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THE BROWNIAN MOTION IN A THERMAL FIELD*

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The diffusion of a Brownian particle in a continuum subject to external potential forces as well as nonhomogeneous thermal field is discussed. Apart from a thermodiffusion phenomenon, a Streater effect in which the potential energy of the particle is converted to a heat due to friction *cf.* R.F. Streater, *Rep. Math. Phys.* **40**, 557 (1997), is taken into account. It is shown that for such a continuum the first law of thermodynamics holds true, and the second law is observed if a relation between the probability density function and temperature is satisfied. The examples of the Brownian motion for particular external fields are given.

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1. Introduction

A thermodiffusion phenomenon in liquids was discovered apparently for the first time by Ludwig in 1856 and independently by Soret in 1879. They observed direct thermodiffusion in which a flow of matter is caused by a temperature gradient. A reciprocal effect, in which a flow of heat is caused by the gradient of the particle concentration was observed by Dufour in 1872, *cf.* [2].

The motion of Brownian particle in an external force field when thermal effects are taken into account can be influenced by the two processes: (*i*) a thermodiffusion process, and (*ii*) a conversion of the potential energy of the particle into heat. It was pointed out by Streater [1,3] that the friction work performed by Brownian particles falling in the gravity field is converted to an irreversible heat source energy, so the diffusion and thermal processes are coupled.

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Also, Streater [4] performed an analysis of the so called Soret–Dufour effects for a special statistical model of gas of molecules with repulsive cores. In this model only one phenomenological (macroscopic) coefficient occurs, namely the diffusion coefficient which has interpretation of the microscopic hopping rate, and the heat conductivity and cross-coefficients are expressed by the diffusion coefficient, density and a maximum density of the diffusing Brownian particles.

It is well known, even from the elementary kinetic theory of gases that the different transport phenomena, such as viscosity, heat conduction and diffusion are interrelated, see *e.g.* [5]. However, the thermodiffusion phenomenon in terms of mean free path has not been analysed in a satisfactory way. For example, Oskar Meyer in his famous considerations on the elementary theory of gas kinetics does not include the thermodiffusion phenomenon, [6]. Even when a theory of thermodiffusion was built for the gases on the basis of the Boltzmann equation by Enskog (1912) and Chapman (1916) such a theory was not accepted until an experimental evidence was gained by Chapman and Dootson in 1917 [7]; the experimental evidence of the reciprocal thermodiffusion effect was found by Clusius and Waldmann only in 1943 [8,9].

The Enskog–Chapman method of analysis of the Boltzmann equation is somehow awkward, and trials to give more immediate and intuitive explanation of the effect were proposed by Frankel in 1940 [10] and Fürth in 1941 [11]. These elementary treatments were discussed by Furry in 1948 [12]. However, a simple elementary explanation of the reciprocal effect is apparently missing in the literature. Such an explanation based on Pohl's method [5] is given in Appendix A.

In the present paper a Brownian motion in which both the thermodiffusion effect and an external potential force exist, is studied, *cf.* [1,13,14]. We do not enter into a micromechanics of the thermodiffusion and only phenomenological coefficients, namely those of diffusion, thermodiffusion and heat conductivity are taken into account.

2. The first law for Brownian particle

Let Ω be a bounded, sufficiently regular domain with boundary $\partial\Omega$, *cf.* Fig. 1. Let the function $f = f(\boldsymbol{x}, t)$ represent the probability density of finding a tagged Brownian particle at $\boldsymbol{x}$ at time t. Consider the motion of the Brownian particle in a fluid at temperature $T = T(\boldsymbol{x})$, under the influence of a conservative field of force $\boldsymbol{F} = -\nabla V$, where V denotes a potential.

In the present paper the temperature T is given in the energetic scale. Its relation to the temperature T^{Kelv} given in the degrees of Kelvin is $T = k_{\mathrm{B}} T^{\mathrm{Kelv}}$, where $k_{\mathrm{B}} = 1.38 \times 10^{-23} \frac{J}{K}$ is the Boltzmann constant.

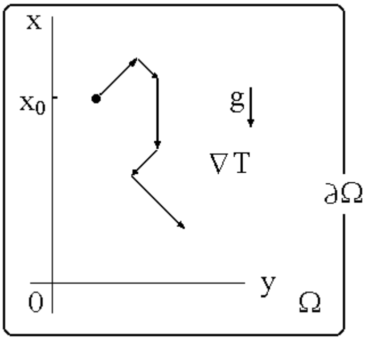

Fig. 1. Motion of a Brownian particle in domain Ω subject to a temperature gradient and a gravitational field

Let $\boldsymbol{j}$ and $\boldsymbol{q}$ denote the flux of Brownian particle diffusion and heat flow, respectively, considered in that domain. The corresponding continuity equations read

$$\frac{\partial f}{\partial t} + j_{i,i} = 0, \qquad C\frac{\partial T}{\partial t} + q_{i,i} = r, \tag{2.1}$$

where $C = C(\boldsymbol{x})$ stands for the specific heat and r denotes a heat source. Moreover, j_i denotes the i-th component of the vector $\boldsymbol{j}$ and the comma denotes differentiation with respect to the spatial variable; thus $j_{i,i} \equiv \mathrm{div}\boldsymbol{j}$, $(i = 1, 2, 3)$.

The term r represents the rate at which the Brownian particle does work which is subsequently converted into heat

$$r = \boldsymbol{j} \cdot \boldsymbol{F} \qquad \text{or} \qquad r = -\boldsymbol{j} \cdot \nabla V. \tag{2.2}$$

We make the following boundary assumptions:

$$\boldsymbol{j} = \boldsymbol{0} \qquad \text{and} \qquad \boldsymbol{q} = \boldsymbol{0} \qquad \text{on} \qquad \partial\Omega. \tag{2.3}$$

Combining equations (2.1) with the second equation of (2.2) we obtain the following continuity relation

$$\frac{\partial e}{\partial t} + j^E_{i,i} = 0, \tag{2.4}$$

where e denotes the energy density and $\boldsymbol{j}^E$ is the current of total energy

$$e \equiv Vf + CT \qquad \text{and} \qquad j^E_i \equiv Vj_i + q_i. \tag{2.5}$$

According to conditions (2.3)

$$\boldsymbol{j}^E = \boldsymbol{0} \qquad \text{on} \qquad \partial\Omega \tag{2.6}$$

and the energy of the system is

$$E \equiv \int\limits_{\Omega} e d\boldsymbol{x} = \int\limits_{\Omega} \left[V(\boldsymbol{x}) f(\boldsymbol{x},t) + C(\boldsymbol{x}) T(\boldsymbol{x},t) \right] d\boldsymbol{x}. \tag{2.7}$$

By integration of (2.4) we find that

$$\frac{\partial E}{\partial t} = \int\limits_{\Omega} j^E_{i,i} d\boldsymbol{x} \tag{2.8}$$

or by virtue of the divergence theorem and vanishing boundary condition (2.6) we get

$$\frac{\partial E}{\partial t} = 0. \tag{2.9}$$

Thus the first law of thermodynamics holds true.

3. The transport relations

Let $\boldsymbol{D}$ and $\boldsymbol{K}$ be the diffusion and heat conductivity tensors, respectively; and let $\boldsymbol{M}$ and $\boldsymbol{N}$ denote the thermodiffusion direct and reciprocal tensors, respectively. In general the tensors $\boldsymbol{M}$ and $\boldsymbol{N}$ are not independent, see Eq. (4.5). We admit that $\boldsymbol{D}$, $\boldsymbol{K}$, $\boldsymbol{M}$ and $\boldsymbol{N}$ are functions of position $\boldsymbol{x}$, time t, temperature T and probability density f. The equations for diffusion and heat fluxes are as follows, *cf.* [1,4,15]

$$\begin{aligned} j_i &= -D_{ij} \left(f_{,j} + \frac{f}{T} V_{,j} \right) - M_{ij} T_{,j}, \\ q_i &= -N_{ij} \left(f_{,j} + \frac{f}{T} V_{,j} \right) - K_{ij} T_{,j}. \end{aligned} \tag{3.1}$$

Substituting the expressions (3.1) into the set of equations (2.1) we get

$$\begin{aligned} \frac{\partial f}{\partial t} &= \left[D_{ij} \left(f_{,j} + \frac{f}{T} V_{,j} \right) + M_{ij} T_{,j} \right]_{,i}, \\ C \frac{\partial T}{\partial t} &= \left[N_{ij} \left(f_{,j} + \frac{f}{T} V_{,j} \right) + K_{ij} T_{,j} \right]_{,i} + r. \end{aligned} \tag{3.2}$$

The first equation of the last set for $\boldsymbol{M} = \boldsymbol{0}$ becomes the diffusion equation with drift known as the Einstein–Smoluchowski equation.

Remark 1

The mean velocity of the Brownian particle is, by the first equation of (2.1) and the divergence theorem,

$$\begin{aligned} v_i &= \frac{\partial}{\partial t}\int\limits_{\Omega} x_i f(\boldsymbol{x},t)d\boldsymbol{x} = \int\limits_{\Omega} x_i \frac{\partial f(\boldsymbol{x},t)}{\partial t} d\boldsymbol{x} = -\int\limits_{\Omega} x_i j_{k,k} d\boldsymbol{x} \\ &= -\int\limits_{\partial\Omega} x_i j_k n_k dA + \int\limits_{\Omega} j_i d\boldsymbol{x}. \end{aligned} \tag{3.3}$$

So, similarly as in [2], $\boldsymbol{v} = \int\limits_{\Omega} \boldsymbol{j} d\boldsymbol{x}$, where the boundary condition (2.3) for $\boldsymbol{j}$ is used, or, by the first equation of the set (3.1),

$$v_i = -\int\limits_{\Omega} \left[D_{ij}\left(f_{,j} + \frac{f}{T}V_{,j}\right) + M_{ij}T_{,j}\right] d\boldsymbol{x}. \tag{3.4}$$

If D_{ij}, M_{ij}, T and ∇V are constants, and $f = 0$ on $\partial\Omega$, the relation (3.3) passes into Einstein's formula

$$v_i = \frac{1}{T} D_{ij} F_j, \tag{3.5}$$

where the relation $\int\limits_{\Omega} f(\boldsymbol{x}) d\boldsymbol{x} = 1$ was used.

4. The second law of thermodynamics

We have the following expression for the entropy of our model

$$S = \int\limits_{\Omega} \left[-f(\boldsymbol{x},t)\ln f(\boldsymbol{x},t) + C(\boldsymbol{x})\ln\frac{T(\boldsymbol{x},t)}{T_0}\right] d\boldsymbol{x}, \tag{4.1}$$

where T_0 denotes a temperature of the initial state. Hence

$$\frac{\partial S}{\partial t} = \int\limits_{\Omega} \left[-\frac{\partial f}{\partial t}\ln f(\boldsymbol{x},t) - \frac{\partial f}{\partial t} + C(\boldsymbol{x})\frac{1}{T}\frac{\partial T}{\partial t}\right] d\boldsymbol{x}$$

or

$$\frac{\partial S}{\partial t} = \int\limits_{\Omega} \left[j_{i,i}\ln f(\boldsymbol{x},t) + j_{i,i} + \frac{1}{T}(-q_{i,i} + r)\right] d\boldsymbol{x}. \tag{4.2}$$

We use the divergence theorem and after use of the boundary conditions (2.3) we get

$$\frac{\partial S}{\partial t} = \int\limits_{\Omega} \left[-j_i \frac{1}{f} f_{,i} - \frac{1}{T^2} T_{,i} q_i + \frac{1}{T} r \right] d\boldsymbol{x}. \tag{4.3}$$

Substituting r as the second alternative from (2.2) into (4.3) we get

$$\frac{\partial S}{\partial t} = \int\limits_{\Omega} \left\{ -j_i \frac{1}{f} \left[f_{,i} + \frac{f}{T} V_{,i} \right] - q_i \frac{1}{T^2} T_{,i} \right\} d\boldsymbol{x}. \tag{4.4}$$

Remark 2

From (4.4) we see that the thermodynamic forces for the diffusion and heat fluxes $\boldsymbol{j}$ and $\boldsymbol{q}$ are

$$\frac{1}{f}\left[\nabla f + \frac{f}{T} \nabla V \right] \qquad \text{and} \qquad \frac{1}{T^2} \nabla T, \text{ respectively.}$$

Thus the proper form of equations for diffusion and heat fluxes (3.1) is as follows

$$\begin{aligned} j_i &= -D_{ij} f \frac{1}{f} \left(f_{,j} + \frac{f}{T} V_{,j} \right) - M_{ij} T^2 \frac{1}{T^2} T_{,j}, \\ q_i &= -N_{ij} f \frac{1}{f} \left(f_{,j} + \frac{f}{T} V_{,j} \right) - K_{ij} T^2 \frac{1}{T^2} T_{,j} \end{aligned}$$

and the symmetry of kinetic coefficients gives

$$M_{ij} T^2 = N_{ij} f. \tag{4.5}$$

Thus, in this condition not only coefficients $\boldsymbol{M}$ and $\boldsymbol{N}$ are involved but also the unknown fields f and T, *cf.* Appendices A and B.
Next, from Eq. $(3.1)_1$ we find

$$f_{,i} + \frac{f}{T} V_{,i} = -\overline{D}_{ij} \left(j_j + M_{jm} T_{,m} \right), \tag{4.6}$$

where $\overline{\boldsymbol{D}} \equiv \boldsymbol{D}^{-1}$ and after Eq. $(3.1)_2$ we can write

$$q_i = N_{ij} \overline{D}_{ik} j_{,k} - \left(K_{im} - N_{ij} \overline{D}_{ik} M_{km} \right) T_{,m}. \tag{4.7}$$

Using (4.6) and (4.7) we find

$$\begin{aligned} j_i \left(f_{,i} + \frac{f}{T} V_{,i} \right) &= -\overline{D}_{ij} j_i j_j - \overline{D}_{ij} M_{jm} j_i T_{,m}, \\ q_i T_{,i} &= N_{ij} \overline{D}_{ik} j_k T_{,i} - \left(K_{im} - N_{ij} \overline{D}_{jk} M_{km} \right) T_{,m} T_{,i}. \end{aligned}$$

Substituting these relations into (4.4) we obtain

$$\frac{\partial S}{\partial t} = \int\limits_{\Omega} \left\{ \frac{1}{f} \overline{D}_{ij} j_i j_j + \left(\frac{1}{f} M_{ij} - \frac{1}{T^2} N_{ij} \right) j_k T_{,i} + \left(K_{im} - N_{ij} \overline{D}_{jk} M_{km} \right) T_{,i} T_{,m} \right\} d\boldsymbol{x}. \tag{4.8}$$

Therefore, if (4.5) is satisfied and the matrix

$$K_{im} - N_{ij} \overline{D}_{jk} M_{km} \tag{4.9}$$

or

$$\begin{bmatrix} \boldsymbol{D} & \boldsymbol{M} \\ \boldsymbol{N} & \boldsymbol{K} \end{bmatrix}$$

is positive definite, the second law of thermodynamics

$$\frac{\partial S}{\partial t} \geq 0 \tag{4.10}$$

holds true in the system.

Remark 3

If $\boldsymbol{D} = \mathbf{0}, \boldsymbol{M} = \mathbf{0}$ and $\boldsymbol{N} = \mathbf{0}$, then Eq. (4.4) becomes

$$\frac{\partial S}{\partial t} = \int\limits_{\Omega} \left\{ -q_i \frac{1}{T^2} T_{,i} \right\} d\boldsymbol{x}$$

or, by Eq. (3.1),

$$\frac{\partial S}{\partial t} = \int\limits_{\Omega} \frac{1}{T^2} K_{ij} T_{,j} T_{,i} d\boldsymbol{x}. \tag{4.11}$$

A function $T = T(\boldsymbol{x})$ which minimizes $\dot{S}$ is to be found from the variational equation

$$\left[\frac{d}{d\lambda} \int\limits_{\Omega} \frac{1}{(T + \lambda \tilde{T})^2} K_{ij} (T_{,i} + \lambda \tilde{T}_{,i})(T_{,j} + \lambda \tilde{T}_{,j}) d\boldsymbol{x} \right]_{\lambda = 0} = 0 \tag{4.12}$$

with the condition $\tilde{T} = 0$ on the boundary $\partial \Omega$. This leads to the nonlinear equation

$$\frac{1}{T^3} K_{ij} \frac{\partial T}{\partial x_i} \frac{\partial T}{\partial x_j} = \frac{\partial}{\partial x_j} \left(\frac{1}{T^2} K_{ij} \frac{\partial T}{\partial x_i} \right). \tag{4.13}$$

On the other hand from the second equation of (3.2) we have

$$C\frac{\partial T}{\partial t} = \left(K_{ij}T_{,j}\right)_{,i} \tag{4.14}$$

and for $\dot{T} = 0$ we get the quasi-linear equation

$$\left(K_{ij}T_{,j}\right)_{,i} = 0. \tag{4.15}$$

Therefore, according to Eq. (4.13) a minimum entropy production condition differs from that describing a stationary distribution of temperature (4.15). This contradicts a Prigogine conjecture [16,17] that for a driven system the rate of entropy production $\dot{S}$ decreases with time towards the minimum. An example supporting this contradiction was presented by Streater in [1].

5. A driven system in a slab

Again, treading in footsteps of [1], we look for a stationary solution far from equilibrium. Consider one-dimensional isotropic model for which a Brownian particle is confined to $0 \leq x \leq 1$.

We impose the condition that the particle current is zero

$$j = 0 \tag{5.1}$$

and that time derivatives vanish. From (2.2) and (5.1), we get

$$r = 0. \tag{5.2}$$

Also we assume that there is a nonzero flow of heat driven by maintaining the ends of the interval $[0,1]$ at different temperatures, T_0 and T_1.

Eqs. (2.1) for our case (1-dim, isotropic) read

$$\begin{aligned} D\left(f_{,x} + \frac{f}{T}V_{,x}\right) + MT_{,x} &= 0, \\ \left[N\left(f_{,x} + \frac{f}{T}V_{,x}\right) + KT_{,x}\right]_{,x} &= 0. \end{aligned} \tag{5.3}$$

Using (4.5) in the first equation of the last set we have

$$D\left(f_{,x} + \frac{f}{T}V_{,x}\right) + N\frac{f}{T^2}T_{,x} = 0. \tag{5.4}$$

Hence after integration we find that

$$f = f_0 \exp\left[\frac{N}{D}\left(\frac{1}{T} - \frac{1}{T_0}\right) - \int\limits_0^x \frac{1}{T(\xi)}V_{,\xi}d\xi\right], \tag{5.5}$$

where f_0 is a normalizing factor. Using (5.4) we write the second equation of the set (5.3) in the form

$$\left[\left(K - \frac{N^2}{D}\frac{f}{T^2}\right)T_{,x}\right]_{,x} = 0. \tag{5.6}$$

After integration we get

$$\left(K - \frac{N^2}{D}\frac{f}{T^2}\right)T_{,x} = a, \tag{5.7}$$

where $a = \text{const}$ and f is given by (5.5). Thus (5.7) is complicated nonlinear integro-differential equation for T which can be solved by approximative methods.

We can write an alternative form of (5.7)

$$T(x) = T_0 + a\int\limits_0^x \frac{d\xi}{K - \dfrac{N^2}{D}\dfrac{f}{T^2}}. \tag{5.8}$$

For $N \to 0$ and $K = \text{const}$ we have an expression from [2]. We can estimate the influence of the thermodiffusion on distribution f considering the simplified situation in which D, N and K are constants. As an example of V we take the potential of a homogeneous gravity field in the form

$$V = gx, \tag{5.9}$$

where $g =$ constant. In the first approximation when the second term in the denominator under the integral in (5.8) is neglected, the temperature is a linear function of x

$$T(x) = T_0 + (T_1 - T_0)x. \tag{5.10}$$

Substituting this expression into (5.5) we get the first approximation of f

$$f = f_0\left(\frac{T}{T_0}\right)^{-\frac{g}{T_1 - T_0}} \exp\left[\frac{N}{D}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]. \tag{5.11}$$

Hence the distribution f is a product of two functions: The first is explicitly non-Gibbsian (as in [1]), and the second with the fraction N/D in exponent has a quasi-Gibbsian character. The examples of the function f given by (5.11) for different parameters g and N/D are given in Fig. 2.

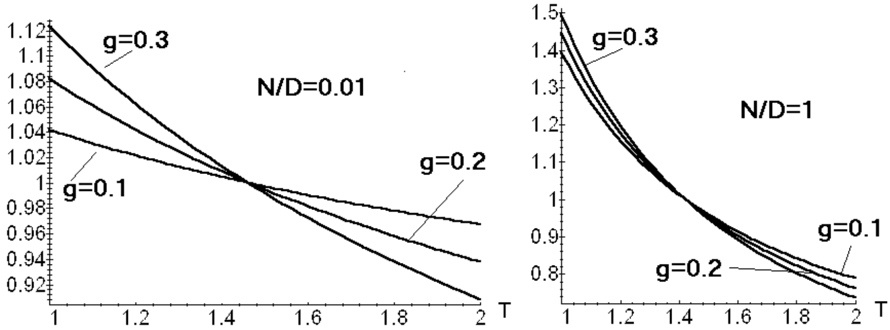

Fig. 2. The non-Gibbsian distribution function *versus* T $(T_0 = 1, T_1 = 2, N/D = 0.01, 1)$ for different values $g = 0.1, 0.2, 0.3$.

6. System in a slab with given temperature

We consider a one-dimensional isotropic model for which a Brownian particle at $t = 0$ is at $x = x_0$, and the particle current $j = 0$ at the bottom of the slab $x = 0$ for $t \geq 0$, see Fig. 1. We assume that the temperature distribution is known $T = T(x)$. Evolution of the distribution function is described by equation $(2.3)_1$ which for 1-dim, isotropic case reads

$$\frac{\partial f}{\partial t} = \left[D \left(f_{,x} + \frac{f}{T} V_{,x} \right) + M T_{,x} \right]_{,x} \tag{6.1}$$

or after using (4.5) we have

$$\frac{\partial f}{\partial t} = \left[D \left(f_{,x} + \frac{f}{T} \mathcal{V}_{,x} \right) \right]_{,x}, \tag{6.2}$$

where

$$\mathcal{V}_{,x} = V_{,x} + \frac{N}{D} \frac{T_{,x}}{T} \tag{6.3}$$

is a given function. If N and D are constants, we have

$$\mathcal{V} = V + \frac{N}{D} \ln \frac{T}{T_0} \tag{6.4}$$

which means that a thermodiffusion leads to a modification of the external potential V. Solution of equations of type (6.2) was discussed by Smoluchowski [18,19], *cf.* also Cherkasov [20] and Ricciardi [21].

Eq. (6.2) can be used as a mathematical model for the considered system. We take into account (5.9) as a potential V and (5.10) as a temperature distribution $T(x)$. Then $T_{,x} = T_1 - T_0$ and we make the approximation

$$\frac{T_{,x}}{T} \approx 2\frac{T_1 - T_0}{T_1 + T_0}.$$

From (6.3) we have

$$D\mathcal{V}_{,x} = Dg + 2\frac{T_1 - T_0}{T_1 + T_0}N. \tag{6.5}$$

In the equation

$$\frac{\partial f}{\partial t} = D\frac{\partial^2 f}{\partial x^2} + \; D\mathcal{V}_{,x}\frac{\partial f}{\partial x} \tag{6.6}$$

we change the scale of length and time as follows:

$$\xi = \frac{x}{x_0} \qquad \tau = \frac{D}{x_0^2}t \tag{6.7}$$

and obtain

$$\frac{\partial f}{\partial \tau} = \frac{\partial^2 f}{\partial \xi^2} + c\frac{\partial f}{\partial \xi}, \tag{6.8}$$

where

$$c = x_0\mathcal{V}_{,x} = \text{const.} \tag{6.9}$$

A solution of Eq. (6.8) for $(\xi,\tau) \in (0,\infty) \times (0,\infty)$ subject to the conditions

$$\begin{array}{ll} f(\xi,0) = \delta(\xi - 1), & \xi \in (0,\infty) \\ \dfrac{\partial f}{\partial \xi}(0,\tau) + cf(0,\tau) = 0, & \tau > 0 \\ f(\xi,\tau) \to 0, & \xi \to \infty, \tau > 0 \end{array} \tag{6.10}$$

takes the form

$$\begin{aligned} f(\xi,\tau) \;=\; & \frac{1}{2\sqrt{\pi\tau}}\left[\mathrm{e}^{\frac{(\xi-1)^2}{4\tau}} - \mathrm{e}^{-\frac{(\xi+1)^2}{4\tau}}\right]\mathrm{e}^{-c\frac{\xi-1}{2}-c^2\frac{\tau}{4}} \\ & +\frac{c}{\sqrt{\pi}}\mathrm{e}^{-c\xi}\int\limits_{\frac{\xi+1-c\tau}{2\sqrt{\tau}}}^{\infty} \mathrm{e}^{-z^2}dz. \end{aligned} \tag{6.11}$$

In Fig. 3 the function $f(\xi,\tau)$ and the corresponding heat source $r = r(\xi,\tau)$ as functions of ξ for a given moment of time are plotted. The interpretation of the heat source function $r = r(\xi)$ shown in Fig. 3 is the following: For $\xi < 1.1$, ($x < 1.1x_0$) a Brownian particle that falls in the gravity

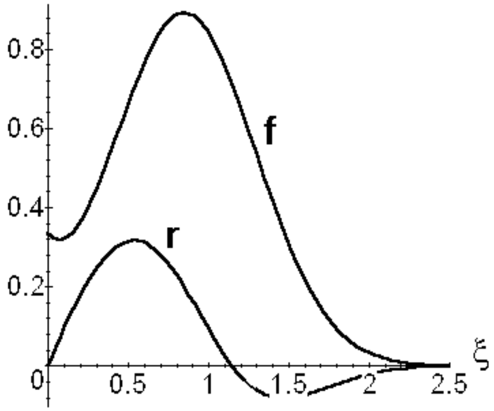

Fig. 3. The distribution f and the heat source r as function of ξ for $\tau = 1.5$, and for $c = 3 \times 10^{-15} J/\breve{x}$ and $g = 0.3 \times 10^{-15} J/\breve{x}$. The unit of f is $(\breve{x})^{-3}$ and the unit of r is $10^{-15} J(\breve{x})^{-3}(\breve{t})^{-1}$, where $\breve{x} \equiv x_0$ and $\breve{t} \equiv x_0^2/D$ are the new units of length and time, *cf.* Eq. (6.7).

field produces a positive amount of heat ($r > 0$). For $1.1 < \xi < \infty$ the particle goes up due to absorption of an environmental heat, which corresponds to $r < 0$ over that interval.

In Figs. 4, 5 and 6 the solution $f(\xi, x_0, \tau)$ as a function of ξ for a set of values of c and for fixed values of time τ is presented.

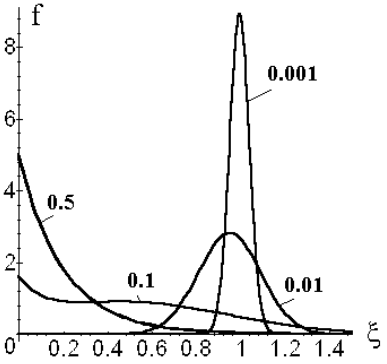

Fig. 4. The distribution f *versus* ξ for $c = 5$ and times $\tau = 0.001, 0.01, 0.1, 0.5$.

It follows from these figures that if

$$g + 2\frac{T_1 - T_0}{T_1 + T_0}\frac{N}{D}$$

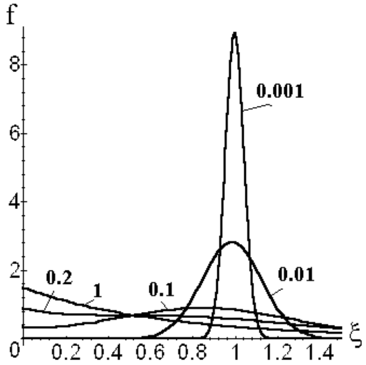

Fig. 5. The distribution f *versus* ξ for $c = 1.5$ and times $\tau = 0.001, 0.01, 0.1, 0.2, 1$.

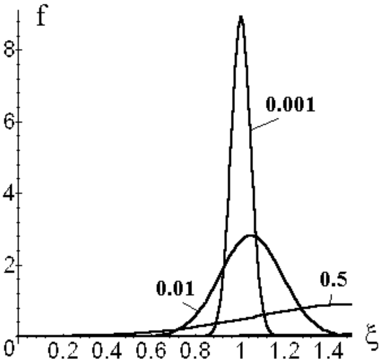

Fig. 6. The distribution f *versus* ξ for $c = -5$ and times $\tau = 0.001, 0.01, 0.1, 0.5$.

changes sign from positive to negative ($T_0 \gg T_1$) then c becomes negative, *cf.* Eqs. (6.5) and (6.9), and the Brown particles move towards a colder part of the region, *i.e.* most of them do not fall down in the gravitational field. This means that in case $c < 0$ the thermodiffusive forces are greater than the gravitational ones.

7. Conclusions

1. A consistent thermodynamic description of the motion of Brownian particles subject to both thermodiffusive forces and the gravity forces, is given following the Einstein–Smoluchowski and Streater approaches to the Brownian particle motion problem, *cf.* [22].

2. In particular, it is shown that the Brownian particles in a gravity field move upward provided the particles absorb the heat from the surrounding, and they fall down when they generate heat in a friction process.
3. A relation (4.5) between the coefficients of direct and reciprocal thermodiffusion is found, and verified using examples from the elementary gas theory (Appendix A) and the rarified gas theory (Appendix B).
4. A generalization of Streater's proposition regarding the Prigogine conjecture to include 3dim nonhomogeneous anisotropic case is also given.

Appendix A

Onsager relations in an elementary thermodiffusion theory

Let n, v, λ and ε be the number density of gas particles, the mean velocity of gas particles, the length of mean free path and the mean energy of a particle, respectively. Then a one-dimensional stream of particles j and of heat q is, respectively

$$j = -\frac{1}{6}\frac{d(nv)}{dx}2\lambda \quad \text{and} \quad q = -\frac{1}{6}\frac{d(\varepsilon v)}{dx}2\lambda, \tag{A.1}$$

where $\varepsilon = nsT$ and s is a number of particle degree of freedom. Since

$$\frac{1}{2}mv^2 \approx \frac{1}{2}sT, \tag{A.2}$$

where m is a mass of particle, we find that

$$v = \sqrt{\frac{sT}{m}}. \tag{A.3}$$

Hence

$$j = -\frac{1}{3}\lambda\left(v\frac{dn}{dx} + n\sqrt{\frac{s}{m}}\frac{1}{2\sqrt{T}}\frac{dT}{dx}\right)$$

and

$$q = -\frac{1}{3}\lambda\left(\frac{1}{2}sTv\frac{dn}{dx} + C_p\frac{dT}{dx}\right), \tag{A.4}$$

where $C_p = nd\varepsilon/dT$. Therefore, the thermodiffusion coefficients

$$M = \frac{1}{3}\lambda n\sqrt{\frac{s}{m}}\frac{1}{2\sqrt{T}} \qquad N = \frac{1}{3}\lambda\frac{1}{2}sTv \tag{A.5}$$

and

$$\frac{M}{N} = \frac{n}{sT^2}. \tag{A.6}$$

This is an expression of the type of Eq. (4.5). In a one-dimensional problem in which $s = 1$ the last equation is identical with (4.5).

Appendix B

Onsager relations in a Enskog–Chapman thermodiffusion theory

The set of thermodiffusion equations as derived from the Boltzmann equation for the gas mixture in which the partial density distribution of one constituent is $n_1 = n_1(\boldsymbol{r}, t)$ and the density distribution of the second constituent is $n_2 = n_2(\boldsymbol{r}, t)$, and the conditions of the constant pressure p prevail, reads

$$\begin{aligned} \boldsymbol{C}_1 - \boldsymbol{C}_2 &= -\frac{n^2}{n_1 n_2}\left(D_{12}\boldsymbol{d}_{12} + D_T \frac{1}{T}\frac{\partial T}{\partial \boldsymbol{r}}\right), \\ \boldsymbol{q} &= -\lambda \frac{\partial T}{\partial \boldsymbol{r}} + nTk_T\left(\boldsymbol{C}_1 - \boldsymbol{C}_2\right), \end{aligned} \tag{B.1}$$

where

$$\boldsymbol{d}_{12} \equiv \frac{\partial n_{10}}{\partial \boldsymbol{r}} - \frac{\rho_1 \rho_2}{p\rho}(\boldsymbol{F}_1 - \boldsymbol{F}_2), \qquad n_{10} \equiv \frac{n_1}{n} \quad \text{and} \quad p = nT, \tag{B.2}$$

cf. Chapman and Cowling [7], Chapter 8. Here, D_{12}, D_T and λ are the coefficients of diffusion, thermal diffusion and thermal conduction, respectively, while k_T is called the thermodiffusion ratio

$$k_T = \frac{D_T}{D_{12}}, \tag{B.3}$$

moreover, $\boldsymbol{C}_1$ and $\boldsymbol{C}_2$ are the mean peculiar velocities (measured relative to the mean mass velocity of the gas) of the particle of the constituent number 1 and of number 2, respectively; the number density of the s-th constituent is $n_s (s = 1, 2)$, the mass of the particle is m_s, the partial density of this constituent is $\rho_s = n_s m_s$ and the density ρ of the whole gas is $\rho = \rho_1 + \rho_2$. The total number density is denoted by $n = n_1 + n_2$. We combine equations of (B.1) and obtain

$$\begin{aligned} \boldsymbol{C}_1 - \boldsymbol{C}_2 &= -\frac{n^2}{n_1 n_2}\left(D_{12}\boldsymbol{d}_{12} + D_T \frac{1}{T}\frac{\partial T}{\partial \boldsymbol{r}}\right), \\ \boldsymbol{q} &= -TD_T \frac{n^3}{n_1 n_2}\boldsymbol{d}_{12} - \left(\lambda + k_T \frac{n^3}{n_1 n_2} D_T\right)\frac{\partial T}{\partial \boldsymbol{r}}. \end{aligned} \tag{B.4}$$

For the case of Brownian particle

$$n_1 \ll n_2 \qquad \text{thus} \quad n_2 \approx n.$$

Then

$$\boldsymbol{d}_{12} = \frac{1}{n}\frac{\partial n_1}{\partial \boldsymbol{r}} - \frac{\rho_1}{nT}(\boldsymbol{F}_1 - \boldsymbol{F}_2)$$

and instead of (B.4) we have the following system

$$\begin{aligned} n_1(\boldsymbol{C}_1 - \boldsymbol{C}_2) &= -\left[\frac{\partial n_1}{\partial \boldsymbol{r}} - \frac{\rho_1}{T}(\boldsymbol{F}_1 - \boldsymbol{F}_2)\right] - nD_T\frac{1}{T}\frac{\partial T}{\partial \boldsymbol{r}}, \\ \boldsymbol{q} &= -TD_T\frac{n}{n_1}\left[\frac{\partial n_1}{\partial \boldsymbol{r}} - \frac{\rho_1}{T}(\boldsymbol{F}_1 - \boldsymbol{F}_2)\right] - \left(\lambda + k_T\frac{n^2}{n_1}D_T\right)\frac{\partial T}{\partial \boldsymbol{r}}. \end{aligned} \tag{B.5}$$

Comparing the system (B.5) with Eq. (2.1) we find

$$M = \frac{n}{T}D_T \qquad N = TD_T\frac{n}{n_1}. \tag{B.6}$$

Hence

$$\frac{M}{N} = \frac{n_1}{T^2}. \tag{B.7}$$

If the distribution function f is identified with the number density n_1 then Eq. (B.7) is identical with Eq. (4.5).

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