

## THEORY OF THERMAL DIFFUSION OF BROWNIAN PARTICLES

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A calculation of the thermal diffusion coefficient of Brownian particles is made by using an idea of Luttinger, who suggested the introduction of an auxiliary dynamical field such that the matter and energy fluxes arising through its action are related to those that arise when there is a temperature gradient in the system. It is shown that the thermal diffusion coefficient  $\tilde{\beta}$  of the Brownian particles is connected with the diffusion coefficient  $D$  by the relation  $\tilde{\beta} = Dn/T$ .

## INTRODUCTION

SERIOUS difficulties are often encountered in the solution of problems of calculating kinetic coefficients in the presence of a temperature gradient (thermoelectric emf, thermal diffusion, thermal conductivity). For example, such difficulties arise when the problem is essentially a quantum one, or even in the classical problem, if the departure of the system from equilibrium is not described by the one-particle distribution function.

There have been several papers<sup>[1,2]</sup> whose purpose was to give a general solution of this problem analogous to the Kubo formula<sup>[3]</sup> in the theory of electric conductivity. The results of these papers are formulas expressing the kinetic coefficients in terms of the correlation functions of the matter and energy fluxes. These formulas, however, are in a certain sense without content, since the method used to derive them does not give any recipe for an unambiguous determination of the operators for the matter and energy fluxes. Actually, the choice of these operators has to be motivated by definite physical conditions, analogous to those that were formulated by Obraztsov<sup>[4]</sup> in the problem of the thermoelectric emf of electrons in a quantizing magnetic field.

There has recently appeared a paper by Luttinger<sup>[5]</sup> in which an auxiliary field is introduced which is chosen so that the matter and energy fluxes that arise in the system under the action of the field are the same as those that arise under the action of a temperature gradient. Among actual fields, a relativistic gravitational field has this property. Despite the fact that the final result derived by Luttinger in general form suffers from the same shortcomings as the papers mentioned

earlier,<sup>[1,2]</sup> the idea of the auxiliary field seems to us to be a very fruitful one.

In the present paper this idea is applied to the problem of thermal diffusion of Brownian particles. It is shown that the thermal diffusion coefficient  $\tilde{\beta}$  is connected with the diffusion coefficient  $D$  by the relation

$$\tilde{\beta} = Dn / T,$$

where  $n$  is the concentration of the particles. For this purpose we introduce in Sec. 1 a purely formal auxiliary field which does not exist in nature. In particular, one could also introduce an actual relativistic gravitational field. By a consistent use of the apparatus of general relativity it can be shown that this leads to the same result for  $\tilde{\beta}$ .

## 1. INTRODUCTION OF THE AUXILIARY FIELD

We consider particles which are in an external field  $\varphi(\mathbf{r})$  and in this field have a Hamiltonian function of the form<sup>1)</sup>

$$\mathcal{H}(\mathbf{p}, \mathbf{r}) = p^2 / 2m(1 + \varphi(\mathbf{r})). \quad (1.1)$$

The equations of motion are the canonical equations

$$\dot{\mathbf{r}} = \mathbf{v} = \frac{\partial \mathcal{H}}{\partial \mathbf{p}} = \frac{\mathbf{p}}{m(1 + \varphi)}, \quad (1.2)$$

$$\dot{\mathbf{p}} = -\frac{\partial \mathcal{H}}{\partial \mathbf{r}} = \frac{mv^2}{2} \frac{\partial \varphi}{\partial \mathbf{r}}. \quad (1.3)$$

From (1.2) and (1.3) it is easy to derive the equation

$$\dot{v}_i = \frac{1}{(1 + \varphi)} \left( \frac{v^2}{2} \frac{\partial \varphi}{\partial x_i} - v_i v_h \frac{\partial \varphi}{\partial x_h} \right). \quad (1.4)$$

<sup>1)</sup>There is evidently no such field in nature, but this is of no importance for what follows.

In a state of thermodynamic equilibrium the distribution function of such a gas is of the form

$$\tilde{f}(\mathbf{p}, \mathbf{r}) = \exp\left\{-\frac{p^2}{2m(1+\varphi)T_0} + \frac{\mu_0}{T_0}\right\}, \quad (1.5)$$

where  $\mu_0$  and  $T_0$  are the thermodynamic chemical potential and the thermodynamic temperature, which in the equilibrium state are independent of the coordinates. The function  $f$  is normalized so that

$$\int \tilde{f}(\mathbf{p}, \mathbf{r}) d\tau_p = n(\mathbf{r}). \quad (1.6)$$

Instead of this function it is convenient to introduce a function  $f$  normalized by the condition

$$\int f(\mathbf{v}, \mathbf{r}) d^3v = n(\mathbf{r}). \quad (1.7)$$

It is easy to see that

$$f(\mathbf{v}, \mathbf{r}) = n \left(\frac{m}{2\pi T}\right)^{3/2} \exp\left\{-\frac{mv^2}{2T}\right\}, \quad (1.8)$$

where

$$T = T_0 / (1 + \varphi), \quad (1.9)$$

$$f = \text{const} \cdot \tilde{f}(1 + \varphi)^3. \quad (1.10)$$

Here  $T$  is the "physical" temperature, determined from the mean square speed of the gas particles. In the equilibrium state it is not a constant, but depends on the coordinates, while

$$T(1 + \varphi) = \text{const}. \quad (1.9')$$

The difference between the physical and thermodynamical temperatures is an unavoidable consequence of the Hamiltonian (1.1). An effect of this sort occurs in nature when there is a relativistic gravitational field.<sup>[6]</sup>

The dependence of the equilibrium temperature on the coordinates can be obtained by substituting (1.5) in (1.6). We get

$$\frac{\mu_0}{T_0} = \ln \frac{n(\mathbf{r}) (2\pi\hbar)^3}{(2\pi m T_0)^{3/2} (1 + \varphi)^{3/2}} = \text{const}. \quad (1.11)$$

From this we find

$$n(\mathbf{r}) (1 + \varphi)^{-3/2} = \text{const}.$$

Let  $\mu(n, T)$  be the "physical" chemical potential of the ideal gas:

$$\mu(n, T) = T \ln \frac{n(2\pi\hbar)^3}{(2\pi m T)^{3/2}}. \quad (1.12)$$

Then

$$\mu_0 / T_0 = \mu / T - 3 \ln(1 + \varphi). \quad (1.13)$$

Let us now proceed to dissipative processes. If a one-component gas is not in a state of thermo-

dynamic equilibrium, an energy flux  $\mathbf{q}$  arises in it which is proportional to the gradient of the thermodynamic temperature. Therefore in the presence of the field  $\varphi$  ( $\varphi \ll 1$ )

$$\mathbf{q} = -\kappa \nabla [T(1 + \varphi)] = -\kappa \nabla T - \kappa T \nabla \varphi, \quad (1.14)$$

where  $\kappa$  is the thermal conductivity coefficient.

In a mixture of gases or in a solid the approach to equilibrium is also accompanied by diffusion and thermal diffusion. In this case there is a particle flux  $\mathbf{i}$  proportional to the gradients of the thermodynamic chemical potential and of the temperature. Using (1.13), we get

$$\mathbf{i} = -\tilde{\alpha} \nabla \left[ \frac{\mu}{T} - 3 \ln(1 + \varphi) \right] - \beta \nabla [T(1 + \varphi)], \quad (1.15)$$

where  $\tilde{\alpha}$  and  $\beta$  are kinetic coefficients, or

$$\mathbf{i} = -\alpha \nabla \mu - \gamma \nabla T - \delta \nabla \varphi; \quad (1.16)$$

$$\gamma = \beta - \alpha \mu / T, \quad \alpha = \tilde{\alpha} / T; \quad (1.17)$$

$$\delta = \beta T - 3\alpha T. \quad (1.18)$$

The coefficient  $\alpha$  is connected with the diffusion coefficient  $D$  by the relation

$$\alpha T / n = D. \quad (1.19)$$

On the other hand, it is easy to calculate  $D$  by means of the Einstein relation. Therefore to calculate  $\gamma$  it is sufficient to determine the coefficient  $\delta$ . In order to do this, we shall argue as follows, following Luttinger.<sup>[5]</sup> Suppose that initially, for  $t \rightarrow -\infty$ , there was no field  $\varphi$ . We then turn it on according to the law  $\varphi = \varphi_0 e^{i\mathbf{k} \cdot \mathbf{r} + s \cdot t}$ , choosing  $s$  so that

$$1 / \tau_M \ll s \ll 1 / \tau, \quad (1.20)$$

where  $\tau$  is the microscopic relaxation time in the system and  $\tau_M$  is the macroscopic time for equalization of concentrations or temperatures ( $\tau_M^{-1} \sim k^2 D$  or  $\tau_M^{-1} \sim k^2 \chi$ , where  $\chi$  is the temperature conductivity). Then initially and also immediately after the turning on of the field the physical temperature  $T$  and the chemical potential  $\mu$  were constants. Thereafter they gradually change, and after the time  $\tau_M$  take the equilibrium values given by (1.9) and (1.13). This means that immediately after the turning on of the field the system was not in a state of equilibrium, since in it there were gradients of the thermodynamic temperature (defined as the derivative of the energy of a volume element with respect to its entropy) and of the chemical potential, which get equalized during the time  $\tau_M$  by the matter and energy fluxes which are set up.

The condition  $s \gg \tau_M^{-1}$  means that we can set

$\mu = \text{const}$  and  $T = \text{const}$  in (1.14) and (1.16) and obtain the coefficients  $\delta$  and  $\kappa$  by calculating the matter and energy fluxes in the field  $\varphi$ , and then, knowing  $\alpha$ , obtain the coefficient  $\gamma$  from (1.17). The condition  $s \ll \tau^{-1}$  is necessary so that the kinetic coefficients will not contain any temporal dispersion, i.e., not depend on  $s$ . The condition  $\tau_M \gg \tau$  is always satisfied if the nonuniformity of the field is sufficiently weak.

We note that the arguments given here are in essence the same<sup>[5]</sup> as those in which the Einstein relation is used.

2. SOME EXAMPLES OF THE SIMPLEST SORT

Let us consider a one-component gas which is in a field  $\varphi$ . Using (1.10), we can obtain the kinetic equation for the function  $f$ , which is of the following form:

$$\frac{\partial f}{\partial t} + \frac{\partial f}{\partial \mathbf{r}} \mathbf{v} - \frac{3}{(1 + \varphi)} f \frac{\partial \varphi}{\partial \mathbf{r}} \mathbf{v} + \frac{\partial f}{\partial \mathbf{v}} \dot{\mathbf{v}} + I(ff_1) = 0. \tag{2.1}$$

Here  $I(ff_1)$  is the usual collision integral for a gas (cf., e.g.,<sup>[7]</sup>), in which the integration is taken over  $d^3v_1$  and over the two collision parameters.

We integrate this equation over  $d^3v$  with the weight factors 1,  $m\mathbf{v}$ , and  $m\mathbf{v}^2/2$ . The results are the system of hydrodynamic equations:

$$\frac{\partial n}{\partial t} + \text{div}(n\mathbf{v}_0) = 0, \tag{2.2}$$

$$\rho \left[ \frac{\partial v_{0i}}{\partial t} + \left( v_{0k} \frac{\partial}{\partial x_k} \right) v_{0i} \right] + \frac{\partial p_{ik}}{\partial x_k} + \frac{1}{(1 + \varphi)} \left[ p_{ik} + \rho v_{0i} v_{0k} - \frac{3}{2} nT \delta_{ik} - \rho \frac{v_0^2}{2} \delta_{ik} \right] \frac{\partial \varphi}{\partial x_k} = 0, \tag{2.3}$$

$$\frac{\partial T}{\partial t} + \mathbf{v}_0 \frac{\partial T}{\partial \mathbf{r}} + \frac{2}{3} \frac{1}{n} \left( \text{div} \mathbf{q} + p_{\alpha\beta} \frac{\partial v_{0\alpha}}{\partial x_\beta} \right) + \frac{2T}{(1 + \varphi)} \mathbf{v}_0 \frac{\partial \varphi}{\partial \mathbf{r}} = 0, \tag{2.4}$$

where

$$n\mathbf{v}_0 = \int f \mathbf{v} d^3v, \quad \rho = nm.$$

$$\frac{3}{2} nT = \int f \frac{m(v - v_0)^2}{2} d^3v,$$

$$p_{\alpha\beta} = m \int f (v_\alpha - v_{0\alpha})(v_\beta - v_{0\beta}) d^3v = nT \delta_{\alpha\beta} - \sigma_{\alpha\beta}';$$

$\sigma'_{\alpha\beta}$  describes the viscosity of the gas, and  $\mathbf{q}$  the flux of energy:

$$\mathbf{q} = \int f \frac{mv^2}{2} (1 + \varphi) \mathbf{v} d^3v.$$

An unusual feature of Eq. (2.3) is that there is a pressure gradient for  $\mathbf{v}_0 = 0$ . It is, however, easy

to see from (1.11) and (1.9) that in equilibrium  $p = nT$  satisfies the equation

$$\frac{\partial p}{\partial x_i} = \frac{1}{2} \frac{nT}{(1 + \varphi)} \frac{\partial \varphi}{\partial x_i},$$

which follows from Eq. (2.3). Equation (2.4) can be rewritten in the form

$$\frac{\partial}{\partial t} (ns_0) + \text{div}(ns_0\mathbf{v}_0) = -\frac{1}{T} \frac{\text{div} \mathbf{q}}{(1 + \varphi)} + \sigma_{\alpha\beta}' \frac{\partial v_{0\alpha}}{\partial x_\beta}, \tag{2.5}$$

where

$$ns_0 = - \int \tilde{f}_p \ln \frac{\tilde{f}_p}{e} d\tau_p$$

is the entropy per unit volume.

We can solve Eq. (2.1) by the Chapman-Enskog method<sup>[7]</sup> and find an explicit expression for the flux  $\mathbf{q}$ . It turns out that

$$\mathbf{q} = -\kappa \nabla [T(1 + \varphi)], \tag{2.6}$$

where  $\kappa$  is the ordinary thermal conductivity of the gas, so that this confirms the phenomenological arguments of Sec. 1.

As a second simple example we consider the calculation of the coefficient  $\gamma$  in Eq. (1.16) for semiconductors with an isotropic and quadratic spectrum of charge carriers. As has already been said, this problem can be solved by making a calculation of the current proportional to  $\nabla\varphi$ . Using the approximation of the relaxation time for simplicity, we get from Eq. (2.1)

$$-\frac{3}{(1 + \varphi)} f^0 \frac{\partial \varphi}{\partial \mathbf{r}} \mathbf{v} + \frac{\partial f^0}{\partial \mathbf{v}} \mathbf{v} = -\frac{f^{(1)}}{\tau}, \tag{2.7}$$

where  $f = f^0 + f^{(1)}$ , and  $f^0$  is the equilibrium distribution function with constant  $T$  and  $\mu$ .

Substituting the value of  $\dot{\mathbf{v}}$  from (1.4), we get

$$\begin{aligned} f^{(1)} &= f^0 \left( 3 - \frac{mv^2}{2T} \right) \frac{\partial \varphi}{\partial \mathbf{r}} \mathbf{v} \tau, \\ i_\alpha &= \frac{1}{3} \frac{\partial \varphi}{\partial x_\alpha} \sum_p f^0 v^2 \left( 3 - \frac{mv^2}{2T} \right) \tau, \\ \delta &= -\frac{1}{3} \sum_p f^0 v^2 \left( 3 - \frac{mv^2}{2T} \right) \tau. \end{aligned} \tag{2.8}$$

The quantity  $\alpha$  can be found independently:

$$\alpha = \frac{1}{3} \sum_p f^0 v^2 \tau. \tag{2.9}$$

Finally, from (1.17) and (1.18) we have the result:

$$\gamma = \frac{1}{3} \frac{1}{T} \sum_p f^0 v^2 \left( \frac{mv^2}{2T} - \frac{\mu}{T} \right) \tau, \tag{2.10}$$

which can easily be obtained by introducing the temperature gradient into the kinetic equation in the usual way.

### 3. THERMAL DIFFUSION OF BROWNIAN PARTICLES

Let us imagine Brownian particles which are in a liquid or gas in which there is a temperature gradient, but no pressure gradient and consequently no mass transfer. Then besides the Brownian motion the particles will have also a directed velocity from the hot end to the cold end. The cause of this motion is as follows. A particle at a given point has equal probabilities of going to the right or the left owing to fluctuations, but if the temperature is higher on the right, then if the particle goes there it will make its next transition more quickly than if it had gone to the left. The result of this is that the particle will be repelled from the hot region into the cold one.

The considerations developed in Sec. 1 enable us to give a theory of this effect without difficulty. For this purpose we are to find the flux of particles in the field  $\varphi$ . When this field is turned on the particles begin to move with acceleration, but owing to the fact that the force of resistance, which we shall call the Stokes force, is proportional to the velocity, this motion becomes a uniform one after a certain time. This velocity can be found from the following arguments.

In the linear approximation in  $\varphi$  and  $\nabla\varphi$  the equation of motion in the field  $\varphi$  is

$$m\dot{v}_i = m\left(\frac{v^2}{2}\delta_{ik} - v_i v_k\right)\frac{\partial\varphi}{\partial x_k} + A_i(t) - 6\pi\eta R v_i. \quad (3.1)$$

Here  $A_i(t)$  is the random force,  $\eta$  is the viscosity of the medium in which the motion occurs, and  $R$  is the radius of the spherical Brownian particle.

Let us average Eq. (3.1) over the time. Since on the average the motion of the particle is uniform,  $\overline{v}_i = 0$ . Moreover,  $\overline{A_i(t)} = 0$ . Then

$$\overline{v}_i = \frac{1}{2} \frac{T}{6\pi\eta R} \frac{\partial\varphi}{\partial x_i}, \quad (3.2)$$

$$\delta = -\frac{1}{2} \frac{nT}{6\pi\eta R}. \quad (3.3)$$

As is known from the theory of the Brownian motion,<sup>[8]</sup>

$$D = T / 6\pi\eta R, \quad \delta = -1/2 Dn. \quad (3.4)$$

Using (1.17)–(1.19), we get

$$\gamma = -\frac{Dn\mu}{T^2} + \frac{5}{2} \frac{Dn}{T}, \quad (3.5)$$

which solves the stated problem.

When there is no field  $\varphi$  the expression (1.16) can also be written in the form

$$\mathbf{i} = -D\nabla n - \tilde{\beta}\nabla T, \quad (3.6)$$

where

$$\beta = \gamma + \alpha\partial\mu / \partial T. \quad (3.7)$$

Using (1.12), we get

$$\tilde{\beta} = Dn / T. \quad (3.8)$$

Consequently (3.6) can be rewritten in the form

$$\mathbf{i} = -T^{-1}D\nabla(nT). \quad (3.9)$$

This means that if a situation is produced in which the flux is zero, the particles are distributed so that the gradient of their osmotic pressure is zero.

We point out that in our opinion this is not a trivial result. For example, it does not hold in the usual problem of the thermal diffusion in a gas mixture with binary collisions, nor for electrons in a solid, where the expression for the thermoelectric emf contains parameters associated with the scattering.

### 4. RIGOROUS THEORY OF THE THERMAL DIFFUSION OF BROWNIAN PARTICLES IN A GAS

The theory expounded in Sec. 3 is not fully consistent, in the sense that we took the medium in which the Brownian motion occurs to be neutral in relation to the field  $\varphi$ . Physically this means that it is assumed that the presence of a thermal flux in the medium has no effect on the motion of the Brownian particles. In this section we shall prove the legitimacy of this assumption for the case in which the medium is a gas. It is reasonable to suppose that replacement of the gas by a liquid cannot lead to the appearance or disappearance of an effect of this sort.

Accordingly, let us consider the Brownian particles and the medium surrounding them as a mixture of two ideal gases. The quantity that plays the role of the chemical potential for such a mixture is<sup>[8]</sup>

$$\mu = \mu_1 / m_1 - \mu_2 / m_2. \quad (4.1)$$

We shall use the index 1 for the Brownian particles, and 2 for the molecules of the medium. The quantities  $\mu_1$  and  $\mu_2$  are given in terms of the concentrations by Eq. (1.12).

In the absence of the field  $\varphi$  the flux of one component relative to the other can be written in the form

$$\mathbf{i} = -\alpha\nabla\mu - \gamma\nabla T. \quad (4.2)$$

By using Eq. (1.13), it is easy to show that the quantities that are constant in the presence of the field  $\varphi$  are

$$\begin{aligned} \mu_0 / T_0 &= \mu / T - (1 / m_1 - 1 / m_2) 3 \ln (1 + \varphi), \\ T_0 &= T(1 + \varphi). \end{aligned}$$

Therefore in this case we must write

$$\begin{aligned} \mathbf{i} &= -\tilde{\alpha} \nabla [\mu / T - 3(1 / m_1 - 1 / m_2) \ln (1 + \varphi)] \\ &\quad - \beta \nabla [T(1 + \varphi)] \end{aligned} \tag{4.3}$$

or

$$\begin{aligned} \mathbf{i} &= -\alpha \nabla \mu - \gamma \nabla T - \delta \nabla \varphi, \\ \gamma &= \delta / T + 3\alpha(1 / m_1 - 1 / m_2) - \alpha \mu / T, \\ \tilde{\alpha} &= \alpha T. \end{aligned} \tag{4.4}$$

Thus we have again expressed the coefficient  $\gamma$  in terms of  $\delta$  and  $\alpha$ . In order to obtain  $\delta$  we must calculate the velocity of one component relative to the other in the field  $\varphi$ .

The motion of the gas surrounding the Brownian particles is determined by Eqs. (2.2)–(2.4). Furthermore it is easy to see that we can turn the field on so rapidly that the motion will occur with constant  $n$ ,  $T$ , and  $p$ . The equation of motion then takes the form

$$n_2 m_2 \mathbf{v}_2 = \frac{1}{2} n_2 T \partial \varphi / \partial \mathbf{r}. \tag{4.5}$$

An analog of this sort of motion is a gas flowing in a gravitational field because the time for establishing the barometric equilibrium distribution [ $\sim (k^2 D)^{-1}$ ] is much longer than the time in which the field has been turned on.

The Brownian particles will move initially with a different acceleration. Very soon, however, the Stokes force will make their acceleration equal to that of the gas. Of course it is necessary that the time for establishing this motion, which in this case plays the role of the time  $\tau$ , be much smaller than the time  $\tau_M$ ; this condition is always satisfied for sufficiently small  $k$ .

The speed of the uniform motion of the two components relative to each other can be found from the following considerations. The equation of motion of the Brownian particles is

$$\begin{aligned} m_1 \dot{v}_{1i} &= m_1 (\frac{1}{2} v^2 \delta_{ih} - v_i v_h) \partial \varphi / \partial x_h \\ &\quad + A_i(t) - 6\pi\eta R (v_{1i} - v_{2i}). \end{aligned} \tag{4.6}$$

We average (4.6) over time, and when we use the fact that

$$\overline{\dot{\mathbf{v}}_1} = \overline{\dot{\mathbf{v}}_2} = \frac{1}{2} \frac{T}{m_2} \frac{\partial \varphi}{\partial \mathbf{r}},$$

we get

$$\overline{\mathbf{v}_1 - \mathbf{v}_2} = \frac{1}{2} \frac{T}{6\pi\eta R} \frac{m_2 - m_1}{m_2} \frac{\partial \varphi}{\partial \mathbf{r}}. \tag{4.7}$$

From this we get

$$\delta = -\frac{1}{2} \frac{T n_1}{6\pi\eta R} \left( 1 - \frac{m_1}{m_2} \right), \tag{4.8}$$

and by using (4.4) we can find  $\gamma$ .

In ignoring the influence of the Brownian particles on the motion of the medium we have actually been assuming that  $n_1 \ll n_2$ ,  $m_1 n_1 \ll m_2 n_2$ . Assuming this also in what follows, we can conveniently take the chemical potential  $\mu$  as a function of the variables  $n_1$ ,  $p$ ,  $T$ , where  $p = (n_1 + n_2)T$ . Then we can rewrite Eq. (4.2) in the form

$$\mathbf{i} = -n_1 D \left( \frac{\nabla n_1}{n_1} + k_p \frac{\nabla p}{p} + k_T \frac{\nabla T}{T} \right), \tag{4.9}$$

where

$$D = \alpha \partial \mu / \partial n_1,$$

$$k_p = \frac{p}{n_1} \left( \frac{\partial \mu}{\partial p} \right)_{n_1, T} \left| \left( \frac{\partial \mu}{\partial n_1} \right)_{p, T} \right|, \tag{4.10}$$

$$k_T = \frac{T}{n_1} \left( \frac{\partial \mu}{\partial T} \right)_{n_1, p} \left| \left( \frac{\partial \mu}{\partial n_1} \right)_{p, T} \right| + \frac{\gamma T}{n_1 D}, \tag{4.11}$$

or, when we substitute (4.4) in (4.1),

$$\begin{aligned} k_T &= \frac{T}{n_1 (\partial \mu / \partial n_1)_{p, T}} \left[ \left( \frac{\partial \mu}{\partial T} \right)_{n_1, p} - \frac{\mu}{T} + 3 \left( \frac{1}{m_1} - \frac{1}{m_2} \right) \right] \\ &\quad + \frac{\delta}{D n_1}. \end{aligned} \tag{4.12}$$

The derivatives that appear in (4.10)–(4.12) can be calculated easily, and we get

$$k_p = -\frac{m_1}{m_2}; \quad k_T = -\frac{1}{2} \frac{m_1}{m_2} + \frac{3}{2} + \frac{\delta}{n_1 D}. \tag{4.13}$$

Substituting (4.8) in (4.13) and using (3.4), we get

$$k_T = 1. \tag{4.14}$$

From here on it is immaterial whether we regard the process as occurring at constant total pressure  $p$  or at constant gas pressure  $n_2 T$ . In the former case  $\nabla p = 0$  exactly in (4.9), and in the latter case this term is of the order of  $n_1^2$ .

Accordingly, we have finally from (4.9) and (4.14)

$$\mathbf{i} = -D \nabla n_1 - T^{-1} D n_1 \nabla T,$$

which is the same as Eq. (3.9).

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