On the Kinetic Theory of the Enskog Fluid. Viscosity and Viscoelasticity, Heat Conduction and Thermal Pressure

G. Schmidt *, W. E. Köhler, and S. Hess
Institut für Theoretische Physik der Universität Erlangen-Nürnberg, Erlangen

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The moment method is applied to the linearized Enskog-Boltzmann equation for a dense gas. Thus an enlarged set of equations of thermo-hydrodynamics is obtained which allows to go beyond ordinary hydrodynamics. The resulting expressions for the density dependent viscosity and heat conductivity coincide with those previously obtained with the help of the Chapman-Enskog solution procedure. In addition, however, the frequency dependence of the viscosity is treated and it is demonstrated that the thermal pressure does not vanish in a dense fluid.

The Boltzmann equation [1, 2] combined with appropriate solution methods [3—8] is the basis for the theoretical treatment of nonequilibrium phenomena, in particular transport processes, in dilute monatomic gases. During the last two decades, the kinetic theory of gases has been extended in essentially three directions, viz. to molecular gases, rarefied gases and dense gases. The derivation of a generalized quantum mechanical Boltzmann equation for a gas of particles with degenerate internal degrees of freedom by Waldmann [5, 9] and Snider [10] opened the way to the kinetic theory of a great variety of nonequilibrium phenomena in dilute polyatomic gases, e.g. spin diffusion and relaxation [11—15], the influence of external magnetic and electric fields on the transport coefficients [16—31] (Senftleben-Beenakker effects [32—34]), flow birefringence [35—39], broadening of spectral lines, in particular depolarized Rayleigh [36, 40] and rotational Raman lines [41, 42]. A number of new effects has been discovered in rarefied polyatomic gases, e.g. the thermomagnetic torque [43] and the thermomagnetic force [44], the thermomagnetic pressure difference [45], the viscomagnetic heat flux [46] and diffusion flux [47] as well as heat flow birefringence [48] and diffusio birefringence [49].

In this field, the kinetic theory not only helped to understand and to explain experimental findings but had also regained its predictive power [30, 36, 45—49]. An essential part of the theoretical progress was based on the extension of the moment method [4] to polyatomic gases as initiated by Waldmann [50] and used by him and his school [12, 51—53].

The moment method is such a handy tool to treat transport processes including dynamic phenomena and allows to proceed beyond hydrodynamics that it seems overdue to apply it also to dense gases. It is the purpose of this article to derive transport-relaxation equations for a number of relevant macroscopic variables from Enskog's version of the Boltzmann equation for hard spheres [54, 3, 55]. The "Enskog fluid" is a model system for dense gases and even liquids which is of great interest for two reasons. Firstly, the theoretical results obtained for this model can be compared with computer calculations for hard sphere fluids [55]. Secondly, and this seems to be even more important, the density dependence of the transport coefficients, viz. heat conductivity and viscosity agrees with the measured values over a surprisingly large range of densities [55—57]. By the present approach, not only these density dependent transport coefficients relevant for the "hydrodynamic regime" are recovered but some new applications can be treated. The dynamic i.e. frequency dependent viscosity and the viscoelasticity of the Enskog fluid are studied. Furthermore, the thermal pressure, usually associated with rarefied gases, is shown to exist in a dense gas or a liquid.

The paper proceeds as follows: In the first section, the Enskog-Boltzmann equation is stated. The moment method (with the thirteen moments corresponding to number density, temperature, velocity, heat

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* Present address: Institut für Technische Chemie der Universität Erlangen-Nürnberg, Erlangen.

Reprint request to Prof. Dr. S. Hess und Dr. W. E. Köhler, Institut für Theoretische Physik der Universität Erlangen-Nürnberg, D-8520 Erlangen.

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flux and friction pressure tensor) is used to derive a set of coupled transport relaxation equations (Sects. 2 and 3), which contain spatial derivatives of "conserved" quantities up to 2nd order. In Sect. 4, the local conservation laws are given and transport relaxation equations for heat flux and friction pressure tensor are discussed. Due to the nonlocal (Enskog) part of the collision term, there are collisional transfer contributions to heat conductivity and viscosity (Sect. 5); the corresponding transport coefficients λ and η are compared with their Boltzmann values. The coefficients of dynamic viscosity and viscoelasticity are also discussed. Finally (in Sect. 6), the thermal pressure is considered. Apart from the usual Burnett contribution it contains a term which does not vanish for high densities.

1. The Enskog-Boltzmann Equation

The nonequilibrium state of the gas is characterized by the one-particle distribution function

$$f = f(t, \boldsymbol{r}, \boldsymbol{c}) \tag{1.1}$$

with the normalization

$$\int f \, \mathrm{d}^3 c = n(t, \boldsymbol{r}) \, . \tag{1.2}$$

As usual, t, $\boldsymbol{r}$, $\boldsymbol{c}$ are the time, position and velocity variables, n is the number density of the gas. The local average $\langle \Psi \rangle$ of a function $\Psi = \Psi(\boldsymbol{c})$ is given by

$$n \langle \Psi \rangle = \int \Psi(\boldsymbol{c}) f(t, \boldsymbol{r}, \boldsymbol{c}) \, \mathrm{d}^3 c \, . \tag{1.3}$$

In the following, it is assumed that f obeys Enskog's version of the Boltzmann equation for a dense gas of hard spheres of diameter d where the nonlocality of the collision term is taken into account.

The velocities of the collision partners are denoted by $\boldsymbol{c}_1$ and $\boldsymbol{c}_2$, the distribution functions $f(t, \boldsymbol{r}, \boldsymbol{c}_i)$ are abbreviated by $f_i(\boldsymbol{r})$, $i = 1, 2$. Then the Enkog equation can be written as

$$\begin{aligned} &\partial f_1(\boldsymbol{r})/\partial t + \boldsymbol{c}_1 \cdot \boldsymbol{\nabla} f_1 + \int d^2 e' \int \mathrm{d}^3 c_2 \, \sigma g \\ &\quad \cdot [\chi(\boldsymbol{r} + \tfrac{1}{2} \delta \boldsymbol{r}) f_1(\boldsymbol{r}) f_2(\boldsymbol{r} + \delta \boldsymbol{r}) \\ &\quad - \chi(\boldsymbol{r} - \tfrac{1}{2} \delta \boldsymbol{r}) f_1'(\boldsymbol{r}) f_2'(\boldsymbol{r} - \delta \boldsymbol{r})] = 0 \end{aligned} \tag{1.4}$$

The second term is the usual flow term which stems from the free flight of the particles between two collisions. In the collision term, primed variables refer to the precollisional state; f_1' and f_2' stand for $f(\ldots \boldsymbol{c}_1')$ and $f(\ldots \boldsymbol{c}_2')$. Due to the conservation of linear momentum and energy one has

$$\boldsymbol{c}_\mathrm{S} \equiv \tfrac{1}{2}(\boldsymbol{c}_1 + \boldsymbol{c}_2) = \boldsymbol{c}_\mathrm{S}' \equiv \tfrac{1}{2}(\boldsymbol{c}_1' + \boldsymbol{c}_2') \tag{1.5}$$

and

$$g = g' \, , \tag{1.6}$$

where g and g' are the magnitudes of the relative velocities

$$\boldsymbol{g} = \boldsymbol{c}_1 - \boldsymbol{c}_2 \, , \quad \boldsymbol{g}' = \boldsymbol{c}_1' - \boldsymbol{c}_2' \, . \tag{1.7}$$

Thus one has

$$\boldsymbol{c}_1^{(\prime)} = \boldsymbol{c}_\mathrm{S} + \tfrac{1}{2} g \, \boldsymbol{e}^{(\prime)} \, , \quad \boldsymbol{c}_2^{(\prime)} = \boldsymbol{c}_\mathrm{S} - \tfrac{1}{2} g \, \boldsymbol{e}^{(\prime)} \, , \tag{1.8}$$

where $\boldsymbol{e}$ and $\boldsymbol{e}'$ are unit vectors parallel to the relative velocities $\boldsymbol{g}$ and $\boldsymbol{g}'$. The difference between the centers of the two colliding spheres is determined by

$$\delta \boldsymbol{r} = d \, \frac{\boldsymbol{e} - \boldsymbol{e}'}{|\boldsymbol{e} - \boldsymbol{e}'|} \, ; \tag{1.9}$$

$$\sigma = \tfrac{1}{4} d^2 \tag{1.10}$$

is the differential cross section for hard spheres with diameter d. The quantity χ which is essentially the pair correlation function takes into account that the binary collision frequency is modified by surrounding particles. It is assumed that χ depends on $\boldsymbol{r}$ only via the number density n. An explicit expression for χ is not needed here but it seems appropriate to mention that the simple analytic expression [56]

$$\chi = (1 - \tfrac{1}{2} y) \quad (1 - y)^{-3} \, ,$$

where $y = n(\pi/6) d^3$ is the fraction of the volume occupied by the spheres can be used successfully over a rather large range of densities. In any case, one has $\chi \to 1$ for $y \to 0$.

2. Expansion of the Distribution Function

In the moment method approach f is expanded about an absolute equilibrium distribution f_0 characterized by constant values n_0 and T_0 for the number density and the temperature, respectively. In the following, it is more convenient to work with the dimensionless velocity variable

$$\boldsymbol{V} = (1/\sqrt{2}) \, c_0^{-1} \, \boldsymbol{c} \, , \tag{2.1}$$

with

$$c_0 = \left(\frac{k_\mathrm{B} T_0}{m} \right)^{1/2} \, , \tag{2.2}$$

(m is the mass of a particle) and to use the distribution function F defined by

$$F \, \mathrm{d}^3 V = f \, \mathrm{d}^3 c \, . \tag{2.3}$$

The Maxwellian equilibrium distribution corresponds to

$$F_0 = n_0 \pi^{-3/2} e^{-V^2} . \tag{2.4}$$

In general, F can be written as

$$F = F_0 (1 + \Phi) , \tag{2.5}$$

where $\Phi = \Phi(t, \boldsymbol{r}, \boldsymbol{V})$ is a measure for the deviation of F from F_0. This quantity is expanded according to

$$\Phi(t, \boldsymbol{r}, \boldsymbol{V}) = \sum_i a^i (t, \boldsymbol{r}) \Phi^i (\boldsymbol{V}) , \tag{2.6}$$

where the Φ^i are orthonormalized functions with the properties

$$\langle \Phi^i \Phi^j \rangle_0 = \delta_{ij} . \tag{2.7}$$

Here $\langle \ldots \rangle_0$ refers to an average evaluated with the equilibrium distribution. In (2.6, 7), it is understood that "i" or "j", in general, stand for a set of labels distinguishing the various expansion functions.

For Φ^i with $\langle \Phi^i \rangle_0 = 0$, the expansion coefficients are given by

$$n \langle \Phi^i \rangle = \int \Phi^i f \, \mathrm{d}^3 c = n_0 a^i , \tag{2.8}$$

i.e. they are the nonequilibrium averages of the pertaining expansion functions.

For practical applications, a finite set of expansion functions is used. In the "13-moment" approximation, the following expansion functions are used: the scalars

$$\Phi^{(1)} = 1 , \quad \Phi^{(2)} = \sqrt{\tfrac{2}{3}} \left(V^2 - \tfrac{3}{2} \right) , \tag{2.9}$$

the vectors

$$\Phi_\mu^{(1)} = \sqrt{2}\, V_\mu , \quad \Phi_\mu^{(2)} = \frac{2}{\sqrt{5}} \left(V^2 - \frac{5}{2} \right) V_\mu , \tag{2.10}$$

and the 2nd rank tensor

$$\Phi_{\mu\nu} = \sqrt{2}\, \overline{V_\mu V_\nu} . \tag{2.11}$$

The symbol $\overline{\ldots}$ refers to the symmetric traceless part of a tensor, e.g.

$$\overline{a_\mu b_\nu} = \tfrac{1}{2} (a_\mu b_\nu + a_\nu b_\mu) - \tfrac{1}{3} a_\lambda b_\lambda \delta_{\mu\nu} , \tag{2.12}$$

for the dyadic constructed from two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$.

The pertaining expansion functions are the scalars

$$\begin{aligned} a^{(1)} &= n_0^{-1} (n - n_0) , \\ a^{(2)} &= \sqrt{\tfrac{3}{2}}\, T_0^{-1} (T - T_0) , \end{aligned} \tag{2.13}$$

the vectors

$$a_\mu^{(1)} = c_0^{-1} v_\mu , \tag{2.14}$$
$$a_\mu^{(2)} = \sqrt{\tfrac{2}{5}} (c_0 n_0 k_\mathrm{B} T_0)^{-1} \langle (\tfrac{1}{2} m c^2 - \tfrac{5}{2} k_\mathrm{B} T_0) c_\mu \rangle ,$$

and the second rank tensor

$$a_{\mu\nu} = \frac{m}{\sqrt{2 k_\mathrm{B} T_0}} \langle \overline{c_\mu c_\nu} \rangle . \tag{2.15}$$

In these expressions the factor $n\, n_0^{-1}$ which would occur according to (2.8) has been replaced by 1 except for $a^{(1)}$. Clearly, the scalar expansion functions are macroscopic variables which determine the relative deviation of the number density and the temperature from their equilibrium values. The vectorial functions are dimensionless velocity and heat flux variables, more specifically, $a_\mu^{(2)}$ is proportional to the "kinetic" contribution to the heat flux. The symmetric traceless 2nd rank tensor $\langle \overline{c_\mu c_\nu} \rangle$ is proportional the kinetic part of the friction pressure tensor.

3. Transport-Relaxation Equations

Insertion of the ansatz (2.5) into the kinetic equation (1.4), its multiplication by the expansion functions $\Phi^i(\boldsymbol{V})$ and subsequent intergration over $\mathrm{d}^3 V$ leads to a set of coupled equations for the expansion functions $a^i(t, \boldsymbol{r})$. These equations are referred to as transport-relaxation equations. In general terms, these equations can be written as

$$\frac{\partial a^i}{\partial t} + \sum_j [c_\mu^{ij} \nabla_\mu + \omega^{ij} + \Omega^{ij}] a^j = 0 . \tag{3.1}$$

The term containing

$$c_\mu^{ij} = \sqrt{2}\, c_0 \langle \Phi^i V_\mu \Phi^j \rangle_0 \tag{3.2}$$

stems from the flow term $\boldsymbol{c} \cdot \boldsymbol{\nabla}$. The quantities ω^{ij} and Ω^{ij} are the local and nonlocal parts of the linearized collision term. In (3.1), terms nonlinear in the quantities specifying the deviation from equilibrium have been disregarded.

The quantity ω^{ij} is given by

$$\omega^{ij} = \langle \Phi^i \omega (\Phi^j) \rangle_0 , \tag{3.3}$$

where $\omega(\Phi)$ is, apart from a factor χ_0 the linearized Boltzmann collision operator for a gas of hard spheres. For two functions Ψ and Φ rather than Φ^i and Φ^j, this collision bracket is given by

$$\begin{aligned} \langle \Psi \omega (\Phi) \rangle_0 &= \omega_0 \{ \Psi_1 (\Phi_1 + \Phi_2 - \Phi_1' - \Phi_2') \} \\ &= \omega_0 \{ \tfrac{1}{2} (\Psi_1 - \Psi_1') (\Phi_1 + \Phi_2 - \Phi_1' - \Phi_2') \} \end{aligned} \tag{3.4}$$

with

$$\Phi_n = \Phi(\boldsymbol{V}_n), \quad \Phi_n{}' = \Phi(\boldsymbol{V}_n{}'), \quad n = 1, 2. \tag{3.5}$$

The abbreviation

$$\{\ldots\} = \pi^{-3/2} \int \mathrm{d}^3 V \, e^{-V^2} (8\pi^2)^{-1} \cdot \int_0^\infty \mathrm{d}\gamma \, \gamma^3 e^{-\gamma^2} \iint \mathrm{d}^2 e \, \mathrm{d}^2 e' \ldots \tag{3.6}$$

has been introduced.

The dimensionless velocity variables $\boldsymbol{V}_1^{(\prime)}, \boldsymbol{V}_2^{(\prime)}$ are related to $\boldsymbol{V}$ and $\gamma \boldsymbol{e}^{(\prime)}$ by

$$\boldsymbol{V}_1 = \frac{1}{\sqrt{2}} (\boldsymbol{V} + \gamma \boldsymbol{e}), \quad \boldsymbol{V}_1{}' = \frac{1}{\sqrt{2}} (\boldsymbol{V} + \gamma \boldsymbol{e}'), \tag{3.7}$$

$$\boldsymbol{V}_2 = \frac{1}{\sqrt{2}} (\boldsymbol{V} - \gamma \boldsymbol{e}), \quad V_2{}' = \frac{1}{\sqrt{2}} (\boldsymbol{V} - \gamma \boldsymbol{e}'). \tag{3.8}$$

These equations are equivalent to (1.5, 7). The quantity ω_0 is a collision frequency, viz.

$$\omega_0 = \chi_0 16 \sqrt{\pi} \, n_0 c_0 \sigma = 4 \sqrt{\pi} \, \chi_0 n_0 c_0 \mathrm{d}^2. \tag{3.9}$$

The symmetry $\langle \Psi \omega(\Phi) \rangle_0 = \langle \Phi \omega(\Psi) \rangle_0$ implies

$$\omega^{ij} = \omega^{ji}. \tag{3.10}$$

The "matrix elements" Ω^{ij} stem from the nonlocal part of the linearized collision term. Analogously to (3.3), one can define a nonlocal collision operator $\Omega(\ldots)$ by

$$\Omega^{ij} = \langle \Phi^i \Omega(\Phi^j) \rangle_0. \tag{3.11}$$

With Ψ and Φ instead of Φ^i and Φ^j this expression is given by

$$\langle \Psi \Omega(\Phi) \rangle_0 = \omega_0 \{\Psi_1 [\Phi_2 (e^{\delta \boldsymbol{r} \cdot \boldsymbol{\nabla}} - 1) - \Phi_2{}' (e^{-\delta \boldsymbol{r} \cdot \boldsymbol{\nabla}} - 1)]\}, \tag{3.12}$$

$$\delta \boldsymbol{r} = d(\boldsymbol{e} - \boldsymbol{e}')(|\boldsymbol{e} - \boldsymbol{e}'|)^{-1} = \mathrm{d}\boldsymbol{u}. \tag{3.13}$$

Clearly Ω^{ij} is a differential operator of infinite order. Expansion of the exponential functions in (3.12) leads to

$$\langle \Psi \Omega(\Phi) \rangle_0 = \langle \Psi \omega_\mu(\Phi) \rangle_0 \nabla_\mu + \langle \Psi \omega_{\mu\nu}(\Phi) \rangle_0 \nabla_\mu \nabla_\nu + \cdots \tag{3.14}$$

with

$$\langle \Psi \omega_\mu(\Phi) \rangle_0 = \omega_0 d \{\Psi_1 u_\mu (\Phi_2 + \Phi_2{}')\} = \omega_0 d \{\tfrac{1}{2} (\Psi_1 - \Psi_1{}') u_\mu (\Phi_2 + \Phi_2{}')\}, \tag{3.15}$$

$$\langle \Psi \omega_{\mu\nu}(\Phi) \rangle_0 = \tfrac{1}{2} \omega_0 d^2 \{\Psi_1 u_\mu u_\nu (\Phi_2 - \Phi_2{}')\} = \tfrac{1}{2} \omega_0 d^2 \{\tfrac{1}{2} (\Psi_1 - \Psi_1{}') \cdot u_\mu u_\nu (\Phi_2 - \Phi_2{}')\}, \tag{3.16}$$

$$\boldsymbol{u} = (\boldsymbol{e} - \boldsymbol{e}')(|\boldsymbol{e} - \boldsymbol{e}'|)^{-1}.$$

For the applications to be considered here, the first and second order gradient terms (3.15, 16) only are taken into account.

In addition to the expression given by (3.12), the nonlocal collision matrix Ω^{ij} contains a term which stems from the spatial dependence of χ (cf. 1.4). This term, however, is relevant only for $j = 1$, i.e. for a^j identical with the relative deviation of the number density from its equilibrium value. This gives rise to the additional contribution

$$\omega_0 \chi_0^{-1} n_0 (\partial \chi_0 / \partial n_0) \{\Phi_1{}^i (e^{\frac{1}{2} \delta \boldsymbol{r} \cdot \boldsymbol{\nabla}} - e^{-\frac{1}{2} \delta \boldsymbol{r} \cdot \boldsymbol{\nabla}})\} \boldsymbol{a}^{(1)}, \tag{3.17}$$

in (3.1); for $a^{(1)}$ see (2.13). Clearly, only terms odd in $\boldsymbol{\nabla}$ occur in (3.17).

In lowest order (3.17) reduces to

$$\omega_0 \mathrm{d} \chi_0^{-1} n_0 (\partial \chi_0 / \partial n_0) \{\Phi_1{}^i \boldsymbol{u}\} \cdot \boldsymbol{\nabla} a^{(1)}. \tag{3.18}$$

Next, the transport-relaxation equations are stated for the expansion coefficient tensors introduced in Section 2. The equations for the scalars are

$$\frac{\partial a^{(1)}}{\partial t} + c_0 \nabla_\mu a_\mu^{(1)} = 0, \tag{3.19}$$

$$\frac{\partial a^{(2)}}{\partial t} + \sqrt{\frac{2}{3}} c_0 (1 + 4\varphi_0) \nabla_\mu a_\mu^{(1)} + \sqrt{\frac{5}{3}} c_0 \left(1 + \frac{12}{5} \varphi_0\right) \nabla_\mu a_\mu^{(2)} - \frac{1}{9} \mathrm{d}^2 \omega_0 \Delta a^{(2)} = 0. \tag{3.20}$$

The terms containing the quantity φ_0 stem from the first-derivative terms of the nonlocal collision operator; φ_0 is the equilibrium value of φ defined by

$$\varphi = \chi y, \quad y = n \frac{\pi}{6} d^3. \tag{3.21}$$

It is recalled that y is the fraction of the available volume occupied by the hard spheres. Its maximum value for a close packed system is

$$y = (\sqrt{2}/6) \pi \approx 0,7.$$

Notice that $\omega_0 d = (24/\sqrt{\pi}) c_0 \varphi_0$.

The vectorial transport-relaxation equations are

$$\frac{\partial a_\mu^{(1)}}{\partial t} + c_0 \left(1 + 8\varphi_0 + 4\varphi_0 \chi_0^{-1} n_0 \frac{\partial \chi_0}{\partial n_0}\right) \nabla_\mu \boldsymbol{a}^{(1)} + \sqrt{\tfrac{2}{3}} c_0 (1 + 4\varphi_0) \nabla_\mu a^{(2)} + \sqrt{2} c_0 (1 + \tfrac{8}{5} \varphi_0) \nabla_\nu a_{\mu\nu} - \tfrac{1}{15} \omega_0 d^2 (\Delta a_\mu^{(1)} + 2 \nabla_\mu \nabla_\nu a_\nu^{(1)}) = 0. \tag{3.22}$$

$$\begin{aligned}\frac{\partial a_\mu^{(2)}}{\partial t} &+ \sqrt{\frac{5}{3}}\, c_0 \left(1 + \frac{12}{5}\varphi_0\right) \nabla_\mu a^{(2)} \\ &+ \frac{2}{5}\sqrt{5}\, c_0 \left(1 + \frac{12}{5}\varphi_0\right) \nabla_\nu a_{\mu\nu} \\ &+ \frac{8}{15}\,\omega_0\, a_\mu^{(2)} \\ &- \frac{1}{30\sqrt{10}}\,\omega_0 d^2 (\Delta a_\mu^{(1)} + 2\nabla_\mu \nabla_\nu a_\nu^{(1)}) = 0 .\end{aligned} \tag{3.23}$$

Finally, the equation for the 2nd rank tensor $a_{\mu\nu}$ is

$$\begin{aligned}\frac{\partial a_{\mu\nu}}{\partial t} &+ \sqrt{2}\, c_0 \left(1 + \frac{8}{5}\varphi_0\right) \overline{\nabla_\nu a_\mu^{(1)}} \\ &+ \frac{2}{5}\sqrt{5}\, c_0 \left(1 + \frac{12}{5}\varphi_0\right) \overline{\nabla_\nu a_\mu^{(2)}} + \frac{4}{5}\,\omega_0\, a_{\mu\nu} \\ &- \frac{2}{15\sqrt{3}}\,\omega_0 d^2\, \overline{\nabla_\mu \nabla_\nu}\, a^{(2)} = 0 .\end{aligned} \tag{3.24}$$

In (3.23, 24), second spatial derivatives of conserved quantities only have been taken into account.

The physical meaning of these transport relaxation equations and some applications are discussed in the following sections.

4. Local Conservation Equations; Transport-Relaxation Equations for the Kinetic Heat Flux and Pressure Tensor

The dimensionless variables $a^{(i)}$, $a^{(2)}$, $a_\mu^{(1)}$ are associated with the number density, temperature and velocity, respectively. Thus Eqs. (3.19, 20, 22) are essentially the (linearized) local conservation equations which can be rewritten as

$$\frac{\partial n}{\partial t} + n_0 \nabla_\mu v_\mu = 0, \tag{4.1}$$

$$n_0 \frac{\mathrm{d}u}{\mathrm{d}t} + P_0 \nabla_\mu v_\mu + \nabla_\mu q_\mu = 0, \tag{4.2}$$

$$m n_0 \frac{\mathrm{d}v_\mu}{\mathrm{d}t} + \nabla_\mu P + \nabla_\nu \overline{p_{\mu\nu}} + \nabla_\mu p = 0, \tag{4.3}$$

where

$$u = \tfrac{3}{2} k_\mathrm{B} T \tag{4.4}$$

is the energy per particle and

$$P = n k_\mathrm{B} T (1 + 4\varphi) \tag{4.5}$$

is the pressure of the hard sphere gas, m is the mass of a particle. Notice that P_0 stands for

$$n_0 k_\mathrm{B} T_0 (1 + 4\varphi_0), \quad \varphi_0 = \chi_0 y_0 .$$

The heat flux $\boldsymbol{q}$ can be decomposed into a kinetic and a collisional transfer contribution $\boldsymbol{q}^\mathrm{kin}$ and $\boldsymbol{q}^\mathrm{ct}$ according to

$$\begin{aligned}\boldsymbol{q} &= \boldsymbol{q}^\mathrm{kin} + \boldsymbol{q}^\mathrm{ct}, \\ \boldsymbol{q}^\mathrm{kin} &= n_0 k_\mathrm{B} T_0 c_0 (1 + \tfrac{12}{5}\varphi_0) \boldsymbol{Q}\end{aligned} \tag{4.6}$$

with

$$Q_\mu = \sqrt{\tfrac{5}{2}}\, a_\mu^{(2)}, \tag{4.7}$$

cf. (2.14), and

$$\boldsymbol{q}^\mathrm{ct} = -\lambda^\mathrm{ct} \boldsymbol{\nabla} T, \tag{4.8}$$

$$\lambda^\mathrm{ct} = \tfrac{1}{6} k_\mathrm{B} n_0 \omega_0 d^2 . \tag{4.9}$$

Similarly, the symmetric traceless part $\overline{p_{\mu\nu}}$ of the friction tensor as it can be inferred from (3.22) can be written as

$$\overline{p_{\mu\nu}} = \overline{p_{\mu\nu}}^\mathrm{kin} + \overline{p_{\mu\nu}}^\mathrm{ct}, \tag{4.10}$$

$$\begin{aligned}\overline{p_{\mu\nu}}^\mathrm{kin} &= n_0 k_\mathrm{B} T_0 (1 + \tfrac{8}{5}\varphi_0) \Pi_{\mu\nu}, \\ \Pi_{\mu\nu} &= \sqrt{2}\, a_{\mu\nu},\end{aligned} \tag{4.11}$$

cf. (2.15).

The collisional transfer contribution $\overline{p_{\mu\nu}}^\mathrm{ct}$ as it follows from (3.22) is

$$\overline{p_{\mu\nu}}^\mathrm{ct} = -2\eta^\mathrm{ct}\, \overline{\nabla_\mu v_\nu} \tag{4.12}$$

with

$$\begin{aligned}\eta^\mathrm{ct} &= \tfrac{1}{15} n_0 m \omega_0 d^2 \\ &= \tfrac{1}{15} n_0 k_\mathrm{B} T_0 c_0^{-2} \omega_0 d^2 .\end{aligned} \tag{4.13}$$

The scalar part p of the friction pressure is

$$p = -\eta_\mathrm{v} \nabla_\mu v_\mu, \quad \eta_\mathrm{v} = \tfrac{5}{3}\eta^\mathrm{ct}. \tag{4.14}$$

The bulk viscosity η_v does not contain a kinetic contribution.

The local conservation equations (4.1–3) with (4.6, 7) and (4.10, 11) have to be complemented by the equations for Q_μ and $\Pi_{\mu\nu}$ which can readily be inferred from (3.23, 24) viz.,

$$\begin{aligned}\partial Q_\mu/\partial t &+ \tfrac{5}{2} c_0 (1 + \tfrac{12}{5}\varphi_0) T_0^{-1} \nabla_\mu T \\ &+ c_0 (1 + \tfrac{12}{5}\varphi_0) \nabla_\nu \Pi_{\mu\nu} + \omega^{(\lambda)} Q_\mu \\ &- \tfrac{1}{16}\omega^{(\lambda)} \mathrm{d}^2 c_0^{-1} (\Delta v_\mu + 2\nabla_\mu \nabla_\nu v_\nu) = 0,\end{aligned} \tag{4.15}$$

$$\begin{aligned}\partial \Pi_{\mu\nu}/\partial t &+ 2(1 + \tfrac{8}{5}\varphi_0) \overline{\nabla_\mu v_\nu} \\ &+ \tfrac{4}{5} c_0 (1 + \tfrac{12}{5}\varphi_0) \overline{\nabla_\mu Q_\nu} \\ &+ \omega^{(\eta)} \Pi_{\mu\nu} - \tfrac{1}{6}\omega^{(\eta)} \mathrm{d}^2 T_0^{-1} \overline{\nabla_\mu \nabla_\nu} T = 0 .\end{aligned} \tag{4.16}$$

The collision frequencies $\omega^{(\lambda)}$ and $\omega^{(\eta)}$ are given by

$$\omega^{(\lambda)} = \tfrac{8}{15}\omega_0, \quad \omega^{(\eta)} = \tfrac{4}{5}\omega_0, \tag{4.17}$$

for ω_0 see (3.9). Apart from the factor χ_0, $\omega^{(\lambda)}$ and $\omega^{(\eta)}$ are the corresponding (local) Boltzmann collision frequencies.

5. Transport Coefficients, Viscoelasticity

In the hydrodynamic regime, the time derivatives, the spatial derivatives of the nonconserved quantities $\boldsymbol{Q}$, $\boldsymbol{\Pi}$, as well as 2nd spatial derivatives of the conserved quantities $\boldsymbol{v}$, T can be disregarded. Then (4.15) and (4.16) reduce to

$$Q_\mu = -\frac{1}{\omega^{(\lambda)}}\,\frac{5}{2}\,c_0\left(1+\frac{12}{5}\,\varphi_0\right)T_0^{-1}\,\nabla_\mu T\,, \tag{5.1}$$

$$\Pi_{\mu\nu} = -\frac{2}{\omega^{(\eta)}}\left(1+\frac{8}{5}\,\varphi_0\right)\overline{\nabla_\mu v_\nu}\,. \tag{5.2}$$

Insertion into (4.6) and (4.10) yields

$$q_\mu = -\lambda\,\nabla_\mu T\,, \quad \overline{p_{\mu\nu}} = -2\,\eta\,\overline{\nabla_\mu v_\nu}\,, \tag{5.3}$$

where the heat conductivity λ and the shear viscosity η are given by

$$\lambda = \lambda^{\text{kin}} + \lambda^{\text{ct}}\,,$$
$$\lambda^{\text{kin}} = \frac{5}{2}\,\frac{k_B}{m}\,\frac{n_0\,k_B\,T_0}{\omega^{(\lambda)}}\left(1+\frac{12}{5}\,\varphi_0\right)^2, \tag{5.4}$$

$$\eta = \eta^{\text{kin}} + \eta^{\text{ct}}\,,$$
$$\eta^{\text{kin}} = \frac{n_0\,k_B\,T_0}{\omega^{(\eta)}}\left(1+\frac{8}{5}\,\varphi_0\right)^2, \tag{5.5}$$

for the collisional-transfer contributions to λ and η, for λ^{ct} and η^{ct}, see (4.9, 13).

These results agree with the corresponding expressions derived previously with the help of the Enskog solution procedure. With

$$\omega^{(\lambda,\eta)} = \chi_0\,\omega_B^{(\lambda,\eta)} \quad\text{and}\quad \chi = \varphi\,y^{-1}\,,$$

cf. (3.21), (5.4, 5) can be rewritten as

$$\lambda^* = \frac{\lambda}{y\,\lambda_B} = \varphi_0^{-1}\left[\left(1+\frac{12}{5}\,\varphi_0\right)^2 + \frac{512}{25\,\pi}\,\varphi_0^2\right], \tag{5.6}$$

$$\eta^* = \frac{\eta}{y\,\eta_B} = \varphi_0^{-1}\left[\left(1+\frac{8}{5}\,\varphi_0\right)^2 + \frac{768}{25\,\pi}\,\varphi_0^2\right]. \tag{5.7}$$

Here, the subscript "B" refers to the "Boltzmann" value of the various quantities. For a discussion of the dependence of the dimensionless transport coefficients λ^*, η^* on φ_0, see [55].

The knowledge of the transport coefficients is sufficient for nonequilibrium phenomena in the hydrodynamic regime. In the following, two applications of the transport-relaxation equations derived in this paper are discussed where some of the approximations which led from (4.15, 16) to (5.1, 2) are abandoned.

Firstly, the frequency dependence of the viscosity and the viscoelasticity are studied. To this purpose, an isothermal fluid is considered, which is subjected to time dependent pressure or velocity gradient. Then (4.16) reduces to

$$\partial\Pi_{\mu\nu}/\partial t + \omega^{(\eta)}\,\Pi_{\mu\nu} = -\,2\left(1+\tfrac{8}{5}\,\varphi_0\right)\overline{\nabla_\mu v_\nu}\,. \tag{5.8}$$

In the case of a periodic time dependence, i.e.

$$\boldsymbol{v} \propto e^{-i\omega t}\,, \quad \Pi_{\mu\nu} \propto e^{-i\omega t}\,,$$

$\Pi_{\mu\nu}$ is related to $\overline{\nabla_\mu v_\nu}$ just as in (5.2) but now with $\omega^{(\eta)}$ replaced by $\omega^{(\eta)} - i\omega$. Thus a dynamic i.e. frequency dependent viscosity

$$\eta(\omega) = \eta^{\text{kin}}\,(1 - i\,\omega\,\tau_\eta)^{-1} + \eta^{\text{ct}} \tag{5.9}$$

is found with η^{kin} given by (5.5) and

$$\tau_\eta = (\omega^{(\eta)})^{-1}\,. \tag{5.10}$$

Alternatively, $\eta(\omega)$ can be written as

$$\eta(\omega) = \eta' + i\,\eta'' \tag{5.11}$$

with

$$\eta' = \eta^{\text{kin}}\,(1 + \omega^2\,\tau_\eta{}^2)^{-1} + \eta^{\text{ct}}\,, \tag{5.12}$$

$$\eta'' = \eta^{\text{kin}}\,\omega\,\tau_\eta\,(1 + \omega^2\,\tau_\eta{}^2)^{-1}\,. \tag{5.13}$$

Clearly, for $\omega\,\tau_\eta \ll 1$ one has

$$\eta'' = 0 \quad\text{and}\quad \eta' = \eta(0) = \eta\,,$$

where η is the viscosity as given by (5.5). On the other hand, η' approaches $\eta^{\text{ct}} < \eta$ for $\omega\,\tau_\eta \ll 1$. This limiting value is zero for the Boltzmann gas. The difference $\eta(0) - \eta(\infty)$ is equal to η^{kin}. For $\omega = \tau_\eta^{-1} = \omega^{(\eta)}$ one has $\eta(0) - \eta'(\omega) = \frac{1}{2}[\eta(0) - \eta(\infty)]$, and η'' assumes its maximum value. Notice that the contribution η^{ct} to the viscosity is frequency independent. This is due to the fact that the collisions are treated as instantaneous events. This corresponds to a transport of momentum "through" a hard sphere with infinite speed.

A complex shear modulus $G(\omega)$ can be defined by

$$G = -\,i\,\omega\,\eta(\omega)\,. \tag{5.14}$$

Its real and imaginary parts (storage and loss moduli) are

$$G' = \omega\,\eta'' = \eta^{\text{kin}}\,\omega^2\,\tau_\eta\,(1 + \omega^2\,\tau_\eta{}^2)^{-1}\,, \tag{5.15}$$

and

$$G'' = -\,\omega\,\eta' \tag{5.16}$$

with η' given by (5.13).

In passing it might be worth mentioning that the viscoelastic properties of the Enskog fluid as described by (4.10) with (4.11) and (5.8) or by the complex viscosity coefficient (5.9) correspond to a rheological model referred to as "Jeffreys body" [58] which is a combination a Newtonian and Maxwell model. In the present case, the Newtonian and Maxwellian parts of the friction pressure are $\overline{\mathbf{p}}^{\mathrm{ct}}$ and $\overline{\mathbf{p}}^{\mathrm{kin}}$, respectively.

6. Thermal Pressure

A spatially inhomogeneous temperature field T can give rise to a (symmetric traceless) pressure tensor $\overline{\mathbf{p}} \propto \overline{\boldsymbol{\nabla}\boldsymbol{\nabla}}\,T$. This thermal pressure was already calculated by Maxwell for the Boltzmann gas with a special interaction potential. More generally, "Burnett effects" of this type have been calculated for "rarefied" monatomic and polyatomic gases. In the latter case, also the influence of external fields was studied theoretically and experimentally [43 to 47]. The existence of a transverse component of the thermal pressure of a polyatomic gas in the presence of a magnetic field is of crucial importance for its experimental detection. The "Burnett" effects as calculated from the Boltzmann equation or the Waldmann-Snider equation are proportional to n_0^{-1}. Thus one might expect that these effects, like the thermal pressure vanish in dense gases and liquids. From the Enskog equation, however, one infers that this is not the case.

More specifically, a stationary situation with $\boldsymbol{v} = 0$ but $T = T(\boldsymbol{r})$ is considered. Then (4.16) leads to

$$\Pi_{\mu\nu} = -\frac{4}{5}\,\frac{c_0}{\omega^{(\eta)}}\left(1+\frac{12}{5}\,\varphi_0\right)\overline{\nabla_\mu Q_\nu} + \tfrac{1}{6}\,\mathrm{d}^2 T_0^{-1}\,\overline{\nabla_\mu \nabla_\nu T}\,. \tag{6.1}$$

With $\boldsymbol{Q}$ approximated by (5.1) and with (4.11),

$$\overline{p_{\mu\nu}} = n_0 k_{\mathrm{B}} T_0 (1+\tfrac{8}{5}\varphi_0) \cdot \left[2\,\frac{c_0^2}{\omega^{(\eta)}\,\omega^{(\lambda)}}\left(1+\frac{12}{5}\,\varphi_0\right)^2 + \frac{1}{6}\,d^2\right] \cdot T_0^{-1}\,\overline{\nabla_\mu \nabla_\nu T} \tag{6.2}$$

is found for the desired thermal pressure. The "Boltzmann" result is recovered from (6.2) with $d = 0$, $\varphi_0 = 0$, and $\chi_0 = 1$ which implies $\omega^{(\cdots)} \propto n_0$ and consequently $\overline{\mathbf{p}} \propto n_0^{-1}$.

The "Enskog" result (6.2) can be rewritten as

$$\overline{p_{\mu\nu}} = n_0\,k_{\mathrm{B}}\,T_0 K\,\mathrm{d}^2\,T_0^{-1}\,\overline{\nabla_\mu \nabla_\nu T}\,, \tag{6.3}$$

where the dimensionless coefficient K is given by

$$K = \frac{1}{6}\left(1+\frac{8}{5}\,\varphi_0\right) \cdot \left[1+\frac{25\,\pi}{512\,\varphi_0^2}\left(1+\frac{12}{5}\,\varphi_0\right)^2\right]. \tag{6.4}$$

Here, use has been made of (4.17) and (3.9). For $\varphi_0 \ll 1$ and $\varphi_0 \gg 1$ one has $K \propto \varphi_0^{-2}$ and $K \propto \varphi_0$, respectively. For the value $\varphi_0 = 5$ which should correspond to a liquid-like density, one has

$$K = \tfrac{3}{2}(1+169\,\pi/512) \approx 3\,.$$

In a liquid, the "kinetic pressure" $n_0 k_{\mathrm{B}} T_0$ ocurring in (6.3) is by about a factor 10^3 larger than the equilibrium pressure P. Thus, in a liquid the thermal pressure is small but nonzero. Its size p^{th} is, by order of magnitude, given by $p^{\mathrm{th}}/p \approx (10d/L)^2\,T_0^{-1}\,\delta T$, where δT is the temperature difference across a typical length scale L (associated with 2nd spatial derivative of T).

Notice, that $\Pi_{\mu\nu} \neq 0$ renders the velocity distribution anisotropic. This, in principle, leads to an anisotropy of a Doppler broadened spectral line [59]. In liquids, Doppler broadening should be observable in Mößbauer-Rayleigh scattering. Furthermore, if $\Pi_{\mu\nu}$ and consequently $\overline{p_{\mu\nu}}$ (cf. 6.2) are spatially inhomogeneous, i.e. if $\overline{\nabla_\mu \nabla_\nu T}$ is not constant, the fluid exerts forces and torques on suspended particles or on walls. The torque on nonspherical particles should lead to a preferential alignment which could be observed via the resulting birefringence. Such a heat-flow birefringence has been calculated and detected experimentally in molecular gases [48]. It would be of interest to search for the corresponding effect in liquids and colloidal suspensions.

Concluding Remarks

In this article, the moment method has been applied to the Enskog-Boltzmann equation. Transport-Relaxation equations have been derived in the 13-moments approximation. Transport processes in the hydrodynamic regime and somewhat beyond viz, frequency dependent viscosity and thermal pressure have been discussed. It should be noticed, however, that the enlarged set of equations of thermohydrodynamics derived here has to be complemented by boundary conditions. The method of Waldmann [60–64] which leads to consistent boundary conditions could also be applied to dense fluids.

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