solved successively, starting with $\mathbf{c}_l^{(0)}$ and then computing $\mathbf{c}_l^{(1)}$, $\mathbf{c}_l^{(2)}$, etc., according to Eq. (A6). However, a closed and explicit form for the coefficients $\mathbf{c}_l^{(n)}$ is not easily obtained in this way.

Let us first rewrite Eq. (A6) by introducing matrices P_l

$$P_0=1,\quad P_l=\tilde{M}_{l-1}\tilde{M}_{l-2}\cdots\tilde{M}_0 , \tag{A9}$$

and new coefficients $\mathbf{y}_l^{(n)}$

$$\mathbf{c}_l^{(n)}=P_l\mathbf{y}_l^{(n)} . \tag{A10}$$

Since the matrix $\tilde{M}_l$ is regular, P_l is regular too, and P_l^{-1} exists. Inserting Eq. (A10) into Eqs. (A6) and (A7) we obtain

$$\mathbf{y}_l^{(n)}-\mathbf{y}_{l-1}^{(n-1)}=H_l\mathbf{y}_{l+1}^{(n-1)}\ , \tag{A11}$$

$$\mathbf{y}_l^{(0)}=\frac{1}{s}\delta_{l,0}\mathbf{e}_1\ , \tag{A12}$$

with

$$H_l=P_l^{-1}\tilde{N}_lP_{l+1}\ . \tag{A13}$$

By induction the following relations can be easily shown:

$$\mathbf{y}_l^{(n)}\equiv 0 \quad \text{for } l>n \text{ and } l<0\ , \tag{A14}$$

$$\mathbf{y}_{2l}^{(2l+1)}\equiv\mathbf{y}_{2l+1}^{(2l)}\equiv 0\ . \tag{A15}$$

Putting $l=n$ in Eq. (A11) and using Eq. (A14) yields

$$\mathbf{y}_n^{(n)}-\mathbf{y}_{n-1}^{(n-1)}=H_n\mathbf{y}_{n+1}^{(n-1)}=0\ , \tag{A16}$$

which implies

$$\mathbf{y}_n^{(n)}=\mathbf{y}_0^{(0)}=\frac{1}{s}\mathbf{e}_1,\quad n\geq 0\ . \tag{A17}$$

next, putting $l=n-2$ in Eq. (A11) and using Eq. (A16), we find

$$\mathbf{y}_{n-2}^{(n)}-\mathbf{y}_{n-3}^{(n-1)}=H_{n-2}\mathbf{y}_{n-1}^{(n-1)}=\frac{1}{s}H_{n-2}\mathbf{e}_1\ , \tag{A18}$$

implying

$$\mathbf{y}_{n-2}^{(n)}=\frac{1}{s}\sum_{j_1=0}^{n-2}H_{j_1}\mathbf{e}_1,\quad n\geq 2\ . \tag{A19}$$

Continuing this process we finally arrive at the following expression:

$$\mathbf{y}_{n-2l}^{(n)}=\frac{1}{s}\sum_{j_1=0}^{n-2l}\sum_{j_2=0}^{j_1+1}\cdots\sum_{j_l=0}^{j_{l-1}+1}H_{j_1}H_{j_2}\cdots H_{j_l}\mathbf{e}_1 \quad \text{for } n\geq 2l,\ l\geq 1\ . \tag{A20}$$

In order to get the Taylor-series expansion of $Q(q,s)$ we use Eq. (2.14)

$$Q(q,s)=\tilde{c}_{0,0}=c_{0,0}=\mathbf{e}_1^T\mathbf{c}_0=\mathbf{e}_1^T\sum_{n=0}^{\infty}(i\tilde{q})^n\mathbf{c}_0^{(n)} =\mathbf{e}_1^T\sum_{n=0}^{\infty}(i\tilde{q})^n\mathbf{y}_0^{(n)}\ . \tag{A21}$$

Finally we make use of Eqs. (A15) and (A20) and obtain

$$Q(q,s)=\frac{1}{s}\sum_{n=0}^{\infty}(-1)^n\tilde{q}^{2n}(\mathbf{e}_1^Ta_{0,n}\mathbf{e}_1)\ , \tag{A22}$$

where the matrix $\alpha_{0,n}$ is given by

$$\alpha_{0,n}=\sum_{j_1=0}^{0}\sum_{j_2=0}^{j_1+1}\cdots\sum_{j_n=0}^{j_{n-1}+1}H_{j_1}H_{j_2}\cdots H_{j_n}\ . \tag{A23}$$

The Taylor-series expansion of $Q(q,s)$ can only be considered as a formal series in powers of q, since in general it does not converge. A convergent representation of Eq. (A21) is given by the continued fraction of the matrices $\tilde{N}_l$ and $\tilde{M}_l$ [see Eq. (3.15)]. Although we lack a mathematical proof for the convergence of this continued fraction we are convinced by numerical computations, which will be presented in a subsequent paper (see also Table I). In Appendix B we will show that the power-series expansion of the continued fraction is identical to Eq. (A22). Finally it should be mentioned that the evaluation of the coefficients $(\mathbf{e}_1^Ta_{0,n}\mathbf{e}_1)$ in Eq. (A22) requires only a finite number of operations due to the special structure of the infinite matrices $\tilde{N}_l$ and $\tilde{M}_l$ [see Eq. (3.5)].

APPENDIX B

In order to get a power-series expansion of the continued fraction given in Eq. (3.15), we start with the sequence of matrices $A_k,\tilde{N}_k,\tilde{M}_k$ $(k=0,1,2,\ldots)$ defined by

$$A_k(z)=(1-z\tilde{N}_kA_{k+1}\tilde{M}_k)^{-1}\ . \tag{B1}$$

We are looking for a power-series expansion of $A_k(z)$ in powers of z

$$A_k(z)=\sum_{n=0}^{\infty}z^n\alpha_{k,n}\ . \tag{B2}$$

Multiplying Eq. (B1) with $[1-z\tilde{N}_kA_{k+1}\tilde{M}_k]$ from the left, inserting Eq. (B2), and comparing equal powers in z, yields the following recursion relation for the coefficients $\alpha_{k,n}$:

$$\alpha_{k,0}=1\ ,$$
$$\alpha_{k,n}=\sum_{l=0}^{n-1}\tilde{N}_k\alpha_{k+1,l}\tilde{M}_k\alpha_{k,n-l-1},\quad n=1,2,\ldots\ . \tag{B3}$$

Equation (B3) can be solved starting with $\alpha_{k,0}$ and then computing successively $\alpha_{k,n}$ for $n=1,2,3,\ldots$. The general expression for $\alpha_{k,n}$ turns out to be

$$\alpha_{k,0}=1\ ,$$
$$\alpha_{k,n}=P_k\sum_{j_1=k}^{k}\sum_{j_2=k}^{j_1+1}\cdots\sum_{j_n=k}^{j_{n-1}+1}H_{j_1}H_{j_2}\cdots H_{j_n}P_k^{-1}\ , \tag{B4}$$

with

$$H_l=P_l^{-1}\tilde{N}_lP_{l+1} \tag{B5}$$

and

$$P_0=1,\quad P_l=\tilde{M}_{l-1}\tilde{M}_{l-2}\cdots\tilde{M}_0\ . \tag{B6}$$

Proof. For the first few n it is easy to show that the $\alpha_{k,n}$, given by Eq. (B4), fulfill Eq. (B3). In order to prove Eq. (B4) for all n we first split up Eq. (B3) as follows:

$$\alpha_{k,n}=\tilde{N}_k\alpha_{k+1,n-1}\tilde{M}_k+\tilde{N}_k\tilde{M}_k\alpha_{k,n-1} +\sum_{l=1}^{n-2}\tilde{N}_k\alpha_{k+1,l}\tilde{M}_k\alpha_{k,n-l-1}\ . \tag{B7}$$

Next we assume that for $s=0,1,\ldots,n-1$ and for all k the $\alpha_{k,s}$'s are given by Eq. (B4). Since the right-hand side (rhs) of Eq. (B7) depends on $\alpha_{k,s}$ with $s=0,1,\ldots,n-1$ only, we can prove by induction that Eq. (B4) is valid for all n. We first consider the coefficient $\alpha_{k+1,n-1}$ on the rhs of Eq. (B7). According to Eq. (B4) we can write

$$\alpha_{k+1,n-1}=P_{k+1}\sum_{j_1=k+1}^{k+1}\sum_{j_2=k+1}^{j_1+1}\cdots\sum_{j_{n-1}=k+1}^{j_{n-2}+1}H_{j_1}H_{j_2}\cdots H_{j_{n-1}}P_{k+1}^{-1}$$

$$=P_{k+1}\sum_{j_1=k+1}^{k+1}\cdots\sum_{j_{n-2}=k+1}^{j_{n-3}+1}\sum_{j_{n-1}=k}^{j_{n-2}+1}H_{j_1}\cdots H_{j_{n-2}}H_{j_{n-1}}P_{k+1}^{-1}$$

$$-P_{k+1}\sum_{j_1=k+1}^{k+1}\cdots\sum_{j_{n-2}=k+1}^{j_{n-3}+1}H_{j_1}\cdots H_{j_{n-2}}\sum_{j_{n-1}=k}^{k}H_{j_{n-1}}P_{k+1}^{-1}$$

$$=P_{k+1}\sum_{j_1=k+1}^{k+1}\cdots\sum_{j_{n-2}=k+1}^{j_{n-3}+1}\sum_{j_{n-1}=k}^{j_{n-2}+1}H_{j_1}\cdots H_{j_{n-2}}H_{j_{n-1}}P_{k+1}^{-1}-\alpha_{k+1,n-2}\tilde{M}_k\alpha_{k,1}\tilde{M}_k^{-1}\,. \tag{B8}$$

Continuing this process of splitting up the first term in Eq. (B8) according to

$$\sum_{j_l=k+1}^{j_{l-1}+1}\cdots=\sum_{j_l=k}^{j_{l-1}+1}\cdots-\sum_{j_l=k}^{k}\cdots$$

$$\text{for } l=n-2,n-3,\ldots,2\,, \tag{B9}$$

we finally obtain the following relation:

$$\alpha_{k+1,n-1}$$

$$=P_{k+1}\sum_{j_1=k+1}^{k+1}\sum_{j_2=k}^{j_1+1}\cdots\sum_{j_{n-1}=k}^{j_{n-2}+1}H_{j_1}H_{j_2}\cdots H_{j_{n-1}}P_{k+1}^{-1}$$

$$-\sum_{l=1}^{n-2}\alpha_{k+1,l}\tilde{M}_k\alpha_{k,n-l-1}\tilde{M}_k^{-1}\,. \tag{B10}$$

If we now insert Eq. (B10) into the right-hand side of Eq. (B7) we find it equal to the following:

$$\tilde{N}_kP_{k+1}\sum_{j_1=k+1}^{k+1}\sum_{j_2=k}^{j_1+1}\cdots\sum_{j_{n-1}=k}^{j_{n-2}+1}H_{j_1}H_{j_2}\cdots H_{j_{n-1}}P_{k+1}^{-1}\tilde{M}_k$$

$$+\tilde{N}_k\tilde{M}_kP_k\sum_{j_1=k}^{k}\sum_{j_2=k}^{j_1+1}\cdots\sum_{j_{n-1}=k}^{j_{n-2}+1}H_{j_1}H_{j_2}\cdots H_{j_{n-1}}P_k^{-1}\,. \tag{B11}$$

Now using the relations

$$\tilde{N}_kP_{k+1}=\tilde{N}_k\tilde{M}_kP_k=P_kH_k \tag{B12}$$

and

$$P_{k+1}^{-1}\tilde{M}_k=P_k^{-1}\,, \tag{B13}$$

we can rewrite (B11) in the following form:

$$P_k\sum_{j_0=k}^{k}\sum_{j_1=k}^{j_0+1}\cdots\sum_{j_{n-1}=k}^{j_{n-2}+1}H_{j_0}H_{j_1}\cdots H_{j_{n-1}}P_k^{-1}\,, \tag{B14}$$

which is identical with Eq. (B4); and this completes our proof.

With the aid of Eqs. (3.14)—(3.16) and the above results we obtain the following power-series expansion for $Q(q,s)$:

$$Q(q,s)=\frac{1}{s}\sum_{n=0}^{\infty}(-1)^n\tilde{q}^{2n}(\mathbf{e}_1^T\alpha_{0,n}\mathbf{e}_1)\,, \tag{B15}$$

where

$$\alpha_{0,n}=\sum_{j_1=0}^{0}\sum_{j_2=0}^{j_1+1}\cdots\sum_{j_n=0}^{j_{n-1}+1}H_{j_1}H_{j_2}\cdots H_{j_n}\,. \tag{B16}$$

Comparing the results of Appendix A and Appendix B we find that the power-series expansion of the continued fraction representation of $Q(q,s)$ is identical with the Taylor series expansion of $Q(q,s)$. Furthermore, a detailed analysis shows that replacing the infinite matrices $\tilde{N}_l$ and $\tilde{M}_l$ by their nth principal minors and truncating the infinite continued fraction after n terms gives the correct power-series expansion of $Q(q,s)$ up to order q^{2n}.

[1]J. H. Ferziger and H. G. Kaper, *Mathematical Theory of Transport Processes in Gases* (North-Holland, Amsterdam, 1972).

[2]R. Dorfmann and H. Van Beijeren, in *Modern Theoretical Chemistry: Statistical Mechanics,* edited by B. J. Berne (Plenum, New York, 1977), p. 65, Part B; see also chapters by G. F. Mazenko and S. Yip, p. 81, and by B. J. Berne, p. 233.

[3]J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1976); and also J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980).

[4]N. G. Van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981).

[5]I. Oppenheim, K. E. Shuler, and G. H. Weiss, *Stochastic Processes in Chemical Physics: The Master Equation* (MIT, Cambridge, Mass., 1977).

[6]O. J. Eder and T. Lackner, Phys. Rev. A **29**, 799 (1984).

[7]J. E. Moyal, J. R. Statist. Soc. **B11**, 150 (1949).

[8]O. Klein, Ark. Mat. Astron. Fys. **16**, 405 (1922).

[9]U. M. Titulaer, Physica **91A**, 321 (1978); **100A**, 234 (1980); **100A**, 251 (1980).

[10]A. K. Das, Physica **98A**, 528 (1979).
[11]N. G. Van Kampen, Can. J. Phys. **39**, 551 (1961).
[12]R. Kubo, K. Matsuo, and K. Kitahara, J. Stat. Phys. **9**, 51 (1973).
[13]O. J. Eder and T. Lackner, Phys. Rev. A **28**, 952 (1983).
[14]T. Lackner and S. Yip, Phys. Rev. A **31**, 451 (1985).
[15]M. R. Hoare, S. Raval, and M. Rahman, Philos. Trans. R. Soc. London, Ser. A **305**, 383 (1982).
[16]C. Wang Chang and G. E. Uhlenbeck, in *Studies in Statistical Mechanics, Vol. V,* edited by J. de Boer and G. E. Uhlenbeck (North-Holland, Amsterdam, 1970); see also C. Cercignani, *Mathematical Methods in Kinetic Theory* (Plenum, New York, 1969).
[17]E. P. Gross and E. A. Jackson, Phys. Fluids **2**, 432 (1959); see also O. L. Deutsch and S. Yip, *ibid.* **17**, 252 (1974); and C. D. Boley and S. Yip, *ibid.* **15**, 1433 (1972).
[18]E. Leutheusser, D. P. Chou, and S. Yip, J. Stat. Phys. **32**, 523 (1983).
[19]S. Yip, Annu. Rev. Phys. Chem. **30**, 547 (1979).
[20]L. Groome, J. W. Dufty, and M. J. Lindenfeld, Phys. Rev. A **19**, 304 (1979).
[21]P. Resibois and M. De Leener, *Classical Kinetic Theory of Fluids* (Wiley, New York, 1977); see also J. R. D. Copley and S. W. Lovesey, Rep. Prog. Phys. **38**, 461 (1975).
[22]T. Lackner and M. Posch (unpublished).
[23]H. S. Wall, *Analytic Theory of Continued Fractions* (Van Nostrand, New York, 1948); see also P. Wynn, Arch. Ration. Mech. Anal. **12**, 273 (1963).
[24]O. J. Eder, T. Lackner, and M. Posch (unpublished).