Simultaneous Brownian Motion of N Particles in a Temperature Gradient

J. M. Rubí\textsuperscript{a} and P. Mazur\textsuperscript{b}

\textsuperscript{a}Departament de Física Fonamental, Facultat de Física,
Universitat de Barcelona, Diagonal 647 08028 Barcelona, Spain
\textsuperscript{b}Instituu-Lorentz, University of Leiden, P.O. Box 9506, 2300 RA Leiden, The Netherlands.

A system of N Brownian particles suspended in a nonuniform heat bath is treated as a thermodynamic system with internal degrees of freedom, in this case their velocities and coordinates. Applying the scheme of non-equilibrium thermodynamics, one then easily obtains the Fokker-Planck equation for simultaneous Brownian motion of N particles in a temperature gradient. This equation accounts for couplings in the motion as a result of hydrodynamic interactions between particles.

I. INTRODUCTION

In a former paper \cite{1}, we reconsidered within the context of nonequilibrium thermodynamics for systems with internal degrees of freedom \cite{2}, the problem of Brownian motion in a temperature gradient and obtained in a simple way, for this case, the Fokker-Planck equation for one Brownian particle. This equation had been originally derived in 1968 by Zubarev and Bashkirov \cite{3} using the more elaborate statistical mechanical methods developed by Zubarev for treating nonequilibrium systems.

More recently Shea and Oppenheim \cite{4} applied statistical mechanical methods based on the use of projection operators to the study of Brownian motion of one particle in a nonequilibrium bath. They obtain a Fokker-Planck equation which, in the presence of a temperature gradient, agrees with the one derived by Zubarev and Bashkirov \cite{3}, and thus also with the one obtained from the nonequilibrium thermodynamic scheme for systems with internal degrees of freedom. The concept of internal degrees of freedom had been introduced already in 1953 into the formalism of nonequilibrium thermodynamics by Prigogine and Mazur \cite{5}, who pointed out that in this way Fokker-Planck-like kinetic equations could be derived.

In this paper we generalize our previous result to the motion of many spherical Brownian particles suspended in a heat bath in the presence of a temperature gradient. In §2 the system of N Brownian particles suspended in a nonuniform heat bath is considered as a system with internal degrees of freedom, consisting of the positions and the velocities of those particles. As a consequence, the probability density function in the phase space of the N Brownian particles plays the role of a thermodynamic density variable of a many component system, for which we give the Gibbs equation, containing the Massieu function conjugated to that density variable. Using Gibbs entropy postulate we are able to express this Massieu function in terms of the N Brownian particle distribution function. In §3 we discuss the form of this distribution function in the state of local equilibrium, in which each particle has a velocity distribution in equilibrium with the temperature at its position.

We are then able not only to state in §4 the conservation laws obeyed by the energy density and the densities of the various components with different internal degrees of freedom, but also to calculate the entropy production accompanying non uniformities, in ordinary coordinate space, as well as in the phase space of the internal degrees of freedom.

In §5 we follow the principles of nonequilibrium thermodynamics to formulate the linear phenomenological laws for the dissipative fluxes occurring in the entropy source strength. These phenomenological laws contain couplings between fluxes pertaining to different particles, which if realized find their origin in hydrodynamic interactions. Substitution of the phenomenological laws into the conservation equations gives rise on the one hand to the desired Fokker-Planck equation for N particles, and on the other to a coupled differential equation for the temperature distribution of the heat bath.

In §6 we discuss the result obtained, also in comparison to - and in the light of - the merits of a more fundamental statistical mechanical approach. Moreover we address the problem why and when the inclusion of internal degrees of freedom in the formalism of nonequilibrium thermodynamics gives rise to valid and acceptable results.
II. THE BROWNIAN GAS AS A THERMODYNAMIC SYSTEM WITH INTERNAL DEGREES OF FREEDOM

Consider a gas of N Brownian particles of mass m suspended in a heat bath at rest with constant mass density $\rho_H$ and fixed total volume V. A nonuniform temperature field $T(r)$ exists in the system (Brownian gas and heat bath) at position r.

The Brownian particles are assumed to be essentially hard spheres and to have no further direct interactions. Their center of mass positions in the heat bath are $R_i$, $i = 1,2,...,N$, their velocities $U_i$. The probability density for the Brownian particles to be at time $t$ in a state defined by a point $\Gamma = (R^N, U^N) = (R_1, R_2, ..., R_N; U_1, U_2, ..., U_N)$ in the 6N dimensional velocity-coordinate space will be denoted by $P^N(\Gamma, t)$ and satisfies the normalization condition

$$\int P^N(\Gamma, t) d\Gamma = 1. \quad (1)$$

The quantity $NmP^N$ then represents the mass density of Brownian particles having velocities $U^N$ and positions $R^N$.

The system itself, Brownian gas and heat bath, has mass density

$$\rho(r, t) = \rho_H + \rho_B(r, t) \equiv \rho_H + \delta \sum_{i} m\delta(R_i - r)P^N(\Gamma, t) = \rho_H + \delta \sum_{i} (m\delta(R_i - r)). \quad (2)$$

Here $\rho_B(r, t)$ is the mass density of the Brownian gas; the bracket $\langle .. \rangle$ denotes an average over the distribution function $P^N(\Gamma, t)$.

The coordinates $R_i$ and velocities $U_i$ may be considered as 6N internal degrees of freedom of the system, in the sense of nonequilibrium thermodynamics [3]. Taking this point of view, which implies that the system can be looked at as a system of many components with mass densities $NmP^N(\Gamma, t)$, the Gibbs equation for the total entropy $S$ of the system may be written as

$$\delta S = \int dr \frac{1}{T(r)} \delta pe - Nm \int d\Gamma \Theta(\Gamma, t) \delta P^N(\Gamma, t), \quad (3)$$

where $e(r, t)$ is the energy per unit of mass and $\Theta$ the Massieu function conjugate to the density $NmP^N$. In writing down equation (3) account has been taken of the fact that $\rho_H$ is constant.

Before carrying out the program of nonequilibrium thermodynamics (which is to calculate in the first place the entropy production occurring in the system as a consequence of the nonequilibrium distribution of temperature and internal degrees of freedom) and thus to derive the Fokker-Planck equation for N Brownian particles in the presence of a temperature gradient, we need to establish an expression for the Massieu function $\Theta(\Gamma)$, relating it to the (thermodynamic) variables $P^N(\Gamma, t)$. For this purpose we make use of Gibbs entropy postulate and write the entropy $S$ with respect to its local equilibrium value in terms of a distribution over possible internal states

$$S = k \int d\Gamma P^N(\Gamma, t) \ln \frac{P^N(\Gamma, t)}{P^N(\Gamma, t)^E} + S^I, \quad (4)$$

Here $P^N(\Gamma, t)$ and $S^I$ are the distribution function and the entropy at local equilibrium. k is Boltzmann’s constant. By local equilibrium we mean that each Brownian particle has at its position a distribution over internal (velocity ) states in equilibrium with respect to the temperature at that point. The entropy $S^I$, which depends only on the temperature distribution and the density distribution of Brownian particles in the heat bath, obeys the standard Gibbs equation

$$\delta S = \int dr \frac{1}{T(r)} \delta pe - \frac{\mu_B}{T} \delta \rho_B, \quad (5)$$

where $\mu_B(r)$ is the chemical potential of the Brownian gas per unit of mass in internal (local) equilibrium at temperature $T(r)$ and density $\rho_B$.

On the other hand we have from expression (4) for the differential of S

$$\delta S = -k \int d\Gamma \ln \frac{P^N(\Gamma, t)}{P^N(\Gamma, t)^E} \delta P^N(\Gamma, t) + \delta S^I. \quad (6)$$

Comparing Eqs. (3) and (6) we find using also Eqs. (2) and (4)
\[ \Theta(\Gamma, t) = \frac{k}{Nm} \ln \frac{P^N(\Gamma, t)}{P^N_{l.e.}(\Gamma)} + \Theta^{l.e.}(\Gamma), \] 

(7)

with

\[ \Theta^{l.e.}(\Gamma) = \frac{1}{N} \sum_i \frac{\mu_B(\mathbf{R}_i)}{T(\mathbf{R}_i)} \] 

(8)

Thus in local equilibrium the Massieu function \( \Theta^{l.e.}(\Gamma) \) is uniform in internal velocity space.

### III. THE N PARTICLE DISTRIBUTION FUNCTION AT LOCAL EQUILIBRIUM

It remains to determine the local equilibrium distribution function \( P^N(\Gamma, t) \). We first note that in full equilibrium (in the absence of a temperature gradient) \( P^N \) is given by the canonical ensemble distribution function

\[ P^N_{eq} = \frac{1}{N!} \exp\left\{ \frac{(F^N - H^N)}{kT} \right\}, \] 

(9)

with \( T \) the equilibrium temperature of the heat bath, \( H^N \) the energy of the N Brownian particles and \( F^N \) the N particle free energy

\[ H^N = \sum_i \frac{1}{2} m U_i^2 ; \] 

(10)

\[ F^N = F^N(T,V) = Nm f_B(T, V/Nm). \] 

(11)

Here \( f_B \) is the free energy of the Brownian gas per unit of mass which (for \( N \) sufficiently large) is a function of temperature and density only.

In Eq.(11) the direct interactions between Brownian particles (even their hard sphere interactions) are neglected, as the system is assumed to be sufficiently dilute.

We shall now take \( P^N \) at local equilibrium to be of the form

\[ P^N_{l.e.} = \prod_i \frac{1}{N} \exp\left\{ \frac{m f_i - H_i}{kT(\mathbf{R}_i)} \right\}, \] 

(12)

with

\[ f_i = f_B(T(\mathbf{R}_i), \rho_e), \quad \rho_e \equiv \frac{Nm}{V}, \] 

(13)

\[ H_i = \frac{1}{2} m U_i^2, \] 

(14)

where \( T(\mathbf{r}) \) is a given non uniform temperature field and \( \rho_e \) the uniform equilibrium particle density.

The free energy \( f_i \), which is determined by inserting (12) into (1) and using Stirling’s approximation, \( \ln N! = N \ln N - N \), has the classical form

\[ f_i = \frac{kT(\mathbf{R}_i)}{m} \left[ \ln \rho_e - \frac{3}{2} \ln \frac{2\pi kT(\mathbf{R}_i)}{m} - 1 \right] = \] 

\[ = \mu_B(\mathbf{R}_i) - p_B(\mathbf{R}_i) \rho_e^{-1}. \] 

(15)

Here \( \mu_B(\mathbf{r}) \) is the explicit form of the previously introduced chemical potential per unit of mass of the ideal Brownian gas and \( p_B(\mathbf{r}) = kT(\mathbf{r}) \rho_e/m \) its - perfect gas - pressure.

Thus \( P^N_{l.e.} \) can be written in the form

\[ P^N_{l.e.} = \prod_i N^{-1} \exp\left( \frac{m(\mu_B(\mathbf{R}_i) - \frac{1}{2} U_i^2)}{kT(\mathbf{R}_i)} \right), \] 

(16)
If expression (16) is inserted into Eq. (7) we obtain for the Massieu function \( \Theta(\Gamma, t) \) the alternative form
\[
\Theta(\Gamma, t) = \frac{k}{N m} \ln P^N(\Gamma, t) + \frac{1}{N} \sum_i \frac{mU_i^2}{2T(R_i)} + \frac{k}{m} \ln N. 
\]

We are now in a position to carry out the nonequilibrium thermodynamics analysis which leads to the derivation of the \( N \) particle Fokker-Planck equation. In the next section we shall establish the basic equations necessary for this derivation.

**IV. CONSERVATION LAWS AND ENTROPY PRODUCTION.**

Let us calculate the rate of change of entropy by differentiating Eq. (3) with respect to time
\[
\frac{dS}{dt} = \int d\Gamma \frac{1}{T(\mathbf{r})} \frac{\partial \rho e}{\partial t} - Nm \int d\Gamma \Theta(\Gamma, t) \frac{\partial P^N(\Gamma, t)}{\partial t}. 
\]

To proceed with the analysis we need the conservation laws obeyed by the energy density \( \rho e \) and the distribution function \( P^N(\Gamma, t) \).

We shall first consider the latter: in \( \Gamma \) space \( P^N \) obeys the continuity equation
\[
\frac{\partial P^N}{\partial t} + \sum_i U_i \cdot \frac{\partial P^N}{\partial R_i} = \sum_i \frac{\partial}{\partial U_i} \cdot J_{U_i},
\]
where the \( J_{U_i} \) are components of fluxes in 3\( N \)-dimensional velocity space, which account for the interaction of the Brownian particles with the heat bath. We have neglected all direct interactions between these particles also in writing down Eq. (19). This is a reasonable approximation since in our dilute system the particle dynamics are overwhelmingly determined by their dissipative interactions with the heat bath. It is indeed our aim to use nonequilibrium thermodynamics to find the laws obeyed by the fluxes \( J_{U_i} \) and thus to derive the equation describing the resulting \( N \) particle random motion problem (also when the heat bath is not uniform).

Next to Eq. (19) we need the law of conservation of energy which can be formulated as follows
\[
\frac{\partial \rho e}{\partial t} = -\nabla \cdot J_q,
\]
where \( J_q \) represents a heat flux defined in the reference frame in which the heat bath is at rest.

Substituting in Eq. (18) the conservation laws (19) and (20) we can write the rate of change of entropy as the sum of two terms
\[
\frac{dS}{dt} = \frac{d_e S}{dt} + \frac{d_i S}{dt}.
\]

The first term \( \frac{d_e S}{dt} \) is the entropy supplied to the system, and is given by
\[
\frac{d_e S}{dt} = -\int d\Omega \cdot \frac{J_q}{T},
\]
while the second term \( \frac{d_i S}{dt} \) represents the total entropy production and is equal to
\[
\frac{d_i S}{dt} = \int d\Gamma \sum_i \{ m \rho_B^{-1}(R_i) P^N(\Gamma) J_{q,i}(R_i) \cdot \nabla T^{-1}(R_i) - J_{U_i} \cdot k \frac{\partial}{\partial U_i} \ln \frac{P^N}{P_{\text{l.e.}}} \}.
\]

In Eq. (22) \( \Omega \) is the surface of the heat bath and \( d\Omega \) a vector of magnitude \( d\Omega \) normal to the surface pointing outward. The vectors \( J_{q,i} \) in Eq. (23) represent modified heat fluxes at the positions of the Brownian particles and are defined as
\[
J_{q,i}(R_i, U_i) = J_q(R_i) - \rho_B(R_i) \frac{1}{2} U_i^2 U_i.
\]

They contain contributions from the kinetic energy flows of the Brownian particles themselves.

In deriving Eq. (22) and (23) use has been made of:
1- Gauss’ theorem in coordinate space and the fact that the Brownian particles are confined to the heat bath,

2- the fact that upon partial integration in velocity space the fluxes \( J_U \) vanish as the velocities \( \pm U_i \) tend to infinity; and

3- the form(s) (7) and/or (17) of the Massieu function \( \Theta(\Gamma) \).

The entropy production (23), which is a positive quantity in accordance with the second law of thermodynamics, is written as an integral over the N-Brownian particle phase space. We shall now demand, in agreement with the extension of nonequilibrium thermodynamics to systems with internal degrees of freedom [5], that not only the integral (23) be positive definite, but also its integrand itself,

\[
\frac{d_i S}{dt} = \int \sigma_T d\Gamma,
\]

\[
\sigma_T = -\sum_i m \rho_B^{-1} \langle R_i \rangle P^N J_{q,i} \cdot T_i^{-2} \nabla T_i - \sum_i J_{U,i} \cdot k \frac{\partial}{\partial U_i} \ln \left( \frac{P^N}{P_{l.e.}} \right) \geq 0.
\]

We have introduced here the notation \( T_i \equiv T(R_i) \). The quantity \( \sigma_T \), the entropy source strength in \( \Gamma \) space, is a sum of products of dissipative fluxes \( J_{q,i} \) and \( J_{U,i} \) respectively, and their conjugate thermodynamic forces, the gradients of temperature in coordinate space and of the Massieu function \( \Theta(\Gamma) \), cf. Eq. (7), in velocity space.

V. PHENOMENOLOGICAL RELATIONS AND THE FOKKER-PLANCK EQUATION FOR N-BROWNIAN PARTICLES.

Following the scheme of nonequilibrium thermodynamics [2] we shall now establish linear phenomenological relations between the fluxes and thermodynamic forces occurring in expression (23) for \( \Gamma \). Since the system is isotropic these relations are

\[
m \rho_B^{-1} P^N J_{q,i} = -\sum_j L_{T_i,T_j} T_j^{-2} \nabla T_j + k \sum_j L_{T_i,U_j} \frac{\partial}{\partial U_j} \ln \left( \frac{P^N}{P_{l.e.}} \right)
\]

\[
J_{U,i} = -\sum_j L_{U_i,T_j} T_j^{-2} \nabla T_j + k \sum_j L_{U_i,U_j} \frac{\partial}{\partial U_j} \ln \left( \frac{P^N}{P_{l.e.}} \right)
\]

Assuming Onsager’s principle of microscopic reversibility to hold for the system studied[1], the coefficients in Eqs. (27) and (28) satisfy the Onsager Casimir reciprocal relations.

\[
L_{T_i,T_j} = L_{T_j,T_i},
\]

\[
L_{U_i,T_j} = -L_{T_j,U_i},
\]

\[
L_{U_i,U_j} = L_{U_j,U_i}.
\]

\(^{1}\)Onsager’s theorem is based on the property of microscopic reversibility which holds for fluctuations, in particular, around equilibrium. But in the system studied we would have to consider correlations of particle velocity fluctuations at different positions and temperatures around a quasi-stationary nonequilibrium state, for which the theorem does not necessarily hold. Nevertheless it seems legitimate to use the theorem when one takes into account that the velocity correlations at two different position \( i \) and \( j \), which find their origin in hydrodynamic interactions, are sufficiently short ranged in space for temperatures to be taken equal as in equilibrium.
Defining the heat conductivity coefficients $\lambda_{ij}$, the thermal acceleration coefficients $\gamma_{ij}$ and the friction coefficients $\beta_{ij}$

$$\lambda_{ij} \equiv \frac{L_{T,T,i} \rho_B}{m P N T_j^2},$$  \hspace{1cm} (32)

$$\gamma_{ij} \equiv \frac{L_{U,U,i}}{P N T_j},$$  \hspace{1cm} (33)

$$\beta_{ij} \equiv \frac{m L_{U,U,i}}{P N T_j},$$  \hspace{1cm} (34)

relations (27) and (28) become taking into account also (30), as well as the fact that in (33) $T_j \simeq T_i$ in good approximation (see also note previous page)

$$m \rho_B^{-1} P N J_{q,i} = - \sum_j m \lambda_{ij} \rho_B^{-1} P N \nabla T_j + \sum_j m \gamma_{ij}(P N U_j + \frac{k T_j}{m} \frac{\partial P N}{\partial U_j}),$$  \hspace{1cm} (35)

$$J_{U,i} = - \sum_j m \gamma_{ij} P N \nabla T_j/T_j - \sum_j m \beta_{ij}(P N U_j + \frac{k T_j}{m} \frac{\partial P N}{\partial U_j}).$$  \hspace{1cm} (36)

Eqs. (35) and (36) (as did Eqs. (27) and (28)) give expression to the fact that the dissipative fluxes at different (particle) positions can be coupled to each other: the coefficients $\beta_{ij}$ represent the well-known mutual friction coefficients of spherical bodies which result (and are calculated) from their hydrodynamic interactions as they move through the fluid they are suspended in. Likewise the coefficients $\gamma_{ij}$ and $\lambda_{ij}$, $i \neq j$ could arise from hydrodynamic interactions. We do not know whether such effects have previously been found. As far as the heat conductivity matrix is concerned its dominant contribution to $\lambda_{ii}$ is the heat conductivity of the heat bath itself, while all other contributions and matrix elements arise from particle motions.

We shall now first formulate, using Eq. (35), the phenomenological law obeyed by the total heat current in the heat bath. For this purpose we multiply both members of (33) by $\delta(R_i - r)$, sum over all particles $i$, and integrate over $\Gamma$-space. We then obtain the following law

$$J'_q(r) = - \int \lambda(r,r') \nabla T(r') dr' + \int \gamma(r,r') \rho_B(r') V_B(r') dr'.$$  \hspace{1cm} (37)

Here the total heat flux $J'_q$ at $r$ is given by (cf. Eq. (24))

$$J'_q(r) = J_q(r) - \sum_i \frac{1}{2} \langle U_i^2 \delta(R_i - r) \rangle,$$  \hspace{1cm} (38)

while $V_B(r')$, is the mean particle velocity,

$$V_B(r) = \rho_B^{-1} \langle \sum_i m U_i \delta(R_i - r) \rangle.$$  \hspace{1cm} (39)

The heat conductivity kernels $\lambda(r,r')$ and $\gamma(r,r')$ are defined by the following averages

$$\lambda(r,r') = \rho_B^{-1} \langle \sum_{ij} \lambda_{ij} \delta(R_i - r) \delta(R_j - r') \rangle,$$  \hspace{1cm} (40)

$$\gamma(r,r') \rho_B(r') V_B(r') = \langle \sum_{ij} \gamma_{ij} m U_i \delta(R_i - r) \delta(R_j - r') \rangle.$$  \hspace{1cm} (41)

These kernels, which for $r \neq r'$ result as stated above from hydrodynamic interactions, can be assumed to be sufficiently short ranged, so that from a truly macroscopic point of view Eq. (37) has the approximate form
\[
\mathbf{J}_q' = -\lambda \nabla T + \gamma \rho_B \mathbf{V}_B,
\]
with the macroscopic heat conductivity
\[
\lambda = \int \lambda(r, r') dr',
\]
and
\[
\gamma = \int \gamma(r, r') dr'.
\]

The last quantity is related to the thermal diffusion coefficient of the Brownian gas (for the exact relation of \(\gamma\) to the thermal diffusion coefficient see eg. ref. [1]).

Substitution of Eq. (42) into the law of conservation of energy (20) gives rise to a differential equation for the temperature which is coupled to the first few Brownian particle velocity moments (cf. also Eq. (38). These moments can be calculated from the N particle distribution function \(P_N(\Gamma, t)\), which in turn is the solution of the differential equation obtained by substitution of Eq. (36) into Eq. (19)

\[
\frac{\partial P_N}{\partial t} + \sum_i U_i \cdot \frac{\partial P_N}{\partial R_i} = \sum_{ij} \frac{\partial}{\partial U_i} [\beta_{ij}(P_N U_j + \frac{kT_j}{m} \frac{\partial P_N}{\partial U_j}) + \gamma_{ij} P_N \frac{1}{T_j} \frac{\partial T}{\partial R_j}].
\]

This is the N particle Fokker Planck equation we set out to derive from the scheme of nonequilibrium thermodynamics as applied to systems with internal degrees of freedom. In the presence of a temperature gradient a coupling occurs, as could be expected, to the value of that gradient at the position of each particle.

In our derivation of Eq. (45), direct interactions between the Brownian particles were completely neglected. It must be pointed out, however, that this derivation can easily be extended to the case that direct interactions \(\phi_{ij}(|R_i - R_j|)\) play a significant role.

To perform that extension the local equilibrium distribution function (12) must be adequately modified replacing Eq. (10) by

\[
H_i = \frac{1}{2} m U_i^2 + \frac{1}{2} \sum_j \phi_{ij},
\]

thus attributing one half of the interaction energy of particle i and particle j to particle i and the other half to particle j. It is then not possible anymore to determine \(f_i\) explicitly in a simple manner. However with \(f_i = \mu_B - p_B \rho_e^{-1}\) and \(P_{N,e}\) therefore given by

\[
P_{N,e} = \prod_i N^{-1} \exp\{[m \mu_B(R_i) - \frac{1}{2} m U_i^2 - \frac{1}{2} \sum_j \phi_{ij} - p_B(R_i) \rho_e^{-1}] / kT(R_i) + 1\},
\]

(which reduces, without direct interactions and the consequent perfect pressure value for \(p_B\), to Eq. (16)) the analysis can proceed as before. One must then take into account the continuity equation obeyed by \(P^N\) in the presence of direct interactions and obtains in a manner completely analogous to the one described above (thereby introducing also a new modified heat current (cf. Eq. (24)) the full Fokker-Planck equation,

\[
\frac{\partial P_N}{\partial t} + \sum_i U_i \cdot \frac{\partial P_N}{\partial R_i} - \sum_{ij} m^{-1} \frac{\partial \phi_{ij}}{\partial R_j} \cdot \frac{\partial P_N}{\partial U_i} = \sum_{ij} \frac{\partial}{\partial U_j} [\beta_{ij}(P_N U_j + \frac{kT_j}{m} \frac{\partial P_N}{\partial U_j}) + \gamma_{ij} P_N \frac{1}{T_j} \frac{\partial T}{\partial R_j}].
\]

The Fokker-Planck equation (48) now remains applicable to systems which are not necessarily dilute.

VI. CONCLUSION AND DISCUSSION

In the preceding sections we considered an ensemble of Brownian particles suspended in a nonuniform heat bath as a system with internal degrees of freedom and applied to it the scheme of nonequilibrium thermodynamics. We showed that it is then a simple matter to obtain the Fokker Planck equation for simultaneous Brownian motion of N particles in the presence of a temperature gradient. In fact the derivation along these lines turns out to be no
more involved than the corresponding one for a single Brownian particle, even though many particle hydrodynamic interactions have to be taken into account. It is the simplicity of the nonequilibrium thermodynamic approach which forms its main attraction, in particular when it concerns, as it does in this case, phenomena which occur somewhere on the interface between macroscopic and microscopic physics.

This thermodynamic approach should be compared to statistical mechanical methods to derive the basic equation describing many particle Brownian motion. In an equilibrium heat bath statistical theories were given by Deutch and Oppenheim [7] and Murphy and Aguirre [6]. While the statistical mechanical treatments are more satisfactory from a fundamental point of view, they do not seem in the present stage to provide substantially more detailed results.

It should be noticed that in the application given above the extension of nonequilibrium thermodynamics to systems with internal degrees of freedom already contains elements of statistical physics beyond those present when the concept was introduced [7]. Thus the theory developed here makes use of the probability density function in the phase space of the N Brownian particles and of Gibbs entropy postulate to relate the entropy of the system to this distribution function.

In their original paper Prigogine and Mazur stated that it was their object, in considering irreversible processes connected to internal degrees of freedom, to extend the domain of applicability of nonequilibrium thermodynamics (d’étendre le domaine d’application de la thermodynamique des phénomènes irréversibles). The question may then be put forward if and why such an extension gives rise to a correct description of irreversible phenomena, as it obviously does in the case studied in this paper. The answer is that an extension to internal degrees of freedom is legitimate as long as the irreversible processes connected to these variables are slow in comparison to a molecular time scale. Think however for a moment that the N particles considered are neither large nor heavy compared to bath molecules but form a marked dilute set of these. In that case the Fokker-Planck equation derived makes no sense for a description of the motion of the molecules concerned, which is such that the Maxwell velocity distribution is attained on a molecular time scale. However, the (slow) long time diffusion regime of the relevant particles may still be described by standard nonequilibrium thermodynamics. We have an illustration here of the limitations for extending that theory: it is an illusion that a small number of added pseudo-thermodynamic variables, whatever their nature, may suffice to adequately describe (with a fundamentally macroscopic discipline) phenomena taking place on the time scale of molecular, or microscopic, events. However when one is confronted with a separation of time scales and some phenomena take place at intermediate times, a proper extended thermodynamic nonequilibrium theory may demonstrate its value in providing the means to easily describe and categorize, together with their symmetries, the irreversibilities which take place.

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