

Brownian Motion of Rotating Particles

SIEGFRIED HESS

Institut für Theoretische Physik der Universität Erlangen-Nürnberg, Erlangen

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A kinetic theory for the Brownian motion of spherical rotating particles is given starting from a generalized Fokker-Planck equation. The generalized Fokker-Planck collision operator is a sum of two ordinary Fokker-Planck differential operators in velocity and angular velocity space respectively plus a third term which provides a coupling of translational and rotational motions. This term stems from a transverse force proportional to the cross product of velocity and angular velocity of a Brownian particle. Collision brackets pertaining to the generalized Fokker-Planck operator are defined and their general properties are discussed. Application of WALDMANN's moment method to the Fokker-Planck equation yields a set of coupled linear differential equations (transport-relaxation equations) for certain local mean values. The constitutive laws for diffusion, heat conduction by Brownian particles and spin diffusion are deduced from the transport-relaxation equations. The transport-relaxations coefficients appearing in them are given in terms of the two friction coefficients for the damping of translational and rotational motions and a third coefficient which is a measure of the transverse force. By the coupling of translational and rotational motions a diffusion flow gives rise to a correlation of linear and angular velocities.

The kinetic theory of dilute gases consisting of particles with spin^{1, 2, 3} and of rough sphere molecules^{4, 5, 6} exhibited two main features that do not occur in the case of monatomic gases: i) thermodynamical fluxes (diffusion flow, heat flow, friction pressure) cause a partial alignment of the spins or internal angular momenta of the particles; ii) this alignment, in turn, influences the values of the transport constants (diffusion constant, heat conductivity, viscosity). Apart from this there are new physical phenomena compared with monatomic gases. One has to deal with spin relaxation (or relaxation of internal angular momentum) and with spin diffusion (or diffusion of internal angular momentum). The kinetic theory also provides methods to calculate the spin relaxation coefficient and the spin diffusion constants.

One might expect similar effects to occur in the case of the Brownian motion of particles with rotational degrees of freedom. For a formal treatment one should start from a generalized Fokker-Planck equation. In order to set up a Fokker-Planck equation one not only has to know the damping of the translational and rotational motions (characterized by 2 friction constants) but also the coupling of

translational and rotational motions. CONDIFF and DAHLER⁷ already studied the Brownian motion of non-spherical particles with rotational degrees of freedom taking into account a linear type of coupling where the friction force and friction torque in the pertaining Langevin equations are linear functions of both the velocity and angular velocity of a Brownian particle. This type of coupling of translational and rotational motions, however, vanishes for particles with three mutually perpendicular symmetry planes⁸. Here we shall deal with a different coupling mechanism consisting in a "transverse force" proportional to the cross product of the velocity and the angular velocity of the Brownian particle. This spin-orbit coupling type of force causes a particle to roll aside if its internal angular velocity is not parallel to its velocity (Magnus effect)⁹. From a hydrodynamical calculation follows that this effect even exists for a sphere¹⁰. Here we assume such a transverse force also to act on particles which are so small that hydrodynamics no longer may be applied. For simplicity we confine our attention to spherical (rotating Brownian) particles. In this case one does not need any angle variables to specify the orientation of a particle in space. Thus the kinetic treatment is rather simple compared with the case

¹ L. WALDMANN, *Nuovo Cim.* **14**, 898 [1959]; *Z. Naturforsch.* **15 a**, 19 [1960].

² F. R. McCourt and R. F. SNIDER, *J. Chem. Phys.* **41**, 3185 [1964].

³ S. HESS and L. WALDMANN, *Z. Naturforsch.* **21 a**, 1529 [1966].

⁴ L. WALDMANN, *Z. Naturforsch.* **18 a**, 1033 [1963].

⁵ D. W. CONDIFF, W. K. LU, and J. S. DAHLER, *J. Chem. Phys.* **42**, 3445 [1965].

⁶ J. L. McLAUGHLIN and J. S. DAHLER, *J. Chem. Phys.* **44**, 4453

⁷ D. W. CONDIFF and J. S. DAHLER, *J. Chem. Phys.* **44**, 3988 [1966].

⁸ J. HAPPEL and H. BRENNER, *Low Reynolds Number hydrodynamics*, Prentice-Hall, Englewood Cliffs, N. J. 1965.

⁹ A. MAGNUS, *Berl. Akad.* 1851.

¹⁰ S. HESS, to be published.



where the linear type of coupling of translational and rotational motions exists (non-spherical particles). But due to the transverse force one finds again those qualitative features known from the kinetic theory of dilute gases of particles with internal degrees of freedom.

In § 1 the generalized Fokker-Planck equation for the rotating spheres is developed. The generalized Fokker-Planck collision operator is a sum of three terms. One of them is the usual Fokker-Planck collision operator containing derivatives with respect to the velocity, another is a term analogous to it but with the linear velocity replaced by the angular velocity. These two collision operators ensure the decay of an arbitrary distribution function to an equilibrium distribution. The third collision term stems from the transverse force. It provides the desired coupling of translational and rotational motions.

Collision brackets pertaining to the generalized Fokker-Planck collision operator are defined in § 2. Their definiteness, symmetries, parity and time reversal properties are discussed. Using the same moment method that Waldmann first applied to the Boltzmann equation for the Lorentzian gas of rough spheres⁴ the generalized Fokker-Planck equation may be cast into a set of linear coupled differential equations ("transport-relaxation equation") for certain mean values characterizing the deviation of the non-equilibrium distribution function from the equilibrium distribution (§ 3, 4). The conservation equation for the number of particles, the constitutive laws for the diffusion flow, for the part of the heat flow that stems from the Brownian particles and for the angular momentum flux tensor ("spin flux" tensor) may be derived from the transport-relaxation equations (§ 5–7). The transport constants, i. e. the diffusion constant, the heat conductivity, the angular velocity diffusion constants and the coefficients characterizing cross effects are expressed in terms of certain collision bracket called relaxation coefficients. The relaxations coefficients, in turn, are explicitly given in terms of the friction constants for translational and rotational motions and a constant depending on the magnitude of the transverse force. It is shown that thermodynamical fluxes cause a partial alignment of the internal angular velocities of Brownian particles. This effect leads to transport constants smaller than those which one obtains by neglecting this alignment.

§ 1. Fokker-Planck Equation

We consider spherical Brownian particles with radius R , mass m and moment of inertia Θ suspended in a fluid with mass density ϱ and viscosity η . The one particle distribution function f of the Brownian particles will depend on time t , on the space coordinate \mathbf{x} , the velocity \mathbf{v} and on the angular velocity \mathbf{w} of a particle:

$$f = f(t, \mathbf{x}, \mathbf{v}, \mathbf{w}). \quad (1.1)$$

The local instantaneous mean value $\langle \Phi \rangle$ of a function $\Phi = \Phi(\mathbf{v}, \mathbf{w})$ is given by

$$\langle \Phi \rangle = \frac{1}{n} \int \Phi(\mathbf{v}, \mathbf{w}) f(t, \mathbf{x}, \mathbf{v}, \mathbf{w}) d^3v d^3w. \quad (1.2)$$

The particle density is

$$n(t, \mathbf{x}) = \int f(t, \mathbf{x}, \mathbf{v}, \mathbf{w}) d^3v d^3w. \quad (1.3)$$

In order to set up the Fokker-Planck equation for f , one has to know the forces and torques acting on a Brownian particle. For spherical particles there will be a friction force

$$\mathbf{K}^f = -m \omega_1 \mathbf{v} \quad (1.4)$$

and a friction torque

$$\mathbf{M}^f = -\Theta \omega_2 \mathbf{w}. \quad (1.5)$$

The friction constants ω_1 and ω_2 (reciprocal times) depend on the viscosity of the fluid and the size of the sphere. If the radius R of the sphere is very large compared with the mean free path in the fluid one may apply hydrodynamics and the friction constants are given by^{8, 11}

$$\omega_1 = m^{-1} 6 \pi \eta R \quad (1.6)$$

and

$$\omega_2 = \Theta^{-1} 8 \pi \eta R^3. \quad (1.7)$$

Here, however, we shall not confine our treatment to the range where hydrodynamics may be applied but consider the friction coefficients ω_1 , ω_2 as given constants. More general, the friction coefficients may be expressed in terms of correlation function integrals^{7, 12}.

With the friction force (1.4) and the friction torque (1.5) alone no coupling of the translational and the rotational motions would occur. The desired

¹¹ L. D. LANDAU and E. M. LIFSHITZ, *Theoretical Physics VI, Fluid Mechanics*, Pergamon Press, London 1959, p. 66.

¹² P. MAZUR, Seminar held at the Summer School on "Fundamental Problems in Statistical Mechanics II" at Noordwijk, Holland, July 1967.

coupling is brought about by the transverse force

$$\mathbf{K}^{\text{tr}} = -\gamma m_t \mathbf{v} \times \mathbf{w}. \quad (1.8)$$

This effect is a kind of spin-orbit coupling since the force (1.8) can be derived from a potential

$$V = \gamma \frac{m_t}{m} m (\mathbf{x} \times \mathbf{v}) \cdot \mathbf{w} = \gamma \frac{m_t}{m} \mathbf{l} \cdot \mathbf{w}. \quad (1.8a)$$

Here $m_t = \frac{4}{3} \pi R^3 \rho$ is the mass of the fluid contained in a volume equal to that of the Brownian particle, γ is a dimensionless constant. From hydrodynamics follows¹⁰ $\gamma = 3/4$. Again we assume γ to be a given constant of similar order of magnitude. It would be desirable to have a derivation of the normal force (1.8) from a microscopic point of view and an expression for γ in terms of a correlation function integral (as it exists for the friction force and torque^{7, 12}).

Knowing the forces and the torque acting on a Brownian particle we now are ready to write down a generalized Fokker-Planck equation

$$\begin{aligned} \frac{\partial f}{\partial t} + \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{x}} - \gamma \frac{m_t}{m} (\mathbf{v} \times \mathbf{w}) \cdot \frac{\partial f}{\partial \mathbf{v}} \\ - \omega_1 \frac{\partial}{\partial \mathbf{v}} \cdot \left(\mathbf{v} + \frac{k T_0}{m} \frac{\partial}{\partial \mathbf{v}} \right) f \\ - \omega_2 \frac{\partial}{\partial \mathbf{w}} \cdot \left(\mathbf{w} + \frac{k T_0}{\Theta} \frac{\partial}{\partial \mathbf{w}} \right) f = 0. \end{aligned} \quad (1.9)$$

Here T_0 is the temperature of the fluid (assumed to be in equilibrium). The last two terms establish the "decay" of the distribution function to an equilibrium distribution f_0 characterized by the temperature T_0 and the density n_0 :

$$\begin{aligned} f_0(\mathbf{v}, \mathbf{w}) = n_0 \left(\frac{\sqrt{m} \Theta}{2 \pi k T_0} \right)^3 \\ \cdot \exp \left\{ -\frac{1}{k T_0} \left(\frac{1}{2} m v^2 + \frac{1}{2} \Theta w^2 \right) \right\}. \end{aligned} \quad (1.10)$$

The third term in (1.9) stems from the transverse force (1.8) and gives the coupling of the rotational and translational motions. It vanishes too in equilibrium.

For convenience we shall now use dimensionless variables:

$$\mathbf{V} = \sqrt{\frac{m}{2 k T_0}} \mathbf{v} = \sqrt{\frac{3}{2}} v_0^{-1} \mathbf{v} \quad \text{with} \quad v_0 = \sqrt{\frac{3 k T_0}{m}}, \quad (1.11)$$

$$\mathbf{W} = \sqrt{\frac{\Theta}{2 k T_0}} \mathbf{w} = \sqrt{\frac{3}{2}} w_0^{-1} \mathbf{w} \quad \text{with} \quad w_0 = \sqrt{\frac{3 k T_0}{\Theta}}. \quad (1.12)$$

For the equilibrium distribution function then holds

$$f_0(\mathbf{v}, \mathbf{w}) d^3 v d^3 w = F_0(\mathbf{V}, \mathbf{W}) d^3 V d^3 W \quad (1.13)$$

$$\text{where} \quad F_0(\mathbf{V}, \mathbf{W}) = n_0 \pi^{-3} e^{-(V^2 + W^2)}.$$

The generalized Fokker-Planck equation now reads

$$\begin{aligned} \frac{\partial f}{\partial t} + \sqrt{\frac{2}{3}} v_0 \mathbf{V} \cdot \frac{\partial f}{\partial \mathbf{x}} - \omega_0 (\mathbf{V} \times \mathbf{W}) \cdot \frac{\partial f}{\partial \mathbf{V}} \\ - \omega_1 \frac{\partial}{\partial \mathbf{V}} \cdot \left(\mathbf{V} + \frac{1}{2} \frac{\partial}{\partial \mathbf{V}} \right) f \\ - \omega_2 \frac{\partial}{\partial \mathbf{W}} \cdot \left(\mathbf{W} + \frac{1}{2} \frac{\partial}{\partial \mathbf{W}} \right) f = 0. \end{aligned} \quad (1.14)$$

The frequency ω_0 is proportional to the thermal angular velocity w_0 :

$$\omega_0 = \sqrt{\frac{2}{3}} \gamma \frac{m}{m_t} w_0. \quad (1.15)$$

Next we write the distribution function f in the form

$$f d^3 v d^3 w = F_0(\mathbf{V}, \mathbf{W}) (1 + \Phi(t, \mathbf{x}, \mathbf{V}, \mathbf{W})) d^3 V d^3 W \quad (1.16)$$

where Φ characterizes the deviation of f from the equilibrium distribution F_0 . The Fokker-Planck equation for Φ reads:

$$\frac{\partial \Phi}{\partial t} + \sqrt{\frac{2}{3}} v_0 \mathbf{V} \cdot \frac{\partial \Phi}{\partial \mathbf{x}} + \Omega(\Phi) = 0. \quad (1.17)$$

The Fokker-Planck "Collision" operator $\Omega(\Phi)$ is the sum of the operators:

$$\Omega_0(\Phi) = -\omega_0 (\mathbf{V} \times \mathbf{W}) \cdot \frac{\partial \Phi}{\partial \mathbf{V}}, \quad (1.18)$$

$$\Omega_1(\Phi) = -\frac{1}{2} \omega_1 F_0^{-1} \frac{\partial}{\partial \mathbf{V}} \cdot \left(F_0 \frac{\partial \Phi}{\partial \mathbf{V}} \right), \quad (1.19)$$

$$\Omega_2(\Phi) = -\frac{1}{2} \omega_2 F_0^{-1} \frac{\partial}{\partial \mathbf{W}} \cdot \left(F_0 \frac{\partial \Phi}{\partial \mathbf{W}} \right). \quad (1.20)$$

For our purposes, equation (1.17) is the most handy form of the generalized Fokker-Planck equation. In the next section some general properties of the "collision brackets" pertaining to the operator Ω shall be studied.

§ 2. Properties of the Fokker-Planck Collision Brackets

We define the Fokker-Planck collision bracket of two functions Ψ and Φ , dependent on \mathbf{V} and \mathbf{W} , by

$$\langle \Psi \Omega(\Phi) \rangle_0 = \frac{1}{n_0} \int d^3V d^3W F_0(\mathbf{V}, \mathbf{W}) \Psi \Omega(\Phi). \quad (2.1)$$

After integrating by parts, one finds from (1.18) – (1.20):

$$\langle \Psi \Omega_0(\Phi) \rangle_0 = -\frac{1}{2} \omega_0 \pi^{-3} \int d^3V d^3W e^{-(V^2+W^2)} \left[\Psi(\mathbf{V} \times \mathbf{W}) \cdot \frac{\partial \Phi}{\partial \mathbf{V}} - \Phi(\mathbf{V} \times \mathbf{W}) \cdot \frac{\partial \Psi}{\partial \mathbf{V}} \right], \quad (2.2)$$

$$\langle \Psi \Omega_1(\Phi) \rangle_0 = \frac{1}{2} \omega_1 \pi^{-3} \int d^3V d^3W e^{-(V^2+W^2)} \frac{\partial \Psi}{\partial \mathbf{V}} \cdot \frac{\partial \Phi}{\partial \mathbf{V}}, \quad (2.3)$$

$$\langle \Psi \Omega_2(\Phi) \rangle_0 = \frac{1}{2} \omega_2 \pi^{-3} \int d^3V d^3W e^{-(V^2+W^2)} \frac{\partial \Psi}{\partial \mathbf{W}} \cdot \frac{\partial \Phi}{\partial \mathbf{W}}. \quad (2.4)$$

Looking at these explicit expressions one immediately can see the symmetry properties of the three types of collision brackets:

$$\langle \Psi \Omega_0(\Phi) \rangle_0 = -\langle \Phi \Omega_0(\Psi) \rangle_0, \quad (2.5)$$

$$\langle \Psi \Omega_i(\Phi) \rangle_0 = \langle \Phi \Omega_i(\Psi) \rangle_0, \quad i=1, 2. \quad (2.6)$$

Furthermore one has for $\Psi = \Phi$:

$$\langle \Phi \Omega_0(\Phi) \rangle_0 = 0, \quad (2.7)$$

$$\langle \Phi \Omega_i(\Phi) \rangle_0 \geq 0, \quad i=1, 2. \quad (2.8)$$

The positive-semidefiniteness of the operators Ω_1 and Ω_2 ensures the decay to equilibrium. On the other hand, the properties (2.5) and (2.7) show that the operator Ω_0 pertaining to the transverse force is a purely “mechanical” operator. Although it gives no direct contribution to the entropy production, we shall see that this term influences the values of the transport constants.

Next we want to study the parity and time reversal behaviour of the collision brackets. For a function Ψ we define a “mirrored” function Ψ_P by

$$\Psi_P(\mathbf{V}, \mathbf{W}) = \Psi(-\mathbf{V}, \mathbf{W}). \quad (2.9)$$

Since Ω is invariant under the exchange $\mathbf{V} \rightarrow -\mathbf{V}$, one has for all Ω_i ($i=0, 1, 2$):

$$\langle \Psi_P \Omega(\Phi_P) \rangle_0 = \langle \Psi \Omega(\Phi) \rangle_0. \quad (2.10)$$

Thus the collision brackets vanish for two functions having different parities.

Similarly we now define a “time reversed” function Ψ_T by

$$\Psi_T(\mathbf{V}, \mathbf{W}) = \Psi(-\mathbf{V}, -\mathbf{W}). \quad (2.11)$$

Using the explicit form of the collision brackets and changing the integration variables, $\mathbf{V}, \mathbf{W} \rightarrow -\mathbf{V},$

$-\mathbf{W}$ one finds:

$$\langle \Psi_T \Omega_0(\Phi_T) \rangle_0 = -\langle \Psi \Omega_0(\Phi) \rangle_0, \quad (2.12)$$

$$\langle \Psi_T \Omega_i(\Phi_T) \rangle_0 = \langle \Psi \Omega_i(\Phi) \rangle_0, \quad i=1, 2. \quad (2.13)$$

The collision bracket pertaining to Ω_0 vanishes for two functions with equal time reversal behaviour, those pertaining to Ω_1, Ω_2 vanish for functions with different time reversal behaviour.

Combining the symmetry properties (2.5), (2.6) with (2.12), (2.13) one finds the general relation holding for all Ω_i ($i=0, 1, 2$):

$$\langle \Psi_T \Omega(\Phi_T) \rangle_0 = \langle \Phi \Omega(\Psi) \rangle_0. \quad (2.14)$$

This equality will give Onsager-Casimir symmetry relations for the transport-relaxation constants.

The properties (2.10) and (2.14) of the collision brackets are typical for particles with internal degrees of freedom. The same relations indeed hold for the linearized Boltzmann collision brackets of rough sphere molecules⁴ and of particles with spin^{1, 3}.

§ 3. Expansion of the Distribution Function

To solve the generalized Fokker-Planck equation we apply a moment method that was used to find an approximate solution of the generalized Boltzmann equation for particles with spin^{1, 3} and rough sphere molecules^{4, 6}. “Solution” of the transport equation here means that one derives a set of coupled linear differential equations (transport-relaxation equations) for certain mean values. The conservation equations, the constitutive laws for the thermodynamical fluxes as well as the transport coefficients

expressed in terms of certain collision brackets (relaxation coefficients) then may be inferred from these transport-relaxation equations.

The first step in the derivation of the transport-relaxation equations from the Fokker-Planck equation is the expansion of the non-equilibrium distribution function. This point shall be discussed in this section using the same notations as in Waldmann's paper on the Lorentzian gas of rough spheres⁴.

$$\begin{aligned} f d^3v d^3w &= F_0 (1 + \Phi) d^3V d^3W \\ &= F_0 [1 + \sum_k (a^{(k)} \Phi^{(k)} + b^{(k)} \Psi^{(k)} + a_\mu^{(k)} \Phi_\mu^{(k)} + b_\mu^{(k)} \Psi_\mu^{(k)} + a_{\mu\nu}^{(k)} \Phi_{\mu\nu}^{(k)} + b_{\mu\nu}^{(k)} \Psi_{\mu\nu}^{(k)} + \dots)] d^3V d^3W. \end{aligned} \quad (3.1)$$

The expansion coefficients $a^{(k)}$, $b^{(k)}$, ... are the time and space dependent mean values of the pertaining $\Phi^{(k)}$, $\Psi^{(k)}$, ... As we shall see immediately the first few of these expansion coefficients characterizing the non-equilibrium state of the system have a simple physical meaning. Retaining the whole complete set of expansion tensors would lead to an infinite system of transport relaxation equations equivalent to the Fokker-Planck equation. Of course, this infinite system cannot be handled, thus we have to truncate it by taking into account the first few expansion tensors and expansion coefficients only. This approximation is entirely satisfactory since one actually needs the first few moments of the distribution function only to characterize the non-equilibrium state of a system in terms of "macroscopic" variables.

The expansion tensors can be ordered according to their rank and their total power in the Cartesian components of \mathbf{V} and \mathbf{W} . Here we shall use expansion tensors up to 2nd rank and 2nd power only with the exception of polar vectors, where expansion tensors up to total power 3 are considered too^{13a}. In table 1 the first few expansion tensors are listed together with their mean values expressed in terms of the usual velocity \mathbf{v} and angular velocity \mathbf{w} . The columns P and T denote the parity and time reversal behaviour of the expansion tensors. The expansion tensors of different rank and parity are orthogonal, those of the same rank and parity obey the following orthonormalization relations:

$$\langle \Phi^{(i)} \Phi^{(k)} \rangle_0 = \langle \Psi^{(i)} \Psi^{(k)} \rangle_0 = \delta^{(ik)}, \quad (3.2)$$

The deviation of the distribution function f from the equilibrium distribution f_0 (see 1.16) shall be expanded with respect to a complete, orthogonal set of Cartesian tensors depending on \mathbf{V} and \mathbf{W} . Scalars, vectors and 2nd rank tensors are denoted by Φ , Φ_μ , $\Phi_{\mu\nu}$ ¹³; pseudo scalars, pseudo vectors and pseudo 2nd rank tensors by Ψ , Ψ_μ , $\Psi_{\mu\nu}$; different expansion tensors of the same rank and parity are distinguished by consecutive supercripts. Thus we write for the distribution function¹³:

$$\langle \Phi_\mu^{(i)} \Phi_\nu^{(k)} \rangle_0 = \langle \Psi_\mu^{(i)} \Psi_\nu^{(k)} \rangle_0 = \delta^{(ik)} \delta_{\mu\nu}, \quad (3.3)$$

$$\langle \Phi_{\mu\nu}^{(i)} \Phi_{\mu'\nu'}^{(k)} \rangle_0 = \langle \Psi_{\mu\nu}^{(i)} \Psi_{\mu'\nu'}^{(k)} \rangle_0 = \delta^{(ik)} \Delta_{\mu\nu, \mu'\nu'}. \quad (3.4)$$

The bracket $\langle \rangle_0$ as in (2.1) denotes the mean value to be taken with the equilibrium distribution function f_0 . The δ 's are usual Kronecker symbols. The isotropic 4th rank tensor $\Delta_{\mu\nu, \mu'\nu'}$ is given by

$$\Delta_{\mu\nu, \mu'\nu'} = \frac{1}{2} (\delta_{\mu\mu'} \delta_{\nu\nu'} + \delta_{\mu\nu} \delta_{\nu\mu'}) - \frac{1}{3} \delta_{\mu\nu} \delta_{\mu'\nu'}. \quad (3.5)$$

The list of mean values in Table 1 shows the physical meaning of the expansion coefficients, e.g. $a^{(1)}$ characterizes the deviation of the particle density $n = n(t, \mathbf{x})$ from its equilibrium value, $a^{(2)}$ and $a^{(3)}$ respectively describe the deviation of the non-equilibrium translational and rotational temperatures from the equilibrium temperature T_0 . These temperatures are defined by

$$\begin{aligned} \frac{3}{2} k T_{\text{trans}} &= \langle \frac{1}{2} m v^2 \rangle \\ \text{and} \quad \frac{3}{2} k T_{\text{rot}} &= \langle \frac{1}{2} \Theta w^2 \rangle. \end{aligned} \quad (3.6)$$

The particle flux $j = n \langle \mathbf{v} \rangle$ is proportional to $\mathbf{a}^{(1)}$, $\mathbf{a}^{(3)}$ and $\mathbf{a}^{(4)}$ give the parts of the translational and rotational heat fluxes that are due to the Brownian particles:

$$\begin{aligned} q_{\text{trans}} &= n \langle (\frac{1}{2} m v^2 - \frac{5}{2} k T_0) \mathbf{v} \rangle, \\ q_{\text{rot}} &= n \langle (\frac{1}{2} \Theta w^2 - \frac{3}{2} k T_0) \mathbf{w} \rangle. \end{aligned} \quad (3.7)$$

The "vector polarization" $w_0^{-1} \langle \mathbf{w} \rangle$ of the rotating particle is characterized by $\mathbf{b}^{(1)}$. The "helicity" $v_0^{-1} w_0^{-1} \langle \mathbf{v} \cdot \mathbf{w} \rangle \propto b^{(1)}$; the "azimuthal spin" $v_0^{-1} w_0^{-1} \langle \mathbf{v} \times \mathbf{w} \rangle \propto \mathbf{a}^{(2)}$ and $b_{\mu\nu}^{(1)}$ are apart from numerical factors the irreducible parts of the "spin-

¹³ Greek subscripts denote Cartesian components of tensors (i.e. vectors, 2nd rank tensors, ...). It is understood that Greek double subscripts have to be summed.

^{13a} For the discussion of heat conductivity expansion vectors up to 4th power have to be taken into account. See note added in proof.

Expansion tensors	<i>P</i>	<i>T</i>	Mean values
Scalars			
$\Phi^{(1)} = 1$	+	+	$a^{(1)} = (n - n_0)/n_0$
$\Phi^{(2)} = \sqrt{\frac{2}{3}} (V^2 - \frac{3}{2})$	+	+	$a^{(2)} = \sqrt{\frac{3}{2}} (T_{\text{trans}} - T_0)/T_0$
$\Phi^{(3)} = \sqrt{\frac{2}{3}} (W^2 - \frac{3}{2})$	+	+	$a^{(3)} = \sqrt{\frac{3}{2}} (T_{\text{rot}} - T_0)/T_0$
Pseudo scalar			
$\Psi^{(1)} = \frac{2}{\sqrt{3}} \mathbf{V} \cdot \mathbf{W}$	-	+	$b^{(1)} = \sqrt{3} \langle \mathbf{v} \cdot \mathbf{w} \rangle / v_0 w_0$
Polar vectors			
$\Phi^{(1)} = \sqrt{2} \mathbf{V}$	-	-	$\mathbf{a}^{(1)} = \sqrt{3} \mathbf{j} / n_0 v_0$
$\Phi^{(2)} = \sqrt{2} \mathbf{V} \times \mathbf{W}$	-	+	$\mathbf{a}^{(2)} = \frac{3}{\sqrt{2}} \langle \mathbf{v} \times \mathbf{w} \rangle / v_0 w_0$
$\Phi^{(3)} = \frac{2}{\sqrt{5}} (V^2 - \frac{5}{2}) \mathbf{V}$	-	-	$\mathbf{a}^{(3)} = \sqrt{\frac{6}{5}} \mathbf{q}_{\text{trans}} / n_0 k T_0 v_0$
$\Phi^{(4)} = \frac{2}{\sqrt{3}} (W^2 - \frac{3}{2}) \mathbf{V}$	-	-	$\mathbf{a}^{(4)} = \sqrt{2} \mathbf{q}_{\text{rot}} / n_0 k T_0 v_0$
$\Phi^{(5)} = 2\sqrt{\frac{2}{5}} \overline{\mathbf{W} \mathbf{W} \cdot \mathbf{V}}$	-	-	$\mathbf{a}^{(5)} = \frac{9}{\sqrt{10}} \langle \overline{\mathbf{w} \mathbf{w} \cdot \mathbf{v}} \rangle / n_0 v_0 w_0^2$
Pseudo vector			
$\Psi^{(1)} = \sqrt{2} \mathbf{W}$	+	-	$\mathbf{b}^{(1)} = \sqrt{3} \langle \mathbf{w} \rangle / w_0$
2nd rank tensors			
$\Phi_{\mu\nu}^{(1)} = \sqrt{2} \overline{V_\mu V_\nu}$	+	+	$a_{\mu\nu}^{(1)} = \frac{3}{2} \sqrt{2} \langle \overline{v_\mu v_\nu} \rangle / v_0^2$
$\Phi_{\mu\nu}^{(2)} = \sqrt{2} \overline{W_\mu W_\nu}$	+	+	$a_{\mu\nu}^{(2)} = \frac{3}{2} \sqrt{2} \langle \overline{w_\mu w_\nu} \rangle / w_0^2$
2nd rank pseudo tensor			
$\Psi_{\mu\nu}^{(1)} = 2 \overline{V_\mu W_\nu}$	-	+	$b_{\mu\nu}^{(1)} = 3 \langle \overline{v_\mu w_\nu} \rangle / v_0 w_0$

Table 1. The first expansion tensors and their mean values.

$$\text{Abbreviation: } \overline{a_\mu b_\nu} = \frac{1}{2} (a_\mu b_\nu + b_\mu a_\nu) - \frac{1}{3} \mathbf{a} \cdot \mathbf{b} \delta_{\mu\nu} = \langle \overline{\mathbf{a} \mathbf{b}} \rangle_{\mu\nu}.$$

flux" tensor:

$$s_{\nu\mu} = n \langle v_\nu \Theta w_\mu \rangle = \frac{1}{\sqrt{3}} \Theta n_0 v_0 w_0 \left(\frac{1}{3} b^{(1)} \delta_{\mu\nu} + \frac{1}{\sqrt{6}} \varepsilon_{\nu\mu\lambda} a_\lambda^{(2)} + \frac{1}{\sqrt{3}} b_{\mu\nu}^{(1)} \right). \quad (3.8)$$

Terms that are quadratic in quantities characterizing the deviation from the equilibrium state have been omitted in the list of mean values (see Table 1). Hence these mean values differ a little from the

corresponding expressions stated in Ref. 3 and 4. By this linearization one obtains linearized hydrodynamical equations.

§ 4. Truncated System of Transport-Relaxation Equations

Plugging the ansatz (3.1) for $\Phi(t, \mathbf{x}, \mathbf{V}, \mathbf{W})$ into the generalized Fokker-Planck equation (1.17), multiplying by $F_0 \Phi^{(k)}$, $F_0 \Psi^{(k)}$, ... and integrating by

$d^3\mathbf{V} d^3\mathbf{W}$ one obtains a system of linear coupled differential equations for the mean values $a^{(k)}$, $b^{(k)}$, The general structure of this system of differential equations (termed transport-relaxation equations) was stated in Ref. 3 and 4. Here we shall write down explicitly the transport-relaxation equations for the moments listed in table 1. Before doing so, a remark is made concerning the collision brackets or relaxation coefficients.

The Fokker-Planck collision operator (1.18 to 1.20) is parity invariant and isotropic, hence tensors of equal parity (see 2.10) and equal rank only may have non-vanishing collision brackets. The pertaining collision brackets are called relaxation coefficients $\omega_{PL}^{(ik)}$ (P : parity, L : rank of the expansion tensor no. i and k) and are defined in the following way:

$$\omega_{+0}^{(ik)} = \langle \Phi^{(i)} \Omega(\Phi^{(k)}) \rangle_0, \quad \omega_{-0}^{(ik)} = \langle \Psi^{(i)} \Omega(\Psi^{(k)}) \rangle_0, \quad (4.1)$$

$$\omega_{-1}^{(ik)} = \frac{1}{3} \langle \Phi_{\mu}^{(i)} \Omega(\Phi_{\mu}^{(k)}) \rangle_0, \quad \omega_{\pm}^{(ik)} = \frac{1}{3} \langle \Psi_{\mu}^{(i)} \Omega(\Psi_{\mu}^{(k)}) \rangle_0, \quad (4.2)$$

$$\omega_{+2}^{(ik)} = \frac{1}{5} \langle \Phi_{\mu\nu}^{(i)} \Omega(\Phi_{\mu\nu}^{(k)}) \rangle_0, \quad \omega_{-2}^{(ik)} = \frac{1}{5} \langle \Psi_{\mu\nu}^{(i)} \Omega(\Psi_{\mu\nu}^{(k)}) \rangle_0. \quad (4.3)$$

Since the number of particles is conserved, one has $\Omega(1) = 0$ and thus

$$\text{scalars:} \quad \omega_{+0}^{(22)} = 2 \omega_1, \quad \omega_{+0}^{(33)} = 2 \omega_2; \quad (4.7)$$

$$\text{pseudo scalar:} \quad \omega_{-0}^{(11)} = \omega_1 + \omega_2; \quad (4.8)$$

$$\text{vectors:} \quad \omega_{-1}^{(11)} = \omega_1, \quad \omega_{-1}^{(12)} = -\omega_{-1}^{(21)} = \omega_0, \quad \omega_{-1}^{(22)} = \omega_1 + \omega_2, \quad (4.9)$$

$$\omega_{-1}^{(33)} = 3 \omega_1, \quad (4.10)$$

$$\omega_{-1}^{(44)} = \omega_1 + 2 \omega_2, \quad \omega_{-1}^{(42)} = -\omega_{-1}^{(24)} = \sqrt{\frac{2}{3}} \omega_0, \quad (4.11)$$

$$\omega_{-1}^{(55)} = \omega_1 + 2 \omega_2, \quad \omega_{-1}^{(52)} = -\omega_{-1}^{(25)} = -\sqrt{\frac{5}{8}} \omega_0; \quad (4.12)$$

$$\text{pseudo vector:} \quad \omega_{+1}^{(11)} = \omega_2; \quad (4.13)$$

$$2^{\text{nd}} \text{ rank tensor:} \quad \omega_{+2}^{(11)} = 2 \omega_1, \quad \omega_{+2}^{(22)} = 2 \omega_2; \quad (4.14)$$

$$2^{\text{nd}} \text{ rank pseudo tensor:} \quad \omega_{-2}^{(11)} = \omega_1 + \omega_2. \quad (4.15)$$

Now we are ready to state the transport-relaxation equations:

$$\begin{aligned} \text{Scalars} \quad & \frac{\partial a^{(1)}}{\partial t} + \frac{v_0}{3} \sqrt{3} \operatorname{div} \mathbf{a}^{(1)} = 0, \\ & \frac{\partial a^{(2)}}{\partial t} + \frac{v_0}{3} \operatorname{div} (\sqrt{2} \mathbf{a}^{(1)} + \sqrt{5} \mathbf{a}^{(3)}) + \omega_{+0}^{(22)} a^{(2)} = 0, \\ & \frac{\partial a^{(3)}}{\partial t} + \frac{v_0}{3} \sqrt{3} \operatorname{div} \mathbf{a}^{(4)} + \omega_{+0}^{(33)} a^{(3)} = 0. \end{aligned} \quad (4.16)$$

$$\omega_{+0}^{(1i)} = \omega_{+0}^{(i1)} = 0. \quad (4.4)$$

Contrary to the Boltzmann equation case here the evaluation of the different relaxation coefficient matrices ω_{PL} is rather simple. They may be expressed very easily in terms of the constants ω_0 , ω_1 , ω_2 characterizing the strength of the interaction between a Brownian particle and the bulk fluid. All expansion tensors are eigenfunctions of the collision operators Ω_1 and Ω_2 , namely

$$\Omega_i(\Phi_{\dots}^{(k)}) = n_i^{(k)} \omega_i \Phi_{\dots}^{(k)}, \quad i = 1, 2. \quad (4.5)$$

Here $\Phi_{\dots}^{(k)}$ stands for anyone of the expansion tensors $\Phi^{(k)}$, $\Psi^{(k)}$, $\Phi_{\mu}^{(k)}$, ...; $n_1^{(k)}$ and $n_2^{(k)}$ denote the power of $\Phi_{\dots}^{(k)}$ in \mathbf{V} and \mathbf{W} respectively. Hence, without the collision operator Ω_0 all relaxation coefficient matrices ω_{PL} would be diagonal. From (2.12) one knows that non-vanishing Ω_0 -collision brackets only exist for tensors of the same rank and parity but different time reversal behaviour. Table 1 shows that non-diagonal relaxation coefficients among the first expansion tensors can occur for the polar vectors (ω_{-1}) only. With (4.5) and by aid of the relation

$$\Omega_0(\Phi_{\mu}^{(2)}) = \omega_0(\Phi_{\mu}^{(1)} + \sqrt{\frac{2}{3}} \Phi_{\mu}^{(4)} - \sqrt{\frac{5}{6}} \Phi_{\mu}^{(5)}) \quad (4.6)$$

one finds the following non-vanishing relaxation coefficients:

$$\text{Pseudo scalar} \quad \frac{\partial b^{(1)}}{\partial t} + \frac{v_0}{3} \operatorname{div} \mathbf{b}^{(1)} + \omega_{-0}^{(11)} b^{(1)} = 0. \quad (4.17)$$

$$\begin{aligned} \text{Polar vectors} \quad & \frac{\partial a_\mu^{(1)}}{\partial t} + \frac{v_0}{3} \operatorname{grad}_\mu (\sqrt{3} a^{(1)} + \sqrt{2} a^{(2)}) + v_0 \sqrt{\frac{2}{3}} \frac{\partial a_{v\mu}^{(1)}}{\partial x_v} + \sum_{k=1}^5 \omega_{-1}^{(1k)} a_\mu^{(k)} = 0, \\ & \frac{\partial a_\mu^{(2)}}{\partial t} + \frac{v_0}{6} \sqrt{6} \operatorname{rot}_\mu \mathbf{b}^{(1)} + \sum_{k=1}^5 \omega_{-1}^{(2k)} a_\mu^{(k)} = 0, \\ & \frac{\partial a_\mu^{(3)}}{\partial t} + \frac{v_0}{3} \sqrt{5} \operatorname{grad}_\mu a^{(2)} + 2 \frac{v_0}{3} \sqrt{\frac{3}{5}} \frac{\partial a_{v\mu}^{(1)}}{\partial x_v} + \sum_{k=1}^5 \omega_{-1}^{(3k)} a_\mu^{(k)} = 0, \\ & \frac{\partial a_\mu^{(4)}}{\partial t} + \frac{v_0}{3} \sqrt{3} \operatorname{grad}_\mu a^{(3)} + \sum_{k=1}^5 \omega_{-1}^{(4k)} a_\mu^{(k)} = 0, \\ & \frac{\partial a_\mu^{(5)}}{\partial t} + \frac{v_0}{5} \sqrt{5} \frac{\partial a_{v\mu}^{(2)}}{\partial x_v} + \sum_{k=1}^5 \omega_{-1}^{(5k)} a_\mu^{(k)} = 0. \end{aligned} \quad (4.18)$$

$$\text{Pseudo vector} \quad \frac{\partial b_\mu^{(1)}}{\partial t} + \frac{v_0}{3} \operatorname{grad}_\mu b^{(1)} - \frac{v_0}{V\epsilon} \operatorname{rot}_\mu \mathbf{a}^{(2)} + \frac{v_0}{3} \sqrt{3} \frac{\partial b_{v\mu}^{(1)}}{\partial x_v} + \omega_{+1}^{(11)} b_\mu^{(1)} = 0. \quad (4.19)$$

$$\begin{aligned} 2^{\text{nd}} \text{ rank tensors} \quad & \frac{\partial a_{\mu\nu}^{(1)}}{\partial t} + \frac{v_0}{3} \sqrt{6} \frac{\partial a_v^{(1)}}{\partial x_\mu} + v_0 \frac{2}{3} \sqrt{\frac{3}{5}} \frac{\partial a_v^{(3)}}{\partial x_\mu} + \omega_{+2}^{(11)} a_{\mu\nu}^{(1)} = 0, \\ & \frac{\partial a_{\mu\nu}^{(2)}}{\partial t} + \frac{v_0}{5} \sqrt{5} \frac{\partial a_v^{(5)}}{\partial x_\mu} + \omega_{+2}^{(22)} a_{\mu\nu}^{(2)} = 0. \end{aligned} \quad (4.20)$$

$$2^{\text{nd}} \text{ rank pseudo tensor} \quad \frac{\partial b_{\mu\nu}^{(1)}}{\partial t} + \frac{v_0}{3} \sqrt{3} \frac{\partial b_v^{(1)}}{\partial x_\mu} + \omega_{-2}^{(11)} b_{\mu\nu}^{(1)} = 0. \quad (4.21)$$

Next we want to give a brief discussion of the “scalar” transport-relaxation equations. Using the meaning of the expansion coefficients given in Table 1 one sees that the first equation of (4.16) is the continuity equation:

$$\frac{\partial n}{\partial t} + \operatorname{div} \mathbf{j} = 0. \quad (4.22)$$

The second and third equations of (4.16) are the relaxation equations for the translational and rotational temperature respectively:

$$\begin{aligned} n_0 \frac{\partial}{\partial t} \frac{3}{2} k T_{\text{trans}} + \operatorname{div} (\mathbf{q}_{\text{trans}} + k T_0 \mathbf{j}) + \omega_{+1}^{(22)} n_0 \frac{3}{2} k (T_{\text{trans}} - T_0) &= 0, \\ n_0 \frac{\partial}{\partial t} \frac{3}{2} k T_{\text{rot}} + \operatorname{div} \mathbf{q}_{\text{rot}} + \omega_{+0}^{(33)} n_0 \frac{3}{2} k (T_{\text{rot}} - T_0) &= 0. \end{aligned} \quad (4.23)$$

Note that both non-equilibrium temperatures decay independently and that no common non-equilibrium temperature $\frac{1}{2} (T_{\text{trans}} + T_{\text{rot}})$ is established after some short relaxation time. This is contrary to the case of the Lorentzian gas⁴, where the sum of translational and rotational energy is conserved.

The constitutive law for the diffusion flux \mathbf{j} and the diffusion constant D may be inferred from the polar vector equations (4.18). This point shall be discussed in the next section. The pseudo vector equation (4.19) is the relaxation equation for the

mean internal angular momentum or mean “porlari-ization”. It contains a divergence of the angular momentum flux tensor (shorter “spin” flux tensor). One obtains the constitutive laws for the irreducible parts of the spin flux tensor and the “spin diffusion” constants from the equations (4.17, 4.18, 4.21). An analysis of this spin diffusion problem shall be given in § 6. Finally in § 7 we will look at the constitutive laws for the translational and rotational heat flow and the cross effect between diffusion and rotational heat flow: thermal diffusion.

§ 5. Diffusion and Azimuthal Polarization

For the discussion of the diffusion problem we assume steady state, i. e. all time derivatives except $\partial n / \partial t$ shall vanish. Furthermore there shall be no gradients except $\text{grad } n \propto \text{grad } a^{(1)}$. For simplicity we take into account expansion tensors up to second power only. Then the equations (4.18) reduce to (using 4.9):

$$\frac{v_0}{3} \sqrt{3} \frac{\partial a^{(1)}}{\partial \mathbf{x}} + \omega_1 \mathbf{a}^{(1)} + \omega_0 \mathbf{a}^{(2)} = 0, \quad (5.1)$$

$$-\omega_0 \mathbf{a}^{(1)} + (\omega_1 + \omega_2) \mathbf{a}^{(2)} = 0.$$

Solving these equations for $\mathbf{a}^{(1)}$ and using the physical meaning of the expansion coefficients $a^{(1)}$ and $\mathbf{a}^{(1)}$ one obtains Fick's law

$$\mathbf{j} = -D \text{grad } n \quad (5.2)$$

with the diffusion constant

$$D = D_{\text{iso}} \left(1 + \frac{\omega_0^2}{\omega_1(\omega_1 + \omega_2)} \right)^{-1}. \quad (5.3)$$

Here
$$D_{\text{iso}} = \frac{1}{3} \frac{v_0^2}{\omega_1} = \frac{k T_0}{m \omega_1} \quad (5.3a)$$

is Einstein's diffusion constant. It is obtained here if one uses an "isotropic" distribution function f neglecting its dependence on the direction of the angular velocity (i. e. $\mathbf{a}^{(2)} = 0$). By (5.3) one has¹⁴

$$D < D_{\text{iso}}. \quad (5.4)$$

This inequality can be understood qualitatively if one remembers that the transverse force (1.8) acting on a Brownian particle causes the particle to travel on a bent orbit if its internal angular velocity \mathbf{w} is not parallel to its velocity \mathbf{v} . Hence a spinning particle with $\mathbf{w} \perp \mathbf{v}$ cannot diffuse as fast as a particle with $\mathbf{w} \parallel \mathbf{v}$. This gives rise to a correlation of linear and angular velocities. Here especially one has to deal with the azimuthal polarization

$$\mathbf{a} = v_0^{-1} \omega_0^{-1} \langle \mathbf{v} \times \mathbf{w} \rangle. \quad (5.5)$$

Equations (5.1) show that there is always an azimuthal polarization linked with the diffusion flow \mathbf{j} (as long as $\omega_0 \neq 0$):

$$\mathbf{a} = \sqrt{\frac{3}{2}} \frac{\omega_0}{\omega_1 + \omega_2} n_0^{-1} v_0^{-1} \mathbf{j}. \quad (5.6)$$

According to the above remarks it is clear that the inequality (5.4) is caused by a partial alignment of the angular velocity of the diffusing particles.

The partial alignment may also be seen by looking at the mean (vector) polarization of particles having a given velocity \mathbf{v}

$$\overline{\mathbf{w}}(\mathbf{v}) = \int w_0^{-1} \mathbf{w} f d^3 w / \int f d^3 w. \quad (5.7)$$

With $f \propto F_0(1 + a^{(1)} + \mathbf{a}^{(1)} \cdot \Phi^{(1)} + \mathbf{a}^{(2)} \cdot \Phi^{(2)})$ one finds

$$\overline{\mathbf{w}}(\mathbf{v}) = \frac{3}{2} v_0^{-1} (1 + n_0^{-1} v_0^{-2} \mathbf{j} \cdot \mathbf{v})^{-1} \mathbf{a} \times \mathbf{v}. \quad (5.8)$$

Using (5.6) for \mathbf{a} one immediately sees that particles flying not parallel to the diffusion flow \mathbf{j} have an angular velocity both perpendicular to their direction of flight \mathbf{v} and the diffusion flow \mathbf{j} . The magnitude of the polarization is determined by the ratio $\omega_0/(\omega_1 + \omega_2)$ and is of order of magnitude ω_0/ω_1 . The relative difference between D and D_{iso} on the other hand is of order of magnitude $(\omega_0/\omega_1)^2$, namely

$$\frac{D_{\text{iso}} - D}{D} = \frac{\omega_0^2}{\omega_1(\omega_1 + \omega_2)}. \quad (5.9)$$

Thus one may say that a polarization of 10% would cause the diffusion constant to differ from D_{iso} by roughly 1%. In order to get a feeling for the magnitude of the azimuthal polarization and the importance of the change in value of the diffusion constant caused by the partial alignment of the angular velocities we take the ratio ω_0/ω_1 from (1.6) and (1.15). With $\Theta = \alpha m R^2$, where α is a number characterizing the distribution of the mass of the Brownian particle over its volume (sphere with radius R), one finds

$$\frac{\omega_0}{\omega_1} = \gamma \sqrt{\frac{2}{27\pi} \alpha^{-1} \frac{m_t}{m} \frac{V_Q k T_0}{\eta}} R^{-1/2}. \quad (5.10)$$

As an example take $\varrho = 1 \text{ g cm}^{-3}$, $T = 300^\circ \text{K}$, $\gamma \approx 1$, $m_f/m \approx 1$, $\alpha \approx \frac{1}{5}$, $\eta = 10^{-3} \text{ g cm}^{-1} \text{ sec}^{-1}$, then one obtains:

$$\frac{\omega_0}{\omega_1} \approx 10^{-4} \left(\frac{R}{1 \text{ cm}} \right)^{-1/2}. \quad (5.11)$$

Thus for a particle with radius $R = 10^{-6} \text{ cm}$ one would have $\omega_0/\omega_1 \approx 10^{-1}$.

These qualitative considerations already indicate that "polyatomic" aspects like the partial alignment of the internal angular velocity are present for very small Brownian particles only, especially in the case of a kinetic theory of polyatomic fluids based on a Fokker-Planck transport equation.

¹⁴ The same inequality holds for the Lorentzian gas of rough spheres, see ref. ⁴.

The polyatomic effects in the diffusion problem as discussed in this section are known since long to occur in the kinetic theory of the Lorentzian gas of particles with spin ¹ and rough spheres ⁴.

§ 6. Relaxation of Internal Angular Momentum, Angular Momentum Flux Tensor

Now we discuss the pseudo-vector equation (4.19). Introducing the internal angular momentum ("spin")

$$s_\mu = \Theta w_\mu \quad (6.1)$$

this equation may be rewritten as

$$\frac{\partial n \langle s_\mu \rangle}{\partial t} + \frac{\partial s_{\nu\mu}}{\partial x_\nu} + \omega_2 n \langle s_\mu \rangle = 0. \quad (6.2)$$

This is a relaxation equation for the mean angular momentum density $n \langle s_\mu \rangle$. For the case of relatively large Brownian particles, where the hydrodynamical values (1.6) and (1.7) hold for the relaxation constants ω_1 and ω_2 , the relaxation constant ω_2 of the angular momentum is of equal order of magnitude as ω_1 . Hence the mean angular momentum will reach its equilibrium value $\langle s_\mu \rangle = 0$ very fast. On the other hand, assuming

$$\omega_2 \ll \omega_1 \quad (6.3)$$

one obtains a classical model for electronic or nuclear spin relaxation in a liquid (where $\omega_1 \geq 10^9 \text{ sec}^{-1}$, $\omega_2 \leq 10^5 \text{ sec}^{-1}$ holds).

The internal angular momentum flux tensor ("spin flux tensor") is $s_{\nu\mu} = n \langle v_\nu s_\mu \rangle$. It may be decomposed into its irreducible parts:

$$s_{\nu\mu} = \frac{1}{3} s \delta_{\mu\nu} + \frac{1}{2} \varepsilon_{\nu\mu\lambda} s_\lambda^{(a)} + \overline{s_{\nu\mu}}, \quad (6.4)$$

where

$$\begin{aligned} s &= s_{\varrho\varrho} = n \langle \mathbf{v} \cdot \mathbf{s} \rangle = \frac{1}{\sqrt{3}} \Theta n_0 v_0 w_0 b^{(1)}, \\ s_\mu^{(a)} &= \varepsilon_{\mu\nu\lambda} s_{\nu\lambda} = n \langle (\mathbf{v} \times \mathbf{s})_\mu \rangle = \frac{1}{3} \sqrt{2} \Theta n_0 v_0 w_0 a_\mu^{(2)}, \\ \overline{s_{\nu\mu}} &= \frac{1}{2} (s_{\nu\mu} + s_{\mu\nu}) - \frac{1}{3} s_{\varrho\varrho} \delta_{\mu\nu} = n \langle v_\nu s_\mu \rangle \\ &= \frac{1}{3} \Theta n_0 v_0 w_0 b_{\nu\mu}^{(1)}. \end{aligned} \quad (6.5)$$

The anti-symmetric part of the spin flux tensor is proportional to the azimuthal polarization.

Next we want to find the constitutive equations for the irreducible parts of the spin flux tensor, i. e. we deal with the spin diffusion problem. Assuming steady state, one may express $b^{(1)}$ by $\text{div } \mathbf{b}^{(1)}$ according to (4.17) and obtains:

$$s = -D_s^{(0)} \text{div } n \langle \mathbf{s} \rangle, \quad (6.7)$$

where the scalar spin diffusion constant $D_s^{(0)}$ is given by

$$D_s^{(0)} = \frac{1}{3} \frac{v_0^2}{\omega_1 + \omega_2}. \quad (6.8)$$

Likewise one infers from (4.21)

$$\overline{s_{\nu\mu}} = -D_s^{(2)} \frac{\partial n \langle s_\mu \rangle}{\partial x_\nu}, \quad (6.9)$$

with the tensor spin diffusion constant

$$D_s^{(2)} = D_s^{(0)}. \quad (6.10)$$

The physical content is richer for the anti-symmetric or vector part of the spin flux tensor since there is a coupling of the polar vectors (see 4.18) that we already encountered in the preceding section. Again we take into account expansion tensors up to second power only and assume steady state, but both $\text{grad } a^{(1)}$ and $\text{rot } \mathbf{b}^{(1)}$ shall be different from zero.

Here one finds

$$\mathbf{s}^{(a)} = -D_s^{(1)} \text{rot } n \langle \mathbf{s} \rangle - D w_0 \Theta \alpha_s \text{grad } n. \quad (6.11)$$

The vector spin diffusion constant $D_s^{(1)}$ is given by

$$D_s^{(1)} = \frac{1}{3} \frac{v_0^2}{\omega_1 + \omega_2} \left(1 + \frac{\omega_0^2}{\omega_1(\omega_1 + \omega_2)} \right)^{-1}. \quad (6.12)$$

The number α_s characterizes the diffusion-spin diffusion cross effect. It may be inferred from (5.6) and (5.2) and turns out to be

$$\alpha_s = \sqrt{\frac{3}{2}} \frac{\omega_0}{\omega_1 + \omega_2}. \quad (6.13)$$

By the way one finds for the diffusion flow \mathbf{j} in the presence of $\text{rot } n \langle \mathbf{s} \rangle$:

$$\mathbf{j} = -D (\text{grad } n - w_0^{-1} \Theta^{-1} \alpha_s \text{rot } n \langle \mathbf{s} \rangle). \quad (6.14)$$

Finally we compare the spin diffusion constants $D_s^{(l)}$ ($l=0, 1, 2$) with the diffusion constants D and D_{iso} . Due to (6.8), (6.10) and (5.3 a) one has

$$D_s^{(0)} = D_s^{(2)} = \left(1 + \frac{\omega_2}{\omega_1} \right)^{-1} D_{\text{iso}}. \quad (6.15)$$

From (6.12) and (5.3) one finds

$$D_s^{(1)} = \left(1 + \frac{\omega_2}{\omega_1} \right)^{-1} D. \quad (6.16)$$

If there is no coupling of translational and rotational motions, i. e. $\omega_0 = 0$, the diffusion constant D equals D_{iso} . Only in this case all three spin diffusion constants $D_s^{(l)}$ are equal. Furthermore one should note that the spin diffusion constant even in this case

is not equal to the diffusion constant D_{iso} but is smaller by the factor $(1 + \omega_2/\omega_1)^{-1}$. This factor, however, may be replaced by 1 for the proper spin relaxation where $\omega_2 \ll \omega_1$ holds.

§ 7. Heat Conduction and Cross Effects

The parts of the translational and rotational heat flows that are due to the Brownian particles (here more appropriately called flows of translational and rotational energies) are proportional to $\mathbf{a}^{(3)}$ and $\mathbf{a}^{(4)}$. These are mean values of expansion tensors of third power that we neglected hitherto. The enlarged set of vector transport-relaxation equations (4.18) with all time derivatives put equal to zero (steady state), will give us the constitutive laws for the heat fluxes and the transport constants expressed in terms of relaxation constants.

Firstly we note that there are no elements in the transport-relaxation coefficient matrix ω_{-1} (see 4.9 to 4.12) which couple $\mathbf{a}^{(3)}$ to any of the other vectors $\mathbf{a}^{(k)}$ ($k=1, 2, 4, 5$). The equation for $\mathbf{a}^{(3)}$ may easily be rewritten as

$$\mathbf{q}_{\text{trans}} = -\lambda_{\text{trans}} \text{grad } T_{\text{trans}}. \quad (7.1)$$

The translational heat conductivity is

$$\lambda_{\text{trans}} = \frac{5}{2} \frac{k}{m} \frac{n_0 k T_0}{3 \omega_1} = \frac{5}{6} k n_0 D_{\text{iso}}. \quad (7.2)$$

For simplicity in all the following discussions we assume the translational temperature T_{trans} to equal T_0 ; then $\mathbf{a}^{(2)}$ and $\mathbf{a}^{(3)}$ vanish and we have to deal with the four vectors $\mathbf{a}^{(1)}$, $\mathbf{a}^{(2)}$, $\mathbf{a}^{(4)}$, $\mathbf{a}^{(5)}$ only. In steady state equations (4.18) now reduce to:

$$v_0 \mathbf{F}^{(i)} + \sum_k \omega_{-1}^{(ik)} \mathbf{a}^{(k)} = 0; \quad i, k = 1, 2, 4, 5. \quad (7.3)$$

The "forces" $\mathbf{F}^{(i)}$ are

$$\begin{aligned} \mathbf{F}^{(1)} &= \frac{1}{\sqrt{3}} \text{grad } \mathbf{a}^{(1)} = \frac{1}{\sqrt{3}} \frac{1}{n_0} \text{grad } n, \\ \mathbf{F}^{(2)} &= \frac{1}{\sqrt{6}} \text{rot } \mathbf{b}^{(1)} \approx \frac{1}{\sqrt{2}} \frac{1}{w_0} \text{rot} \langle \mathbf{w} \rangle, \\ \mathbf{F}^{(4)} &= \frac{1}{\sqrt{3}} \text{grad } \mathbf{a}^{(3)} \approx \frac{1}{\sqrt{2}} \frac{1}{T_0} \text{grad } T_{\text{rot}}, \\ \mathbf{F}^{(5)} &= 0. \end{aligned} \quad (7.4)$$

Introducing the "free path" matrix l_{-1} by

$$l_{-1} = v_0 (\omega_{-1})^{-1} \quad (7.5)$$

equations (7.3) may be solved for the fluxes $\mathbf{a}^{(i)}$:

$$\mathbf{a}^{(i)} = - \sum_k l_{-1}^{(ik)} \mathbf{F}^{(k)}. \quad (7.6)$$

Using the physical meaning of the vectors $\mathbf{a}^{(k)}$ as stated in Table 1, equations (7.6) may be written more explicitly:

$$\begin{aligned} \mathbf{j} &= - \frac{1}{3} v_0 l_{-1}^{(11)} \text{grad } n - \frac{n_0}{\sqrt{6}} \frac{v_0}{w_0} l_{-1}^{(12)} \text{rot} \langle \mathbf{w} \rangle - \frac{n_0}{\sqrt{6}} \frac{n_0}{T_0} l_{-1}^{(14)} \text{grad } T_{\text{rot}}, \\ n \mathbf{a} &= - \frac{1}{3} \sqrt{\frac{2}{3}} l_{-1}^{(21)} \text{grad } n - \frac{n_0}{3} \frac{1}{w_0} l_{-1}^{(22)} \text{rot} \langle \mathbf{w} \rangle - \frac{n_0}{3} \frac{1}{T_0} l_{-1}^{(24)} \text{grad } T_{\text{rot}}, \\ \mathbf{q}_{\text{rot}} &= - \frac{1}{\sqrt{6}} k T_0 v_0 l_{-1}^{(41)} \text{grad } n - \frac{n_0}{2} \frac{k T_0 v_0}{w_0} \text{rot} \langle \mathbf{w} \rangle - \frac{n_0}{2} k v_0 l_{-1}^{(44)} \text{grad } T_{\text{rot}}, \\ n_0 \frac{\langle \mathbf{w} \mathbf{w} \cdot \mathbf{v} \rangle}{w_0^2 v_0^2} &= - \frac{1}{9} \sqrt{\frac{10}{3}} l_{-1}^{(51)} \text{grad } n - \frac{\sqrt{5}}{9} \frac{v_0}{w_0} l_{-1}^{(52)} \text{rot} \langle \mathbf{w} \rangle - \frac{\sqrt{5}}{9} \frac{n_0}{T_0} l_{-1}^{(54)} \text{grad } T_{\text{rot}}. \end{aligned} \quad (7.7)$$

The relation (2.14) implies certain symmetry properties of the ω_{-1} matrix, these in turn lead to the following Onsager-Casimir relations for the $l_{-1}^{(ik)}$:

$$\begin{aligned} l_{-1}^{(ik)} &= l_{-1}^{(ki)} \quad \text{for } i, k = 1, 4, 5; \\ l_{-1}^{(2i)} &= -l_{-1}^{(i2)} \quad \text{for } i = 1, 4, 5. \end{aligned} \quad (7.8)$$

For vanishing $\text{grad } T_{\text{rot}}$ the equations for \mathbf{j} and the azimuthal spin \mathbf{a} as given by (7.7) may be compared with equations (5.2), (6.11) and (6.14). The diffusion constant D , the spin diffusion constant $D_s^{(1)}$

and the number α_s may now be expressed in terms of $l_{-1}^{(11)}$, $l_{-1}^{(22)}$ and $l_{-1}^{(12)} = -l_{-1}^{(21)}$. A comparison of the values of these constants taken from (7.7) with those obtained in the preceeding sections (where vectors of third power were neglected) shows that the values given by (5.3) and (6.13) are exact up to terms of order $(\omega_0/\omega_1)^2$. This accuracy seems to be satisfactory since we expect ω_0/ω_1 to be rather small. In the same approximation (6.12), however,

has to be replaced by

$$D_s^{(1)} = D_s^{(0)} \left(1 - \frac{\omega_0^2}{(\omega_1 + \omega_2) \omega_1} - \frac{3}{2} \frac{\omega_0^2}{(\omega_1 + \omega_2) (\omega_1 + 2\omega_2)} \right).$$

Next we look at the third equation of (7.7). Here the rotational heat conductivity is

$$\lambda_{\text{rot}} = \frac{1}{2} k n_0 v_0 l_{-1}^{(44)}. \quad (7.9)$$

Neglecting terms of higher order of magnitude than $(\omega_0/\omega_1)^2$ one finds

$$\lambda_{\text{rot}} = \lambda_{\text{rot, iso}} \left(1 - \frac{2}{3} \frac{\omega_0^2}{(\omega_1 + \omega_2) (\omega_1 + 2\omega_2)} \right). \quad (7.10)$$

Similar to the diffusion case the transport constant λ_{rot} is smaller than the pertaining isotropic value

$$\begin{aligned} \lambda_{\text{rot, iso}} &= \frac{1}{2} k n_0 \frac{v_0^2}{\omega_1 + 2\omega_2} \\ &= \frac{3}{2} k n_0 \left(1 + 2 \frac{\omega_2}{\omega_1} \right)^{-1} D_{\text{iso}} \end{aligned} \quad (7.11)$$

obtained without partial alignment of the angular velocity (i. e. $\mathbf{a}^{(2)} = 0$).

We also note that there is a diffusion-thermo effect. Its magnitude is determined by

$$l_{-1}^{(41)} = l_{-1}^{(14)} \approx - \sqrt{\frac{2}{3}} \frac{v_0}{\omega_1} \frac{\omega_0^2}{(\omega_1 + \omega_2) (\omega_1 + 2\omega_2)}. \quad (7.12)$$

Of course, the thermal diffusion effect then also exists. For vanishing rot $\langle \mathbf{w} \rangle$ the equation for the diffusion flow \mathbf{j} is:

$$\mathbf{j} = -D \text{grad } n - n_0 D_{\text{iso}} T_0^{-1} \alpha \text{grad } T_{\text{rot}}. \quad (7.13)$$

The thermal diffusion constant is

$$\alpha \approx - \frac{\omega_0^2}{(\omega_1 + \omega_2) (\omega_1 + 2\omega_2)}. \quad (7.14)$$

Note that α is of order $(\omega_0/\omega_1)^2$, α_s (see 6.13) on the other hand is of order ω_0/ω_1 . This stems from the fact that there is a non-vanishing ω_{-1} -matrix element giving a direct coupling of $\mathbf{a}^{(1)}$ and $\mathbf{a}^{(2)}$ yet the coupling of $\mathbf{a}^{(1)}$ and $\mathbf{a}^{(4)}$ is an indirect one (via $\mathbf{a}^{(2)}$) since $\omega_{-1}^{(14)} = \omega_{-1}^{(41)} = 0$.

A look at the equations (7.7) shows that there are a few more cross effects besides those we already discussed. Among these is the spin-diffusion thermo or thermal spin-diffusion cross effect. Due to it a

gradient of the rotational temperature causes an azimuthal polarization and thus a partial alignment of the angular velocities of the Brownian particles. The magnitude of this effect is determined by a l_{-1} -matrix element of order ω_0/ω_1 , namely:

$$l_{-1}^{(24)} = -l_{-1}^{(42)} = \sqrt{\frac{5}{6}} \frac{v_0}{\omega_1 + \omega_2} \frac{\omega_0}{\omega_1 + 2\omega_2}. \quad (7.15)$$

Final Remarks

i) The simple model for the Brownian motion of particles with internal rotational degrees of freedom presented here has shown all essential features one already encountered in the kinetic theory for dilute polyatomic gases¹⁻⁶. Yet there is one difference. Starting from a generalized Boltzmann equation for particles with spin or rough spheres one finds non-diagonal elements in the ω_{-1} relaxation coefficient matrix that couple the vectors $\mathbf{a}^{(1)}$, $\mathbf{a}^{(3)}$, $\mathbf{a}^{(4)}$ directly to $\mathbf{a}^{(5)}$. Thus the thermodynamical fluxes cause a correlation of velocity and tensor polarization (proportional to $\mathbf{a}^{(5)}$) that is of equal order of magnitude as (or even more important than) the azimuthal polarization (proportional to $\mathbf{a}^{(2)}$). Contrary to the azimuthal polarization, the partial tensor polarization tends to increase the values of the transport constants over the corresponding isotropic values. This effect could be simulated for the Brownian motion too by assuming the existence of a friction force proportional to $\overline{w_\mu w_\nu v_\nu}$. In the generalized Fokker-Planck equation this force would give rise to an additional term proportional to

$$f_0^{-1} \overline{W_\mu W_\nu} \frac{\partial}{\partial V_\mu} \left(f_0 \frac{\partial \Phi}{\partial V_\nu} \right)$$

and would account for a direct coupling of the diffusion flow and $\mathbf{a}^{(5)}$. But besides the above mentioned type of force one expects the generalized Langevin equations also to contain friction force terms proportional to $v^2 v_\mu$, $w^2 v_\mu$ as well as friction torque terms proportional to $v^2 w_\mu$, $w^2 w_\mu$ and $v_\mu v_\nu w_\nu$ that might be of equal importance. Hence one would obtain 6 additional terms in the generalized Fokker-Planck collision operator. A kinetic treatment of this more general equation is straightforward but does not seem to be very appealing; the more as little is known about the values of the 6 required proportionality constants.

ii) Assuming the Brownian particles to have a magnetic moment proportional to their internal

angular velocity an external magnetic field \mathbf{H} will cause a precession of the angular velocities.

Hence the Fokker-Planck equation will contain an additional term proportional to $(\mathbf{H} \times \mathbf{w}) \cdot \partial f / \partial \mathbf{w}$. The influence of the magnetic field on the magnetic moments of the Brownian particles would lead to a non-isotropic diffusion tensor depending on the magnetic field (Senftleben-effect for diffusion). This point, however, shall be discussed in a subsequent paper.

Note added in proof

According to (7.2) one might suppose that the translational heat conductivity λ_{trans} is not affected by the coupling between rotational and translational motions. This, however, is not true. From the relation

$$\Omega_0(\Phi^{(3)}) = -\omega_0 \Phi^{(6)} \quad (7.16)$$

where
$$\Phi^{(6)} = \frac{2}{\sqrt{5}} (\mathbf{V}^2 - \frac{5}{2}) \mathbf{V} \times \mathbf{W}$$

is an expansion vector of forth power which has not been included in Table 1 one readily infers that the correct result for λ_{trans} [up to terms of order $(\omega_0/\omega_1)^2$] is

$$\lambda_{\text{trans}} = \lambda_{\text{trans, iso}} \left(1 - \frac{\omega_0^2}{3 \omega_1 (3 \omega_1 + \omega_2)} \right). \quad (7.17)$$

Here $\lambda_{\text{trans, iso}}$ is given by (7.2).

To the same approximation (7.10) has to be replaced by

$$\lambda_{\text{rot}} = \lambda_{\text{rot, iso}} \left(1 - \frac{2}{3} \frac{\omega_0^2}{(\omega_1 + 2 \omega_2) (\omega_1 + \omega_2)} - \frac{5}{3} \frac{\omega_0^2}{(\omega_1 + 2 \omega_2) (\omega_1 + 3 \omega_2)} \right) \quad (7.18)$$

on account of

$$\Omega_0(\Phi^{(4)}) = -\sqrt{\frac{2}{3}} \omega_0 \Phi^{(2)} - \sqrt{\frac{5}{3}} \omega_0 \Phi^{(7)}. \quad (7.19)$$

Again
$$\Phi^{(7)} = \frac{2}{\sqrt{5}} (\mathbf{W}^2 - \frac{5}{2}) \mathbf{V} \times \mathbf{W}$$

is a vector of forth power which is not contained in Table 1.

Likewise the relation

$$\Omega_0(\Psi_{\mu\nu}^{(1)}) = \sqrt{\frac{3}{2}} \omega_0 \Psi_{\mu\nu}^{(2)} \quad (7.20)$$

with
$$\Psi_{\mu\nu}^{(2)} = 2 \sqrt{\frac{2}{3}} (\mathbf{W}(\mathbf{W} \times \mathbf{V}))_{\mu\nu}$$

implies that (6.10) should be replaced by

$$D_s^{(2)} = D_s^{(0)} \left(1 - \frac{3}{2} \frac{\omega_0^2}{(\omega_1 + \omega_2) (\omega_1 + 2 \omega_2)} \right). \quad (7.21)$$

Equations (4.6), (7.20) and (7.16), (7.19) clearly indicate that expansion tensors up to third and forth power respectively have to be taken into account in order to evaluate the spin-diffusion constants and heat conductivities up to terms of order $(\omega_0/\omega_1)^2$. On the other hand, to obtain the diffusion constant to the same approximation, inclusion of expansion tensors up to second power proved sufficient.

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