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FOKKER-PLANCK EQUATION FOR BROWNIAN MOTION OF ROTATING SPHERICAL PARTICLES

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The Langevin equation to derive the Fokker-Planck equation is used for the Brownian motion of particles in translational motion. The Fokker-Planck equation for the Brownian motion of particles which have, in addition to the translational velocity also an angular velocity, has not, so far, been derived. This can apparently be explained by the fact that in the case of the rotational motion, the Langevin equation for the translational motion velocity vector must be supplemented by a corresponding equation for an angular velocity vector. The latter equation must contain, in addition to the systematic moment of reaction linearly dependent on the angular velocity of rotation itself, a random moment rapidly varying with time. Moreover, to ensure the compatibility of two differential vector equations within the system, additional relations which must be introduced, must connect not only the coefficients of the systematic reactions, but also the random vectors varying rapidly with time.

In [1], the Boltzmann's equation for a mixture of two gases was used to derive a Fokker-Planck equation for a translational motion of Brownian particles. The same method can be applied to the Brownian motion of spherical particles which have, in addition to the translational velocities, angular velocities of self-rotations. In this case there is no need to introduce additional relations connecting the random rapidly varying vectors.

In the present paper we derive the Fokker-Planck equations for a new model of rotating spherical molecules which was used in [2].

1. We derive the basic Boltzmann's equation for the Brownian motion of rotating spherical particles, as in [1], we consider a mixture of two gases in a homogeneous state, disregarding the action of external forces. We shall call the particles of the first gas the Brownian particles. The mass of such a particle is much greater than the mass of a particle of the second gas, and their number per unit volume is much smaller than that of the particles of the second gas, i. e.

$$m_2/m_1 = \varepsilon \ll 1, \quad n_2/n_1 \gg 1 \tag{1.1}$$

Using these assumptions we can dispense with one of the Boltzmann's equations and retain the equation the right-hand side of which contains a single integral of collisions of the Brownian particles with the particles of the second gas. This basic equation can be written in the form (see [3])

$$\frac{\partial f_1}{\partial t} = n_2\sigma^2 \int\limits_{(\boldsymbol{\omega}_2)} \int\limits_{(\mathbf{c}_2)} \int\limits_{(\mathbf{k})} (f_1'f_2' - f_1f_2)(\mathbf{c}_1 - \mathbf{c}_2)\,\mathbf{k}d\mathbf{k}\,d\mathbf{c}_2 d\boldsymbol{\omega}_2 \tag{1.2}$$

where $\mathbf{c}_1$ and $\mathbf{c}_2$ are the velocity vectors of the translational motion of the particles, $\boldsymbol{\omega}_2$ is the angular velocity vector of rotation of the particles of the second gas, $\mathbf{k}$ is the unit direction vector from the center of the Brownian particle to the center of the particle of the second gas at the instant of their direct collision, f_1 and f_2 are the velocity distribution functions of the particles in the mixture before their direct collision, f_1' and f_2' are the same functions before their reverse collision, and σ is the sum of the radii of the spherical particles, i.e.

$$\sigma = a_1 + a_2$$

Repeating the arguments used in [1] we can show that for the particles of the second gas, we can use an expression for the Maxwellian velocity distribution function of the limiting thermodynamic state of equilibrium of the second gas, of the form

$$f_2 = \frac{(m_2 I_2)^{3/2}}{(2\pi k T_2)^3} \exp\left(-\frac{m_2 c_2^2 + I_2 \omega_2^2}{2kT_2}\right) \tag{1.3}$$

where I_2 is the axial moment of inertia of a particle of the second gas and T_2 is the partial temperature of this gas.

Introducing the differences in the projections on the fixed axes of the vectors $\mathbf{c}_1'$, $\mathbf{c}_1$, $\boldsymbol{\omega}_1'$ and $\boldsymbol{\omega}_1$, i.e.

$$\Delta c_{1i} = c_{1i}' - c_{1i}, \quad \Delta\omega_{1i} = \omega'_{1i} - \omega_{1i} \tag{1.4}$$

we can write the velocity distribution function of the Brownian particles before their reverse collision with the light particles, in the form of a Taylor series

$$f_1' = f_1 + \sum_{\mu=1} \frac{1}{\mu!}\left[\sum_{i=1}^{i=3}\left(\Delta c_{1i}\frac{\partial}{\partial c_{1i}} + \Delta\omega_{1i}\frac{\partial}{\partial \omega_{1i}}\right)^{(\mu)}(f_1)\right] \tag{1.5}$$

setting now

$$I_1 = m_1\varkappa_1, \quad I_2 = m_2\varkappa_2 = \varepsilon m_1 \varkappa_2 \tag{1.6}$$

and using the law of conservation of the sum of the kinetic energies during the reverse collision between the particles in question, we obtain

$$c_2'^2 + \varkappa_2\omega_2'^2 = c_2^2 + \varkappa_2\omega_2^2 - \frac{1}{\varepsilon}[(2\mathbf{c}_1 + \Delta\mathbf{c}_1)\Delta\mathbf{c}_1 + \varkappa_1(2\boldsymbol{\omega}_1 + \Delta\boldsymbol{\omega}_1)\cdot\Delta\boldsymbol{\omega}_1] \tag{1.7}$$

Substituting (1.7) into the corresponding equation for f_2', we obtain

$$f_2' = f_2 + f_2\sum_{\mu=1}\frac{1}{\mu!}\left\{\frac{m_2}{2\varepsilon kT_2}[(2\mathbf{c}_1 + \Delta\mathbf{c}_1)\cdot\Delta\mathbf{c}_1 + \varkappa_1(2\boldsymbol{\omega}_1 + \Delta\boldsymbol{\omega}_1)\cdot\Delta\boldsymbol{\omega}_1]\right\}^{\mu} \tag{1.8}$$

The series in the right-hand side of (1.8) represent the expansion of f_2' in powers of $\sqrt{\varepsilon}$ provided that we assume the velocities $\mathbf{c}_2$ and ω_2 to be of the order of unity, the velocities of the Brownian particles of the order of $\sqrt{\varepsilon}$, and the differences $\Delta\mathbf{c}_1$ and $\Delta\boldsymbol{\omega}_1$ of the order of ε.

Substituting the expressions (1.5) and (1.8) and writing out the terms of the order of smaller powers of ε, we can obtain

$$f_1'f_2' - f_1f_2 = f_2\left\{\left(\frac{\partial f_1}{\partial \mathbf{c}_1}\cdot\Delta\mathbf{c}_1 + \frac{\partial f_1}{\partial \boldsymbol{\omega}_1}\cdot\Delta\boldsymbol{\omega}_1\right)\left[1 + \frac{m_2}{\varepsilon kT_2}(\mathbf{c}_1\cdot\Delta\mathbf{c}_1 + \varkappa_1\boldsymbol{\omega}_1\cdot\Delta\boldsymbol{\omega}_1\right] + \right. \tag{1.9}$$

$$f_1\frac{m_2}{2\varepsilon kT_2}[(2\mathbf{c}_1 + \Delta\mathbf{c}_1)\cdot\Delta\mathbf{c}_1 + \varkappa_1(2\boldsymbol{\omega}_1 + \Delta\boldsymbol{\omega}_1)\cdot\Delta\boldsymbol{\omega}_1] +$$

$$\frac{1}{2}f_1\left(\frac{m_2}{kT_2}\right)^2\left[\left(\frac{\mathbf{c}_1\cdot\Delta\mathbf{c}_1}{\varepsilon}\right)^2 + \varkappa_1^2\left(\frac{\boldsymbol{\omega}_1\cdot\Delta\boldsymbol{\omega}_1}{\varepsilon}\right)^2 + 2\frac{\varkappa_1}{\varepsilon^2}\mathbf{c}_1\cdot\Delta\mathbf{c}_1\boldsymbol{\omega}_1\cdot\Delta\boldsymbol{\omega}_1\right] +$$

$$\left.\frac{1}{2}\sum_{i=1}^{i=3}\sum_{j=1}^{j=3}\left(\Delta c_{1i}\Delta c_{1j}\frac{\partial^2 f_1}{\partial c_{1i}\partial c_{1j}} + \Delta\omega_{1i}\Delta\omega_{1j}\frac{\partial^2 f_1}{\partial\omega_{1i}\partial\omega_{1j}} + 2\Delta c_{1i}\Delta\omega_{1j}\frac{\partial^2 f_1}{\partial c_{1i}\partial\omega_{1j}}\right)\right\}$$

2. The authors of [3] discuss a Bryan model of a rotating molecule with an absolutely rough spherical surface, while in [2] a new model of a rotating molecule is introduced under the assumption that its surface is absolutely elastic. The following laws are obeyed in both cases : (1) the law of conservation of the sum of kinetic energies of the rotating particles in collision: (2) the law of conservation of the volume element of the 12-dimensional space of velocities during the collision of the particles; (3) the law of mutual conversion of the proportions of the kinetic energy due to the rotational motions of the particles into certain proportions of the kinetic energy due to their translational motions. The above models differ from each other in the fact that in the Bryan model the impulses due to collisions are represented by their single principal vector, while in the new model the impulses distributed over some small area near the initial point of contact between the particles are reduced to the principal vector and their principal moment. One of the two conditions of absolute elasticity of the surfaces of the colliding particles coincides with the condition of absolute elastic roughness in the Bryan model, and the second condition is reduced to the equality of differences of the angular velocities of these particles before and after collisions but with the sign reversed. For the model of rotating molecules with absolutely elastic surfaces, the formulas of relations of the thermal velocities $\mathbf{c}_1'$ and $\boldsymbol{\omega}_1'$ before the reverse collision with the thermal velocities $\mathbf{c}_1$ and $\boldsymbol{\omega}_1$ before the direct collision are represented in the form

$$\mathbf{c}_1 - \mathbf{c}_1 = \Delta\mathbf{c}_1 = \frac{2\varepsilon}{(1+\varepsilon)(\varkappa_1+\varepsilon\varkappa_2)+\varepsilon(a_1+a_2)^2}\times \tag{2.1}$$

$$\Big\{(\varkappa_1+\varepsilon\varkappa_2)(\mathbf{c}_2-\mathbf{c}_1)+(a_1+a_2)(\varepsilon\varkappa_2\boldsymbol{\omega}_2+\varkappa_1\boldsymbol{\omega}_1)\times\mathbf{k}+\frac{\varepsilon}{1+\varepsilon}(a_1+a_2)^2\times$$

$$[(\mathbf{c}_2-\mathbf{c}_1)\cdot\mathbf{k}]\,\mathbf{k}\Big\}$$

$$\boldsymbol{\omega}_1' - \boldsymbol{\omega}_1 = \Delta\boldsymbol{\omega}_1 = -\frac{2\varepsilon(a_1+a_2)}{(1+\varepsilon)(\varkappa_1+\varepsilon\varkappa_2)+\varepsilon(a_1+a_2)^2}\times$$

$$\Big\{\mathbf{k}\times(\mathbf{c}_2-\mathbf{c}_1)-\frac{\varkappa_2(1+\varepsilon)}{a_1+a_2}(\boldsymbol{\omega}_2-\boldsymbol{\omega}_1)+(a_1+a_2)\,\boldsymbol{\omega}_1-$$

$$\frac{a_1+a_2}{\varkappa_1+\varepsilon\varkappa_2}\,\mathbf{k}\,[\mathbf{k}\cdot(\varepsilon\varkappa_2\boldsymbol{\omega}_2+\varkappa_1\boldsymbol{\omega}_1)]\Big\}$$

Since, in what follows we shall compute the whole of the right-hand side of (1.2) taking into account the terms of order not higher than ε, and the expression (1.9) includes factors accompanying $\partial f_1 / \partial \mathbf{c}_1$ and $\partial f_1 / \partial \boldsymbol{\omega}_1$ which are of the order of $1 / \sqrt{\varepsilon}$, we must retain in the right-hand sides of (2.1) terms with the order of smallness of $\varepsilon^{3/2}$. We can therefore replace the exact formulas (2.1) by the approximate expressions of the form

$$\Delta\mathbf{c}_1 = 2\varepsilon\,(\mathbf{c}_2-\mathbf{c}_1+\sigma\boldsymbol{\omega}_1\times\mathbf{k}) \tag{2.2}$$

$$\Delta\boldsymbol{\omega}_1 = -\frac{2\varepsilon}{\varkappa_1}\,[\sigma\mathbf{k}\times(\mathbf{c}_2-\mathbf{c}_1)-\varkappa_2\boldsymbol{\omega}_2+(\varkappa_2+\sigma^2)\,\boldsymbol{\omega}_1-\sigma^2\mathbf{k}\,(\boldsymbol{\omega}_1\cdot\mathbf{k})]$$

3. The integration in the right-hand side of (1.2) over the elementary solid angle $d\mathbf{k}$ must be carried out within a hemisphere the center of which coincides with the center of a fixed Brownian particle at the instant of its direct collision with a particle of the second gas, and the symmetry axis of this hemisphere must be perpendicular to the vector of relative velocity $\mathbf{c}_2 - \mathbf{c}_1$ of the particle of the second gas impinging on the Brownian particle. Choosing the angles in appropriate manner, we have

$$d\mathbf{k} = \sin \alpha d\alpha d\varphi \tag{3.1}$$

The limits of integration over the angle α formed by the vector $\mathbf{k}$ and the direction of the vector difference $\mathbf{c}_1 - \mathbf{c}_2$ will be 0 and $\pi / 2$, and the limits for the angle φ will be 0 and 2π. In particular we have

$$\int_{(\mathbf{k})} (\mathbf{c}_1 - \mathbf{c}_2)\cdot \mathbf{k} d\mathbf{k} = \pi \,| c_1 - c_2 | \tag{3.2}$$

The modulus of relative velocity $| c_1 - c_2 |$ in (3.2) can be expanded into a Newton's binomial in the form

$$| c_1 - c_2 | = c_2 - \frac{\mathbf{c}_1 \cdot \mathbf{c}_2}{c_2} + \frac{c_1^2}{2c_2} - \frac{(\mathbf{c}_1 \cdot \mathbf{c}_2)^2}{2c_2^3} + \cdots \tag{3.3}$$

When Eqs. (2.2) and (3.2) are used, terms of the order of smallness higher than the first order of ε appear in the right-hand side of (1.2). Because of this it is expedient to expand separately, before integrating over the solid angle $d\mathbf{k}$ the terms of the integrand expression in (1.2) and retain only the terms which are of first order in ε . To find the projections $\Delta\omega_{1i}$ on the fixed axes x_1, x_2 and x_3 we must use a table [4] of the direction cosines of the fixed Brownian particle axes ξ_1, ξ_2 and ξ_3 and compute the projections of the unit vector $\mathbf{k}$ on the fixed axes. Using these computations, we obtain

$$k_1 = \sin \alpha \cos \varphi \cos \psi - \sin \alpha \sin \varphi \sin \psi \cos \theta + \cos \alpha \sin \theta \sin \psi \tag{3.4}$$

$$\int_0^{2\pi} d\varphi \int_0^{\pi/2} k_1^2 \cos \alpha \sin \alpha d\alpha = \frac{\pi}{4} (1 + \sin^2 \theta \sin^2 \psi) \tag{3.5}$$

where θ is the angle between ξ_3 and x_3, ψ is the angle between ξ_1 and x_1 and the axis ξ_1 is the nodal line. The volume elements of the spaces $\mathbf{c}_2$ and $\boldsymbol{\omega}_2$ are given in spherical coordinates, e.g.

$$dc_2 = c_2^2 \sin \theta_2 \, dc_2 d\theta_2 d\psi_2$$

The formulas governing the passage from the angles θ and ψ to the angles θ_2 and ψ_2 have the form

$$\cos \theta = - \cos \theta_2 \left(1 + \frac{\mathbf{c}_1 \cdot \mathbf{c}_2}{c_2}\right) + \frac{c_{13}}{c_2} + O(\varepsilon) \tag{3.7}$$

$$\sin \theta \sin \psi = - \sin \theta_2 \cos \psi_2 \left(1 + \frac{\mathbf{c}_1 \cdot \mathbf{c}_2}{c_2}\right) + \frac{c_{11}}{c_2} + O(\varepsilon)$$

$$\sin \theta \cos \psi = \sin \theta_2 \sin \psi_2 \left(1 + \frac{\mathbf{c}_1 \cdot \mathbf{c}_2}{c_2}\right) - \frac{c_{12}}{c_2} + O(\varepsilon)$$

4. Substituting (1.9) into the right-hand side of (1.2), using (2.2) and the corresponding expansions of the separate terms of the integrand expression in (1.2) which were considered in Sect. 3, and computing the numerous quadratures, we obtain the following Fokker-Planck equation :

$$\frac{\partial f_1}{\partial t} = \beta_1 f_1 + \beta_2 \mathbf{c}_1 \cdot \frac{\partial f_1}{\partial \mathbf{c}_1} + \beta_3 \boldsymbol{\omega}_1 \cdot \frac{\partial f_1}{\partial \boldsymbol{\omega}_1} + \beta_4 \Delta_{c_1} f_1 + \beta_5 \Delta_{\omega_1} f_1 \tag{4.1}$$

where Δ_{c_1} and Δ_{ω_1} are the Laplace operators in the vector spaces $\mathbf{c}_1$ and $\boldsymbol{\omega}_1$, and the coefficients have the form

$$\beta_1 = 4\varepsilon \left(4 + 3 \frac{\varkappa_2}{\varkappa_1} + 2 \frac{\sigma^2}{\varkappa_1}\right) n_2 \sigma^2 \sqrt{\frac{2\pi k T_2}{m_2}} \tag{4.2}$$

$$\beta_2 = \frac{16}{3} \varepsilon n_2 \sigma^2 \sqrt{\frac{2\pi k T_2}{m_2}}$$

$$\beta_3 = 2\varepsilon \left(2 \frac{\varkappa_2}{\varkappa_1} + \frac{4}{3} \frac{\sigma^2}{\varkappa_1}\right) n_2 \sigma^2 \sqrt{\frac{2\pi k T_2}{m_2}}$$

$$\beta_4 = \frac{16}{3}\sqrt{2\pi}\,\varepsilon^2\left(\frac{kT_2}{m_2}\right)^{3/2} n_2\sigma^2$$

$$\beta_5 = 4\sqrt{2\pi}\,\varepsilon^2\left(\frac{\varkappa_2}{\varkappa_1{}^2} + \frac{2}{3}\frac{\sigma^2}{\varkappa_1{}^2}\right) n_2\sigma^2\left(\frac{kT_2}{m_2}\right)^{3/2}$$

Equations (4.2) yield the relations

$$\beta_1 = 3(\beta_2 + \beta_3), \quad \beta_4 = \frac{kT_2}{m_2}\varepsilon\beta_2, \quad \beta_5 = \frac{kT_2}{m_2\varkappa_1}\varepsilon\beta_3$$

which can be used to obtain the Fokker-Planck equation (4.1) for rotating particles with absolutely elastic surfaces in the form

$$\frac{\partial f_1}{\partial t} = \frac{\partial}{\partial \mathbf{c}_1}\left(\beta_2 f_1 \mathbf{c}_1 + \beta_2\frac{kT_2}{m_2}\varepsilon\frac{\partial f_1}{\partial \mathbf{c}_1}\right) + \frac{\partial}{\partial \boldsymbol{\omega}_1}\left(\beta_3 f_1 \boldsymbol{\omega}_1 + \beta_3\frac{kT_2}{m_2\varkappa_1}\varepsilon\frac{\partial f_1}{\partial \boldsymbol{\omega}_1}\right) \quad (4.3)$$

When $\partial f_1 / \partial t = 0$, Eq. (4.3) is satisfied by the Maxwell function of velocity distribution of the equilibrium thermodynamic state the form of which coincides with (1.3) when the subscript 2 is replaced by subscript 1. The Fokker-Planck equation enables us to construct the functions of thermodynamic equilibrium and to find the form of the velocity distribution functions for the state near to the thermodynamic equilibrium in the manner shown in [5].

Comparing Eqs. (4.3) with the Fokker-Planck equation for the particles in translational motion [1], we can establish that the terms of (4.3) referring to the translational velocity have identical structure and the coefficient β_2 becomes equal to $2\beta_t$ when $\sigma = a$. The structure of the terms with angular velocity of rotation is the same as the structure of the terms with translational velocity, but the coefficient β_3 contains, apart from the quantities appearing in β_2, also the moments of inertia of the Brownian particles and of the particles belonging to the surrounding medium.

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