BROWNIAN MOTION IN THE PRESENCE OF A TEMPERATURE GRADIENT

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Abstract

By considering an ensemble of Brownian particles suspended in a heat bath as a thermodynamic system with an internal degree of freedom it is possible to obtain the Fokker-Planck equation for Brownian motion in a temperature gradient, by applying the scheme of non-equilibrium thermodynamics. We recover explicitly the equations derived in particular by Zubarev and Bashkirov using statistical mechanical and kinetic methods. In addition when the temperature gradient does not have an externally imposed magnitude we obtain the differential equation for the temperature field, which is coupled to the Fokker-Planck equation.
1 Introduction

In 1965, Nicolis [1] considered the problem of Brownian motion in a temperature gradient by kinetic methods and derived an expression for the thermal diffusion coefficient in this system. A few years later, in 1968, Zubarev and Bashkirov [2] reconsidered this problem using the methods developed by Zubarev for treating non-equilibrium systems. They explicitly derive the Fokker-Planck equation for this case. In addition they recovered Nicolis’ expression for the thermal diffusion coefficient. On the other hand Prigogine and Mazur [3], [4] introduced already in 1953 the concept of internal degrees of freedom into the formalism of non-equilibrium thermodynamics and pointed out that in this way Fokker-Planck like equations could be obtained. Meixner [5] gave a more general framework for the derivation of kinetic equations within this context.

In this paper we apply the non-equilibrium thermodynamic method of internal degrees of freedom to Brownian motion in a temperature gradient and thus derive in a simpler way the Fokker-Planck equation for this case. We do not consider the temperature gradient as given but establish also the coupled differential equation for the temperature field. In section 2 we consider the Brownian particles suspended in a nonuniform heat bath as a system with an internal degree of freedom, the velocity \( \vec{u} \) of the particles. We state the corresponding Gibbs equation for the total differential of entropy per unit volume and give the conservation laws for mass and energy. The entropy balance equation is established in section 3, where we also give expressions for the entropy flux and the entropy source strength. In section 4 we follow the principles of non-equilibrium thermodynamics to formulate the linear phenomenological laws for the dissipative fluxes occurring in the entropy source strength, also for those pertaining to the internal coordinate space. By substitution we then obtain the Fokker-Planck equation and the coupled differential equation for the temperature field. Finally, in section 5 we discuss the thermal-diffusion regime in which the Fokker-Planck equation may be replaced by a simpler differential equation for the density of the Brownian particles.

2 The Brownian gas as a thermodynamic system with an internal degree of freedom

Consider a dilute ‘gas’ of Brownian particles of mass \( m \) suspended in a heat bath at rest with constant mass density \( \rho_H \). The Brownian gas has an internal degree of freedom -internal coordinate- namely the velocity \( \vec{u} \) of a Brownian particle. The mass density of the Brownian particles of velocity \( \vec{u} \) at position \( \vec{r} \) and time \( t \) in the heat bath is \( \rho(\vec{u}, \vec{r}, t) \) while

\[
f(\vec{u}, \vec{r}, t) = \rho(\vec{u}, \vec{r}, t)/m
\]
is the probability density for the Brownian particles in velocity-coordinate space, which may be viewed as an internal thermodynamic variable.

The system, Brownian gas and heat bath, has mass density \( \rho(\vec{r}, t) \)

\[
\rho = \rho_H + \rho_B = \rho_H + m \int f(\vec{u}, \vec{r}, t) d\vec{u},
\]

and energy \( e(\vec{r}, t) \) and entropy \( s(\vec{r}, t) \) per unit of mass.

Since \( \rho_H \) is constant, the Gibbs equation for this system can be written as

\[
\delta \rho s = \frac{1}{T} \delta pe - \frac{m}{T} \int \mu(\vec{u}, \vec{r}, t) \delta f(\vec{u}, \vec{r}, t) d\vec{u}
\]

(2.3)

where \( \delta \) denotes the total differential of a quantity and where \( \mu(\vec{u}, \vec{r}, t) \) is the chemical potential per unit mass of the Brownian gas component with internal coordinate \( \vec{u} \); \( T(\vec{r}) \) is the temperature of the heat bath at position \( \vec{r} \).

The chemical potential \( \mu(\vec{u}, \vec{r}, t) \) is related to the energy \( e \) and entropy \( s \) by

\[
\int \rho(\vec{u}, \vec{r}, t) \mu(\vec{u}, \vec{r}, t) d\vec{u} + \rho_H \mu_H = \rho e - T \rho s + p
\]

(2.4)

Here \( \mu_H \) is the chemical potential of the heat bath and \( p \) the system’s hydrostatic pressure.

For the quantities \( \rho(\vec{u}, \vec{r}, t) = f(\vec{u}, \vec{r}, t)/m \) and \( e \), conservation laws may be written down. Let us first deal with conservation of mass. For the rate of change with time of \( f(\vec{u}, \vec{r}, t) \), one may formally write

\[
\frac{\partial f}{\partial t} = -\vec{v} \cdot \frac{\partial f}{\partial \vec{r}} - \frac{\partial}{\partial \vec{u}} \cdot \vec{J}_\vec{u} = -\vec{u} \cdot \frac{\partial f}{\partial \vec{r}} - \frac{\partial}{\partial \vec{u}} \cdot \vec{J}_\vec{u}
\]

(2.5)

where \( \vec{J}_\vec{u} \) represents a flux in velocity space which results from the interaction with the heat bath (there is no external field of force acting on the Brownian particles).

Integrating eq. (2.5) over velocity \( \vec{u} \) we obtain the law of conservation of mass for the Brownian particles

\[
\frac{\partial \rho_B}{\partial t} = -\nabla \cdot \rho_B \vec{v}_B
\]

(2.6)

where \( \rho_B \) is the mass density of the Brownian particles, c.f. eq.(2.2), and \( \vec{v}_B(\vec{r}, t) \),

\[
\vec{v}_B(\vec{r}, t) = \rho_B^{-1} \int \rho(\vec{u}, \vec{r}, t) \vec{u} d\vec{u},
\]

(2.7)
their mean velocity.

The law of conservation of energy can be formulated as follows

$$\frac{\partial \rho e}{\partial t} = -\nabla \cdot \vec{J}_q \quad (2.8)$$

where $\vec{J}_q$ represent a heat flux defined in the reference frame in which the heat bath is at rest.

In the next section we shall derive, using the Gibbs equation (2.3) and the conservation laws (2.5) and (2.8), the entropy balance equation for the Brownian gas.

## 3 Entropy balance and entropy source strength

Before deriving an expression for the entropy production in the system described in section 2, we note that the Brownian gas, i.e. the suspension of Brownian particles in the heat bath, may be considered to be a many component ideal solution of 'components' with mass density $\rho(\vec{u}, \vec{r}, t)$ and that the thermodynamic potential $\mu(\vec{u}, \vec{r}, t)$ is therefore of the form (with $k$ Boltzmann’s constant)

$$\mu(\vec{u}, \vec{r}, t) = \frac{kT}{m} ln f(\vec{u}, \vec{r}, t) + C(\vec{u}, \vec{r}, t) \quad (3.1)$$

The potential function $C(\vec{u}, \vec{r}, t)$ which depends on the internal coordinate $\vec{u}$, can in principle still be a function of the local thermodynamic state variables $T(\vec{r})$ and $\rho_B(\vec{r}, t)$.

Consider now the gas to be in local equilibrium, i.e. in the state of internal equilibrium which would be reached if the system were locally insulated at temperature $T(\vec{r})$ and mass density $\rho_B(\vec{r}, t)$. The chemical potential $\mu(\vec{u}, \vec{r}, t)$ and the distribution function $f(\vec{u}, \vec{r}, t)$ must then satisfy the following requirements:

1. Since entropy at constant energy and constant density of Brownian particles has in that state a maximum as a function of the internal states $\rho(\vec{u}, \vec{r}, t)$, $\mu^{\text{eq}}(\vec{u}, \vec{r}, t)$ is uniform in velocity space and equal to $\mu_B(\vec{r}, t)$ the thermodynamic potential of a Brownian ideal gas at temperature $T(\vec{r})$ and density $\rho_B(\vec{r}, t)$

$$\mu^{\text{eq}}(\vec{u}, \vec{r}, t) = \mu_B \equiv \frac{kT}{m} \left( ln \frac{\rho_B}{m} - \frac{3}{2} \ln \frac{2\pi kT}{m} \right) \quad (3.2)$$

2. The distribution function $f(\vec{u})$ is Maxwellian at local equilibrium and is given by
\[ f^{l,eq}(\vec{u}, \vec{r}, t) = \exp\left( \mu_B - \frac{1}{2}u^2 \right) m/kT \] \quad (3.3)

If we then substitute eqs. (3.2) and (3.3), for local equilibrium into eq. (3.1), we find for \( C(\vec{u}) \)

\[ C(\vec{u}) = \frac{1}{2}u^2 \] \quad (3.4)

and therefore that the chemical potential may be written as

\[ \mu(\vec{u}, \vec{r}, t) = \frac{kT}{m} \ln f(\vec{u}, \vec{r}, t) + \frac{1}{2}u^2, \] \quad (3.5)

or equivalently

\[ \mu(\vec{u}, \vec{r}, t) = \mu_B + \frac{kT}{m} \ln \left( \frac{f}{f^{l,eq}} \right) \] \quad (3.6)

Let us now calculate the rate of change of entropy per unit volume by differentiating eq. (2.3) with respect to time

\[ \frac{\partial \rho_s}{\partial t} = \frac{1}{T} \frac{\partial \rho e}{\partial t} - m \int \frac{\mu(\vec{u}, \vec{r}, t)}{T} \frac{\partial f(\vec{u}, \vec{r}, t)}{\partial t} \] \quad (3.7)

Using the conservation laws (2.5) and (2.8) as well as eqs. (3.5) and (3.6), expressing \( \mu(\vec{u}, \vec{r}, t) \) in terms of \( \rho(\vec{u}, \vec{r}, t) = mf(\vec{u}, \vec{r}, t) \), this equation may be written in the form of a balance equation

\[ \frac{\partial \rho_s}{\partial t} = -\nabla \vec{J}_s + \sigma, \quad \sigma > 0 \] \quad (3.8)

where the entropy flux \( \vec{J}_s \) and the entropy source strength \( \sigma \), which is a positive quantity in accordance with the second law of thermodynamics, are given by

\[ \vec{J}_s = \vec{J}_q/T - k \int f(\vec{u}, \vec{r}, t)(\ln f(\vec{u}, \vec{r}, t) - 1)\vec{u}d\vec{u} \] \quad (3.9)

\[ \sigma = -\vec{J}_q T^{-2}\nabla T - k \int \vec{J}_q \cdot \frac{\partial}{\partial \vec{u}} \ln \left( \frac{f}{f^{l,eq}} \right) d\vec{u} \] \quad (3.10)

The modified heat flux \( \vec{J}_q \)
\[ \vec{J}_q' = \vec{J}_q - m \int \frac{1}{2} u^2 \bar{u} f(\bar{u}, \bar{r}, t) d\bar{u} \]  

contains a contribution to transfer of heat which is due to the motion of the Brownian particles. In deriving eq. (3.9) for the entropy flux use has been made of the identity

\[ k \int \bar{u} \cdot \frac{\partial f}{\partial \bar{r}} \ln f d\bar{u} = k \frac{\partial}{\partial \bar{r}} \cdot \int \bar{u} f \ln f d\bar{u} - k \int \bar{u} \cdot \frac{\partial f}{\partial \bar{r}} d\bar{u} \]
\[ = k \frac{\partial}{\partial \bar{r}} \cdot \int \bar{u} f (\ln f - 1) d\bar{u} \]  

Furthermore, to obtain the second term in eq. (3.10), a partial integration over velocity space has been performed, using the fact that the flux \( \vec{J}_{\bar{u}} \) vanishes as \( \bar{u} \to \pm \infty \).

The entropy source strength \( \sigma \) consists of two contributions: the first represents the entropy created by heat conduction in the heat bath in the presence of Brownian particles, the second, caused by the motion of the Brownian particles in the heat bath, arises so to say from diffusion in velocity space, the space of the internal degree of freedom.

4 Phenomenological relations and the Fokker-Planck equation for Brownian motion in a temperature gradient

Following the principles of nonequilibrium thermodynamics \[4\], the 'linear' phenomenological relations -linear relations between the fluxes and thermodynamic forces occurring in the entropy production \( \text{(3.10)} \) - are, since the system is isotropic and assuming locality \[3\], \[4\] in velocity space,

\[ \vec{J}_q = -L_{TT} \nabla T / T^2 - \int k L_{T\bar{u}} \frac{\partial}{\partial \bar{u}} \ln \left( \frac{f}{f^{\text{eq.}}} \right) d\bar{u} \]  

\[ \vec{J}_{\bar{u}} = -L_{\bar{a}T} \nabla T / T^2 - k L_{\bar{a}\bar{u}} \frac{\partial}{\partial \bar{u}} \ln \left( \frac{f}{f^{\text{eq.}}} \right) \]  

where the phenomenological coefficients obey the Onsager-Casimir symmetry relations

\[ L_{\bar{a}T} = -L_{T\bar{a}} \]  

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The assumption of locality in velocity space characterizes the specific physical nature of
the system considered and is appropriate for Brownian motion.

With $\lambda = \frac{L_{TT}}{T^2}$ a heat conductivity coefficient and defining the friction coefficients $\gamma$ and $\beta$

$$\gamma \equiv \frac{L_{\vec{u}T}}{fT}, \quad \beta \equiv \frac{mL_{\vec{u}u}}{fT}$$

relations (4.1) and (4.2), taking into account relation (4.3), become

$$\vec{J}_q = -\lambda \nabla T + m \int \gamma \left( f\vec{u} + \frac{kT \partial f}{m \partial \vec{u}} \right) d\vec{u}$$

(4.5)

$$\vec{J}_u = -\gamma f \nabla T/T - \beta \left( f\vec{u} + \frac{kT \partial f}{m \partial \vec{u}} \right)$$

(4.6)

Considering $\gamma$ and $\beta$ to be independent of $\vec{u}$ in first approximation and substituting

eq. (4.6) into the conservation law (2.5), we obtain the Fokker-Planck equation for the
Brownian motion in a heat bath with a non-uniform temperature distribution

$$\frac{\partial f}{\partial t} = -\vec{u} \cdot \frac{\partial f}{\partial \vec{r}} + \beta \frac{\partial}{\partial \vec{u}} \left( f\vec{u} + \frac{kT \partial f}{m \partial \vec{u}} \right) + \frac{\gamma}{T} \frac{\partial}{\partial \vec{u}} \left( f \frac{\partial T}{\partial \vec{r}} \right)$$

(4.7)

This equation is coupled to the differential equation obtained by substituting eq. (4.5)
into the energy conservation law (2.8)

$$\frac{\partial \rho e}{\partial t} = \lambda \frac{\partial^2 T}{\partial \vec{r}^2} - m \gamma \frac{\partial}{\partial \vec{r}} \left( f\vec{u} + \frac{kT \partial f}{m \partial \vec{u}} \right) d\vec{u} = \lambda \frac{\partial^2 T}{\partial \vec{r}^2} - \gamma \frac{\partial}{\partial \vec{r}} \cdot \rho_B \vec{v}_B$$

(4.8)

In writing down eq. (4.8) we have neglected the small contribution to the heat flux arising
from the kinetic energy of the Brownian particles. Equation (4.7) coincides, using their
definitions of constants and variables, with the Fokker-Planck equation derived by Zubarev
and Bashkirov by statistical mechanical methods, except for one term. This term which
these authors show to be proportional to the effective volume of the Brownian particle and
as a consequence of negligible magnitude, can of course, due to its extreme microscopic
nature, not be found within the framework of a thermodynamic theory. The two equations
(4.7) and (4.8) completely specify the coupled evolutions of the temperature field and
the velocity-coordinate probability distribution of the Brownian particles. However after
times much larger than the characteristic time $\beta^{-1}$, the system enters the diffusion and
thermal diffusion regime for which the evolution is governed by a simpler set of equations.
We shall discuss this regime in the next section.
5 The thermal diffusion regime

Before discussing the equations which describe the long time behaviour of the Brownian particles and the heat bath, we shall derive the equation expressing, for the Brownian particles alone, the law of conservation of momentum, an equation which we did not need before. This equation will enable us to simplify the equation of motion of the Brownian gas for $t \gg \beta^{-1}$ (see also in connexion with the developments in this section ref. [4] ch X, § 8).

Using the definition (2.7) as well as the continuity equation (2.5) for the distribution function $f(\vec{u}, \vec{r}, t)$ one obtains the following equation of motion for the mean velocity $\vec{v}_B(\vec{r}, t)$:

$$\rho_B \frac{d\vec{v}_B}{dt} = -\nabla \cdot \vec{P}_B(\vec{r}, t) + m \int \vec{J}_{\vec{u}} d\vec{u}$$  (5.1)

Here the hydrodynamic time derivation $d/dt$ for the Brownian gas is defined as

$$\frac{d}{dt} \equiv \frac{\partial}{\partial t} + \vec{v}_B \cdot \frac{\partial}{\partial \vec{r}}$$  (5.2)

while its pressure tensor $\vec{P}_B$ is given by

$$\vec{P}_B(\vec{r}, t) = m \int f(\vec{u} - \vec{v}_B)(\vec{u} - \vec{v}_B)d\vec{u}$$  (5.3)

Substituting into eq. (5.1) the phenomenological equation (4.6) (which gave rise to the Fokker-Planck equation (4.7)) the equation of motion becomes

$$\frac{d\vec{v}_B}{dt} + \rho_B^{-1} \nabla \cdot \vec{P}_B(\vec{r}, t) + \gamma \nabla T/T = -\beta \vec{v}_B.$$  (5.4)

As is well-known, in the diffusion regime, i.e. for times long compared to the characteristic time $\beta^{-1}$, the Brownian gas, due to collisions with the molecules of the heat bath, will reach a state of internal equilibrium (i.e. eq.). In this state the distribution function is approximately a Maxwellian corresponding to a density $\rho_B(\vec{r}, t)$ and temperature $T(\vec{r})$ and a non-vanishing mean velocity $\vec{v}_B(\vec{r}, t)$. It is then given by

$$f(\vec{u}, \vec{r}, t) \simeq f^{eq}(\vec{u}, \vec{r}, t) \equiv \exp\{m[\mu_B - \frac{1}{2}(\vec{u} - \vec{v}_B)^2]/kT\}$$  (5.5)

The pressure tensor $\vec{P}_B$, eq. (5.3) then reduces to the gas pressure $p_B$. 

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\[ \vec{P}_B = p_B \vec{U}, \quad p_B = \rho_B kT/m, \]  

(5.6)

with \( \vec{U} \) the unit tensor. At the same time, the inertia term at the left hand side of eq. (5.4) becomes negligibly small so that this equation, using also eq. (5.6), can be written, with \( \vec{J}_D \equiv \rho_B \vec{v}_B \), as

\[ \vec{J}_D = -D \nabla \rho_B - D_T \nabla T/T \]  

(5.7)

where the diffusion coefficient \( D \) and the thermal diffusion coefficient \( D_T \) are defined respectively as

\[ D = \frac{kT}{m \beta} \]  

(5.8)

\[ D_T = \rho_B D \left( 1 + \frac{\gamma m}{kT} \right) \]  

(5.9)

The form (5.9) for \( D_T \) agrees with the one obtained by Zubarev and Bashkirov, and earlier by Nicolis, by other methods.

Let us finally discuss the form the entropy production \( \sigma \), eq. (3.10), takes in the diffusion and thermal diffusion regime. We have stated that in this regime \( f(\vec{u}, \vec{r}, t) \) is approximately given by eq. (5.5) and that in eq. (5.4), or the equivalent eq. (5.1), the inertia term may be neglected, while the pressure tensor becomes diagonal. The following relation therefore holds in the diffusion regime

\[ m \int \vec{J}_q \cdot d\vec{u} = \nabla p_B \]  

(5.10)

and one then shows with eqs. (3.3) and (5.5) that \( \sigma \) reduces to

\[ \sigma = -\vec{J}_q \cdot \nabla T/T^2 - \vec{J}_D \cdot \nabla p_B/\rho T \]  

(5.11)

Using also eq. (5.6), eq. (5.11) may be written as

\[ \sigma = -\vec{J}_q \cdot \nabla T/T^2 - \vec{J}_D \cdot \frac{(k/m) \nabla \rho_B}{\rho_B} \]  

(5.12)

where a new modified heat flux \( \vec{J}_q \) has been defined by
\[ \vec{J}_q = \vec{J}_q + p_B \rho_B^{-1} \vec{J}_D \]  

(5.13)

Equation (5.12), as does eq. (5.11), enables one to identify coupled thermodynamic fluxes and forces in ordinary space for which Onsager symmetry relations must hold. Let us then, with our previous results (5.9) and (5.7) for \( \vec{J}_q \) and \( \vec{J}_D \) write down the resulting phenomenological law for \( \vec{J}_q \). This law is

\[ \vec{J}_q = -\tilde{\lambda} \nabla T - D_T T \frac{k}{m \rho_B} \nabla \rho_B \]  

(5.14)

Here the heat conductivity coefficient \( \tilde{\lambda} \) at uniform density of the Brownian gas is given by

\[ \tilde{\lambda} = \lambda + k \frac{D_T}{m D \rho_B} \]  

(5.15)

We note that the coefficients occurring in eqs. (5.7) and (5.14) have as expected the correct Onsager symmetry.

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