Stochastic model for the dynamics of interacting Brownian particles.

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Abstract
Using the scheme of mesoscopic nonequilibrium thermodynamics, we construct the one- and two- particle Fokker-Planck equations for a system of interacting Brownian particles. By means of these equations we derive the corresponding balance equations. We obtain expressions for the heat flux and the pressure tensor which enable one to describe the kinetic and potential energy interchange of the particles with the heat bath. Through the momentum balance we analyze in particular the diffusion regime to obtain the collective diffusion coefficient in terms of the hydrodynamic and the effective forces acting on the Brownian particles.

1 Introduction

Brownian effects are ubiquitous in many examples of soft condensed matter physics for which the system can be modelled as a set of interacting degrees of freedom in contact with a heat bath. They play a very important role when one infers macroscopic behaviors from the mesoscopic level of description, a route utilized frequently in the study of complex systems. Many examples, as colloidal suspensions, polymers, micelles, etc., share those characteristics.

The dynamics at the mesoscopic level is governed by a set of Langevin processes or equivalently by the corresponding $N$-particle Fokker-Planck equation. One may arrive at the formulation of those equations by using different methods, but the inherent complexity of the description of the dynamics of many interconnected degrees of freedom makes it necessary to adopt simple schemes. The method we use to analyze the dynamics of a system of interacting Brownian particles, is based upon a mesoscopic approach proposed recently to obtain
the Fokker-Planck equation for the $N$-particle distribution function \[5\]. It applies the scheme of nonequilibrium thermodynamics to derive the kinetic equation describing the evolution of the $N$-particle probability distribution function \[6, 7\].

One then considers a system of $N$ Brownian particles diluted in a solvent, which acts as a thermal bath. The velocity of the particles are viewed as internal thermodynamic variables. Such a description, is based on the existence of dissimilar time scales for the Brownian particles and permits to proceed with an analysis in the phase space of the macroparticles. The local equilibrium hypothesis is introduced at the phase space level and from it one derives the entropy balance equation. The resulting entropy production accounting for the irreversible processes taking place in the phase space allows us to identify the fluxes and forces in a similar manner as in the thermodynamic of the irreversible processes \[7\].

In the linear regime for the dependence of fluxes on the forces one obtains the Fokker-Planck equations \[5, 8\]. This theory has been applied to the case of interacting Brownian particles under a temperature gradient, and to the thermocapillary migration of Brownian droplets \[10\]. For the case of Brownian motion under stationary flow, the mesoscopic approach permits to obtain a Fokker-Planck equation which exhibits violation of the fluctuation-dissipation theorem \[11\], i.e., the diffusion coefficient does not obey the Stokes-Einstein law. In addition, this formalism has been applied to obtain kinetic equations for polymer dynamics \[12\].

The above approach offers a mesoscopic framework for which simply by applying the scheme of nonequilibrium thermodynamics in phase space it is possible to derive kinetic equations of the Fokker-Planck or Smoluchowski types to analyze the dynamics. Our goal in this paper is to apply that method to describe the dynamics of interacting Brownian particles in the approximation of pair additive interactions.

The paper has been organized in the following way. In section 2, we perform a contraction of the description of the $N$-body problem to two tracer particles, where their velocities are the internal degrees of freedom from the thermodynamic point of view. Section 3 is devoted to obtain the Fokker-Planck equations for the one- and two particles distribution functions. In section 4 we discuss the hydrodynamic regime, whereas in section 5 we analyze the diffusion regime from the momentum balance equation. Finally, in section 6, we present some concluding remarks.

### 2 Conservation laws for the probability distribution functions

We consider a set of $N$ interacting Brownian particles of mass $m$ suspended in a solvent which plays the role of a heat bath at rest. We associate to each Brownian particle a phase coordinate vector $\mathbf{x}_i$ that denotes its position $\mathbf{r}_i$,
and its velocity $u_i$ in phase space, i.e. $x_i = (r_i, u_i)$. Hence, the phase space occupied by the $N$ particles is the one spanned by the values of the vector $\Gamma = (x_1, x_2, ... x_N) \equiv (x^N)$. The probability density for the $N$ particles to be at point $\Gamma$ at time $t$ is denoted by $P^{(N)}(\Gamma, t)$ and satisfies the normalization condition,

$$\int P^{(N)}(\Gamma, t) d\Gamma = 1.$$  \hspace{1cm} (1)

The entropy of the Brownian particles is given through the Gibbs entropy postulate,

$$S = -k \int P^{(N)}(\Gamma, t) \ln \frac{P^{(N)}(\Gamma, t)}{P^{eq.}(\Gamma)} d\Gamma + S_{eq.},$$  \hspace{1cm} (2)

where $S_{eq.}$ is its equilibrium value, $k$ is Boltzmann’s constant and $P^{eq.}(\Gamma)$ the $N$-particle equilibrium probability density. In the framework of mesoscopic non-equilibrium thermodynamics [5, 7], the phase coordinates of the set of $N$ Brownian particles play the role of internal degrees of freedom. The Gibbs equation is formulated as follows,

$$\delta S = -k T \int \mu(\Gamma, t) \delta P^{(N)}(\Gamma, t) d\Gamma,$$  \hspace{1cm} (3)

where $\mu(\Gamma, t)$ is the non-equilibrium $N$-particle chemical potential, $T$ is the heat bath temperature which we assume constant and $\delta$ stands for the exact total differential. The rate of variation of the entropy is then given by

$$\frac{\partial S}{\partial t} = -k T \int \mu(\Gamma, t) \frac{\partial}{\partial t} P^{(N)}(\Gamma, t) d\Gamma.$$  \hspace{1cm} (4)

Quite generally, we may assume that $P^{(N)}(\Gamma, t)$ satisfies the continuity equation,

$$\frac{\partial P^{(N)}}{\partial t} + \sum_{i=1}^{N} u_i \cdot \frac{\partial P^{(N)}}{\partial r_i} - m^{-1} \sum_{i,j}^{N} \phi_{ij} \frac{\partial P^{(N)}}{\partial u_i} \cdot \frac{\partial P^{(N)}}{\partial u_j} = - \sum_{i=1}^{N} \frac{\partial}{\partial u_i} \cdot J^{(N)}_{u_i},$$  \hspace{1cm} (5)

where $\phi_{ij}$ represents the direct interaction potential between particles. The energy and momentum dissipative interchange between particles and the solvent is taken into account through the fluxes $J^{(N)}_{u_i} = J^{(N)}_{u_i}(x^N)$.

From the $N$-particle continuity equation (5), after integrating over $N$-s phase coordinates, we obtain the reduced continuity equations,

$$\frac{\partial P^{(s)}}{\partial t} + \sum_{i=1}^{s} u_i \cdot \frac{\partial P^{(s)}}{\partial r_i} - m^{-1} \int \sum_{i,j=1}^{s} \phi_{ij} \frac{\partial P^{(s)}}{\partial u_i} \cdot \frac{\partial P^{(s)}}{\partial u_j} d\mathbf{x}_{s+1}...d\mathbf{x}_N = - \sum_{i=1}^{s} \frac{\partial}{\partial u_i} \cdot J^{(s)}_{u_i},$$  \hspace{1cm} (6)
with $P^{(s)} = P^{(s)}(x^s, t)$

$$P^{(s)}(x_1, x_2, \ldots x_s, t) = \frac{N!}{(N - s)!} \int^{(N-s)} P^{(N)} dx_{s+1} \ldots dx_N, \quad (7)$$

the reduced distribution function and

$$J^{(s)}_{u_i} = \int J^{(N)}_{u_i} dx_{s+1} \ldots dx_N, \quad (8)$$

the reduced fluxes in phase space.

In particular, we are interested in the case of the one- and two-particle distribution functions, hence from the above equation we can obtain, the continuity equations,

$$\frac{\partial}{\partial t} P^{(1)} + u_1 \cdot \frac{\partial}{\partial r_1} P^{(1)} - m^{-1} \int \frac{\partial \phi_{12}}{\partial r_1} \cdot \frac{\partial P^{(2)}}{\partial u_1} dx_2 = - \frac{\partial}{\partial u_1} \cdot J^{(1)}_{u_1} \quad (9)$$

and

$$\frac{\partial}{\partial t} P^{(2)} + 2 \sum_{i=1} u_i \cdot \frac{\partial P^{(2)}}{\partial r_i} - m^{-1} \sum_{i,j=1}^{2} \frac{\partial \phi_{ij}}{\partial r_i} \cdot \frac{\partial P^{(2)}}{\partial u_i} = - \sum_{i=1}^{2} \frac{\partial}{\partial u_i} \cdot J^{(2)}_{u_i}. \quad (10)$$

These equations present the usual drift terms and conservative interaction contributions on the left hand side. In eq. (9) the third term expresses the mean force over a Brownian particle due to the presence of other particles. On the other hand, eq. (10) includes the effect of the direct forces felt by a pair of particles. The right hand side of each equation accounts for the dissipative interaction of the particles with the solvent through the corresponding currents. At this stage, we have provided the continuity equations for the reduced probability densities $P^{(1)}$ and $P^{(2)}$, where the fluxes $J^{(i)}_{u_i}$ appear as unknown functions. One of the features of the mesoscopic nonequilibrium thermodynamics approach presented here, is to find out the expressions of $J^{(1)}_{u_1}$ and $J^{(2)}_{u_i}$, which will be obtained from the entropy production in the next section.

### 3 Fokker-Planck equations for the one- and two-particle distribution functions

The simplest model of N-interacting particles can be implemented by only considering interactions between pairs. This approximation implies a substantial simplification which in terms of our mesoscopic description concerns the analysis of the dynamics through the one and two-particle distribution functions. In this section we will derive the kinetic equations of the Fokker-Planck type, accounting for the evolution of those distribution functions.
To proceed, we factorize the N-particle distribution function $P^{(N)}(x^N, t)$ as follows

$$P^{(N)}(x^N, t) = P^{(1)}(x_1, t)P^{(1)}(x_2, t)\ldots P^{(1)}(x_N, t)g^{(N)}(x^N, t), \quad (11)$$

where $P^{(1)}(x_i, t)$ represents the reduced distribution function for $s = 1$; moreover, $g^{(N)}(x^N, t)$ is the N-particle dynamic correlation function. In a similar manner, as for the equilibrium situation [13-15], we propose a factorization for the correlation function $g^{(N)}(x^N, t) = g^{(N)}(x_1, x_2, \ldots, x_N, t)$ as follows,

$$g^{(N)} = g^{(2)}(x_1, x_2, t) \ldots g^{(2)}(x_{N-1}, x_N, t) \delta g^{(3)}(x_1, x_2, x_3, t) \ldots \delta g^{(3)}(x_{N-2}, x_{N-1}, x_N, t) \ldots \delta g^{(N)}(x_1, \ldots, x_N, t). \quad (12)$$

Here, $\delta g^{(3)}(x_1, x_2, x_3, t)$ is defined through the relation

$$g^{(3)}(x_1, x_2, x_3, t) = g^{(2)}(x_1, x_2, t)g^{(2)}(x_1, x_3, t)g^{(2)}(x_2, x_3, t)\delta g^{(3)}(x_1, x_2, x_3, t), \quad (13)$$

such that when $\delta g^{(3)}(x_1, x_2, x_3, t) = 1$, it reduces to the so-called Kirkwood’s superposition approximation, and $g^{(4)}$ is defined similarly, through $\delta g^{(N)}$. In the above factorization for $g^{(N)}$, we have $1/2 N (N-1)$ pairs, $1/3! N (N-1) (N-2)$ triplets, etc. so that

$$\ln P^{(N)} = \sum_{i=1}^{N} \ln \left( P^{(1)}(x_i, t) \right) + \ln g^{(N)}(x^N, t)$$

$$= N \ln P^{(1)}(x_1, t) + \frac{N}{2} (N-1) \ln g^{(2)}(x_1, x_2, t) + \frac{N}{3!} (N-1) (N-2) \ln \delta g^{(3)}(x_1, x_2, x_3, t) + \ldots \quad (14)$$

Similarly, for the equilibrium case [13-15], we have

$$\ln P^{(N)}_{eq}(x^N) = N \ln P^{(1)}_{eq}(x_1) + \frac{N}{2} (N-1) \ln g^{(2)}_{eq}(r_1, r_2) + \ldots \quad (15)$$

Substitution of these two last equations in (2), yields the expression of the Gibbs entropy postulate,

$$S = -Nk \int P^{(1)}(x_1, t) \ln \frac{P^{(1)}(x_1, t)}{P^{(1)}_{eq}(x_1)} dx_1$$

$$- \frac{N (N-1)}{2} k \int P^{(2)}(x_1, x_2, t) \ln \left( \frac{g^{(2)}(x_1, x_2, t)}{g^{(2)}_{eq}(r_1, r_2)} \right) dx_1 dx_2 +$$

$$\ldots + S_{eq}. \quad (16)$$
It is worth mentioning that a similar expression, for the non-equilibrium entropy, has been obtained for a kinetic description of a dense gas \[18\] and its equilibrium counterpart has also been used for a calculation of the thermodynamic entropy \[14, 15\]. In addition, this statistical entropy expression has been recently reformulated in terms of the potentials of mean force between particles \[20\], and their graphical representation has been presented for the excess entropy \[21\].

Similarly to the \(N\)-particle case, we formulate the Gibbs equation as follows,

\[
\delta S = \frac{N m}{T} \int \mu^{(1)}(x_1, t) \delta P^{(1)}(x_1) \, dx_1 \\
- \frac{N (N - 1) m^2}{2T} \int \mu^{(2)}(x_1, x_2, t) \delta P^{(2)}(x_2) \, dx_2 \, dx_1,
\]

(17)

where \(\mu^{(1)} + \mu^{(2)}\) represents the non-equilibrium chemical potential per unit mass of the suspended particles. Their general forms are given by,

\[
\mu^{(1)}(x_1, t) = \frac{k T}{m} \ln P^{(1)}(x_1, t) + \Psi^{(1)}(x_1, t) \quad \text{(18)}
\]

and

\[
\mu^{(2)}(x_1, x_2, t) = \frac{k T}{m} \ln g^{(2)}(x_1, x_2, t) + \Psi^{(2)}(x_1, x_2, t), \quad \text{(19)}
\]

where \(\Psi^{(1)}\) and \(\Psi^{(2)}\) are unknown potential functions.

At equilibrium, the distribution functions must satisfy the next expressions,

\[
P^{(1)}_{eq.}(u_1) = \exp \left[ \frac{m}{k T_{eq}} \left( \mu_{id}^{B_{eq}} - \frac{u_1^2}{2} \right) \right], \quad \text{(20)}
\]

where we have defined the distribution function in a reference frame moving with the mean velocity of Brownian particles and

\[
g^{(2)}_{eq}(r_1, r_2) = \exp \left[ \frac{m}{k T_{eq}} \left( \mu_{exc}^{B_{eq}} (r_1, r_2) - \phi^{eff}_{12}(r_1, r_2) \right) \right]. \quad \text{(21)}
\]

Here \(\mu_{id}^{B_{eq}}\) and \(\mu_{exc}^{B_{eq}}(r_1, r_2)\) correspond to the ideal and excess parts of the chemical potential of the Brownian particles at equilibrium with the solvent. On the other hand, according to the above definition of the pair correlation function we can identify the effective pair interaction potential, namely, \(\phi^{eff}_{12}(r_1, r_2) = \phi_{12}(r_1, r_2) - \mu_{B_{eq}}^{exc}(r_1, r_2)\), where \(-\mu_{B_{eq}}^{exc}\) stands for the indirect part of the work, corresponding to the free energy change, to transport the Brownian particles at a certain separation, accounting for the static interaction of the particles with the solvent. For the particular case when the effective interaction \(\phi^{eff}_{12}(r_1, r_2)\) has spherical symmetry, \(g^{(2)}_{eq}\) only depends on the distance separation modulus of the two particles \(r_{12} = |r_{12}| = |r_2 - r_1|\), i.e. \(g^{(2)}_{eq}(|r_2 - r_1|)\) \[19\].
If we now substitute (20) and (21) in (18) and (19), such that in this limit case $\mu^{(1)} = \mu_{\text{id}}^{\text{Beq}}$ and $\mu^{(2)} = \mu_{\text{exc}}^{\text{Beq}}$, and using the definition of the total chemical potential at equilibrium $\mu_{\text{Beq}}^{\text{tot}} = \mu_{\text{id}}^{\text{Beq}} + \mu_{\text{exc}}^{\text{Beq}}$, one obtains the expressions

$$\Psi^{(1)} = \frac{\eta_1^2}{2}, \quad (22)$$

and

$$\Psi^{(2)} = \phi_{12}. \quad (23)$$

With this identification, we can rewrite expressions (18) and (19) as follows,

$$\mu^{(1)} = \frac{kT}{m} \ln \left( \frac{f^{(1)}}{f_{eq}^{(1)}} \right) + \mu_{\text{id}}^{\text{Beq}}, \quad (24)$$

and

$$\mu^{(2)} = \frac{kT}{m} \ln \left( \frac{g^{(2)}}{g_{eq}^{(2)}} \right) + \mu_{\text{exc}}^{\text{Beq}}. \quad (25)$$

After substitution of these expressions in the entropy functional (17), using the definition of mass density $\rho_B = m \int f^{(1)} du_1$ for the Brownian particles and considering that the heat bath density $\rho_H$ is constant, we can identify through the Gibbs entropy postulate (16) the equilibrium entropy,

$$\delta S_{eq} = -\frac{\mu_{\text{Beq}}^{\text{tot}}}{T} \delta \rho_B. \quad (26)$$

This means that eq. (17) with (24) and (25) is consistent with the Gibbs entropy postulate (16) formulated at the pair correlation level.

We now proceed to analyze the evolution in time of Gibbs local entropy $S(r_1, t)$. To reach this purpose, from eq. (17) we obtain the rate of change of entropy per unit volume,

$$\frac{\partial}{\partial t} S(r_1, t) = -mN \int \frac{\mu^{(1)}}{T} \frac{\partial}{\partial t} P^{(1)} du_1 - m^2 N^2 (N - 1) \int \frac{\mu^{(2)}}{T} \frac{\partial}{\partial t} P^{(2)} du_1 du_2 dr_2. \quad (27)$$

Working out the first term in this expression, after substituting eq. (9) we have,

$$- m \int \frac{\mu^{(1)}}{T} \frac{\partial}{\partial t} P^{(1)} du_1 = - \frac{\partial}{\partial r_i} J_s^{(1)}(r_1, t) + \sigma^{(1)}(r_1, t). \quad (28)$$

Here

$$J_s^{(1)}(r_1, t) = Nk \int u_1 P^{(1)} \left( \frac{m}{kT} \mu^{(1)} - 1 \right) du_1$$

7
\[ \frac{N(N-1)}{2T} \int \left( \frac{\partial \phi_{12}}{\partial r_{12}} \right) \frac{\mathbf{r}_{12} \cdot \mathbf{r}_{12}}{r_{12}} \int_0^1 P^{(2)}(\alpha) \frac{\partial \mu^{(1)}}{\partial \mathbf{u}_1} d\alpha d\mathbf{u}_2 d\mathbf{u}_1 \]  

is the first contribution to the entropy flux, with \( \int_0^1 P^{(2)}(\alpha) d\alpha = \int_0^1 P^{(2)}(\mathbf{r}_1 - [1 - \alpha] \mathbf{r}_j, \mathbf{u}_1, \mathbf{r}_1 + \alpha \mathbf{r}_j, \mathbf{u}_2, t) d\alpha \), as results from assuming that \( P^{(2)} \) is a slow varying function of \( \mathbf{r}_1 \) and it admits a Taylor’s expansion around the distance separation between particles \( \mathbf{r}_{1j} \) \[2\]. The first contribution to the entropy production is then given by,

\[ \sigma^{(1)}(\mathbf{r}_1, t) = -Nk \int \mathbf{J}^{(1)}_{\mathbf{u}_1} \cdot \frac{\partial}{\partial \mathbf{u}_1} \ln \left( \frac{P^{(1)}}{P^{(1)}_{\text{eq}}} \right) d\mathbf{u}_1. \]  

We now analyze the two-particle term in eq. (27) using eq. (10). After some algebra we obtain the next identity

\[ -m^2 \int \frac{\mu^{(2)}}{T} \frac{\partial}{\partial t} P^{(2)} d\mathbf{u}_1 d\mathbf{u}_2 d\mathbf{r}_2 = -\frac{\partial}{\partial \mathbf{r}_1} \cdot \mathbf{J}_s^{(2)}(\mathbf{r}_1, t) + \sigma^{(2)}(\mathbf{r}_1, t), \]  

where

\[ \mathbf{J}_s^{(2)}(\mathbf{r}_1, t) = -\frac{N(N-1)m^2}{2T} \int P^{(2)} \mu^{(2)} d\mathbf{u}_1 d\mathbf{u}_2 d\mathbf{r}_2 \]

\[ + \frac{N(N-1)m^2}{2T} \int (\mathbf{u}_1 + \mathbf{u}_2) \cdot \frac{\mathbf{r}_{12} \mathbf{r}_{12}}{2r_{12}} \frac{\partial}{\partial r_{12}} \mu^{(2)} \int_0^1 P^{(2)} d\alpha d\mathbf{u}_1 d\mathbf{u}_2 d\mathbf{r}_{12} \]

\[ - \frac{N(N-1)}{2T} \sum_{i,j=1}^2 \frac{\partial \phi_{ij}}{\partial r_{ij}} \mathbf{r}_{ij} \cdot \mathbf{r}_{ij} \int_0^1 P^{(2)} d\alpha \frac{\partial \mu^{(2)}}{\partial \mathbf{u}_1} d\mathbf{u}_1 d\mathbf{u}_2 d\mathbf{r}_{ij}, \]

(32)

is the two-particle entropy flux and

\[ \sigma^{(2)}(\mathbf{r}_1, t) = -\frac{N(N-1)}{2} k \int \mathbf{J}_{\mathbf{u}_1}^{(2)} \cdot \frac{\partial}{\partial \mathbf{u}_1} \ln \left( \frac{g^{(2)}}{g^{(2)}_{\text{eq}}} \right) d\mathbf{u}_1 d\mathbf{u}_2 d\mathbf{r}_2 \]

\[ - \frac{N(N-1)}{2} k \int \mathbf{J}_{\mathbf{u}_2}^{(2)} \cdot \frac{\partial}{\partial \mathbf{u}_2} \ln \left( \frac{g^{(2)}}{g^{(2)}_{\text{eq}}} \right) d\mathbf{u}_1 d\mathbf{u}_2 d\mathbf{r}_2, \]  

(33)

is the corresponding two-particle entropy production.

A previous analysis on simultaneous motion of \( N \)-Brownian particles leads to the next global entropy production \[5\],

\[ \sigma(t) = \int \sigma^{(N)} d\mathbf{x}^N = \sum_{i=1}^N \int \mathbf{J}_{\mathbf{u}_i}^{(N)} \cdot k \frac{\partial}{\partial \mathbf{u}_i} \ln \left( \frac{P^{(N)}}{P^{(N)}_{\text{eq}}} \right) d\mathbf{x}^N. \]  

(34)
Inserting in this expression the distribution functions \( \ln P^{(N)} \) and \( \ln P^{(eq)}_{\text{eq}} \), given through eqs. (14) and (15) we obtain an alternative expression for the global entropy production, i.e.,

\[
\int \sigma^{(N)} d\mathbf{x}^N =
\]

\[
= Nk \int J_{u_1}^{(1)} \cdot \frac{\partial}{\partial u_1} \ln \left( \frac{P^{(1)}}{P^{(eq)}} \right) d\mathbf{u}_1 d\mathbf{r}_1 +
\]

\[
\frac{N (N - 1)}{2} k \sum_{j=1}^{2} \int J_{u_i}^{(2)} \cdot \frac{\partial}{\partial u_i} \ln \left( \frac{g^{(2)}}{g^{eq}} \right) d\mathbf{u}_2 d\mathbf{r}_{12} d\mathbf{u}_1 + \ldots
\]  (35)

Where we have taken into account the definition of the reduced fluxes, eq. (8).

We notice that the local entropy production \( \sigma (\mathbf{r}_1, t) = \sigma^{(1)} (\mathbf{r}_1, t) + \sigma^{(2)} (\mathbf{r}_1, t) \) can be identified in the integrand of eq. (35). This means that consistently we can use the integrand of the eq. (34) as the local entropy production, and afterwards the hypothesis that the fluxes \( J^{(N)}_{u_i} \) are coupled to the thermodynamic forces \( \frac{\partial}{\partial u_i} \ln \left( \frac{P^{(N)}}{P^{(eq)}} \right) \), giving rise to the next phenomenological equations,

\[
J_{u_i}^{(N)} = -k \sum_{j \neq i}^{N} L u_{i,j} \frac{\partial}{\partial u_i} \ln \left( \frac{P^{(N)}}{P^{(eq)}} \right). \quad (36)
\]

Defining the friction coefficients as

\[
\beta_{ij} = \frac{m L_{u_i u_j}}{P^{(N)} T^{eq}}, \quad (37)
\]

we can give an alternative and more useful expression for the fluxes \( J_{u_i}^{(N)} \), namely,

\[
J_{u_i}^{(N)} = - \sum_{j \neq i}^{N} \beta_{ij} \left( P^{(N)} u_j + \frac{kT^{eq}}{m} \frac{\partial P^{(N)}}{\partial u_j} \right). \quad (38)
\]

Particularly, for the one and two-particle description the corresponding fluxes are,

\[
J_{u_1}^{(1)} = \beta_{11} \left( P^{(1)} u_1 + \frac{kT^{eq}}{m} \frac{\partial P^{(1)}}{\partial u_1} \right), \quad (39)
\]

and

\[
J_{u_i}^{(2)} = \sum_{i,j=1}^{2} \beta_{ij} \left( P^{(2)} u_i + \frac{kT^{eq}}{m} \frac{\partial P^{(2)}}{\partial u_i} \right). \quad (40)
\]

Inserting now these expressions into the continuity equations (9) and (10) one obtains the desired Fokker-Planck equations,
\[
\frac{\partial}{\partial t} P^{(1)} + \mathbf{u}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} P^{(1)} - m^{-1} \int \frac{\partial \phi_{12}}{\partial \mathbf{r}_1} \cdot \frac{\partial P^{(2)}}{\partial \mathbf{u}_1} d\mathbf{u}_2 d\mathbf{r}_2 = \frac{\partial}{\partial \mathbf{u}_1} \cdot \beta_{11} \left( P^{(1)} \mathbf{u}_1 + \frac{kT_{eq}}{m} \frac{\partial P^{(1)}}{\partial \mathbf{u}_1} \right)
\] 

(41)

and

\[
\frac{\partial}{\partial t} P^{(2)} + \sum_{i=1}^{2} \mathbf{u}_i \cdot \frac{\partial P^{(2)}}{\partial \mathbf{r}_i} - m^{-1} \sum_{i,j=1}^{2} \frac{\partial \phi_{ij}}{\partial \mathbf{r}_i} \cdot \frac{\partial P^{(2)}}{\partial \mathbf{u}_i} = \sum_{i,j=1}^{2} \frac{\partial}{\partial \mathbf{u}_i} \cdot \beta_{ij} \left( P^{(2)} \mathbf{u}_i + \frac{kT_{eq}}{m} \frac{\partial P^{(2)}}{\partial \mathbf{u}_i} \right).
\]

(42)

The analysis of these equations, deserves some comments. The third term on the left hand side of eq. (41) represents the local equilibrium mean effective interaction potential applied at the point \(\mathbf{r}_1\), where we have included the instantaneous interaction of a Brownian particle placed at \(\mathbf{r}_1\), with the solvent. If we do not take into account this mean field term, coming from the interactions of a cloud of Brownian particles around \(\mathbf{r}_1\), including the local structure of the solvent, we recover the usual one-particle Fokker-Planck equation [23].

With respect to eq. (42), the effective interactions \(-m^{-1} \sum_{i,j=1}^{2} \frac{\partial \phi_{ij}}{\partial \mathbf{r}_i} \cdot \frac{\partial P^{(2)}}{\partial \mathbf{u}_i}\) are applied in a non-local manner over the two tracer particles placed at \(\mathbf{r}_1\) and \(\mathbf{r}_2\), respectively. The friction tensor is taken by pairs now with respect to the two selected particles. This Fokker-Planck equation coincides with the one obtained first by Mazo [24] and more recently by Piasecki et al [25]. This last one was derived for a system of two-Brownian hard spheres immersed in a hard-sphere solvent.

When the velocities of the Brownian particles thermalize the system reaches the state of local equilibrium. For this case, the dynamical description of the Brownian particles would be represented by the evolution equations for the one- and two-particle local equilibrium distribution functions. Hence, the right hand sides of the continuity equations (9) and (10) should be replaced by \(-\frac{\partial J^{(1)}_{\mathbf{r}_1}}{\partial \mathbf{r}_1}\) and \(-\sum_{i=1}^{2} \frac{\partial J^{(2)}_{\mathbf{r}_i}}{\partial \mathbf{r}_i}\), respectively. Following a similar analysis as the one performed in this section, we would obtain the expressions for the fluxes \(J^{(1)}_{\mathbf{r}_1}\) and \(J^{(2)}_{\mathbf{r}_i}\). The final result would correspond to a couple of equations of Smoluchowski type. Such approach has allowed the calculation of the long time self-diffusion coefficient of hard sphere suspensions and, the corresponding comparison with Brownian dynamics simulations [26].

The one- and two-particles Fokker-Planck equations describe the dynamics of the system at mesoscopic level, under the assumption of pair interactions. These expressions can be used to analyze the hydrodynamic regime of the Brownian gas. This will be the goal of the next section.
4 Hydrodynamic equations

Our purpose in this section is to derive the complete set of hydrodynamic equations describing macroscopically the dynamics of the gas of Brownian particles. For simplicity in our notation, we will omit the dependences of the different quantities in \((r_1, t)\). The conservation law for the mass of the particles follows from the definition of the density

\[
\rho_B = m \int P^{(1)}(u_1) du_1.
\]

We take the temporal derivative of this expression and use the continuity equation (9). After integrating by parts the resulting equation and using the fact that the current \(J_{u_1}^{(1)}\) decays very rapidly when increasing the velocity, one obtains the conservation law

\[
\frac{\partial \rho_B}{\partial t} = - \frac{\partial}{\partial r_1} \cdot \rho_B v_B.
\]

We can proceed in a similar way \([8]\) with the definition of the momentum density of the Brownian particles

\[
\rho_B v_B = m \int u_1 P^{(1)}(u_1) du_1.
\]

By taking the time derivative of this equation and using the one-particle Fokker-Planck equation (41), we obtain a preliminary balance equation for the momentum density,

\[
\frac{\partial \rho_B v_B}{\partial t} + \frac{\partial}{\partial r_1} \cdot \left( \overleftrightarrow{v}_B \rho_B v_B \right) = - \int P^{(2)} \frac{\partial \phi_{12}}{\partial r_1} d\mathbf{r}_2 d\mathbf{u}_2 d\mathbf{u}_1 - \beta_{11} \rho_B v_B.
\]

Here

\[
\overleftrightarrow{v}_B = m \int P^{(1)} (u_1 - v_B) (u_1 - v_B) du_1,
\]

is the kinetic part of the pressure tensor for the Brownian particles, with \(\beta_{11}\) the friction coefficient, such that \(\beta_{11} \rho_B v_B\) takes into account the momentum exchange between the Brownian particles and the bath.

Now, we admit that the distribution function \(P^{(2)}\) varies slowly with the space coordinates as it should be for a concentrated suspension. Expanding the probability density \(P^{(2)}\) around the distance \(r_{12} = r_2 - r_1\) between particles \([27]\), we may approximate

\[
\int P^{(2)} \frac{\partial \phi_{12}}{\partial r_1} d\mathbf{r}_2 \approx
\]
\[ \approx -\frac{\partial}{\partial r_1} \frac{m}{2} \int r_1 r_{12} \frac{\phi_{12}'(r)}{r_{12}} \int_0^1 P^{(2)}(r_1 - [1 - \alpha] r_{12}, r_1 + \alpha r_1, u_1, u_2, t) \, d\alpha \, dr_{12}, \]  

(48)

with \( \phi_{12}'(r_{12}) = \frac{\partial \phi_{12}}{\partial r_{12}} \). This relation enables us to identify the potential component of the pressure tensor, namely,

\[ \vec{P}^\phi_B = -\frac{m}{2} \int r_1 r_{12} \frac{\phi_{12}'(r_{12})}{r_{12}} \times \left( \int_0^1 P^{(2)}(r_1 - [1 - \alpha] r_{12}, r_1 + \alpha r_{12}, u_1, u_2, t) \, d\alpha \right) \, dr_1 du_1 du_2. \]  

(49)

By means of the above identity, the momentum balance (46) can be rewritten in the usual manner \[22, 28\],

\[ \rho_B \frac{d\vec{v}_B}{dt} = -\frac{\partial}{\partial r_1} \cdot \vec{P}_B - \beta_{11} \rho_B \vec{v}_B, \]  

(50)

with

\[ \vec{P}_B = \vec{P}^k_B + \vec{P}^\phi_B, \]  

(51)

the total pressure tensor of the Brownian particles and \( \frac{d}{dt} = \frac{\partial}{\partial t} + \vec{v}_B \cdot \frac{\partial}{\partial r_1} \) the hydrodynamic derivative. This expression for the pressure tensor is consistent with the one obtained by Felderhof \[29\] (eqs. 3.11 and 3.14 of such reference), who used the N-particle Fokker-Planck equation for its derivation.

In order to complete our scheme, we need to obtain the balance equation for the density of internal energy of the “gas” of Brownian particles \( \rho_B u_B \). This quantity splits up into kinetic and potential contributions

\[ \rho_B u_B = \rho_B u^k_B + \rho_B u^\phi_B, \]  

(52)

where

\[ \rho_B u^k_B = \frac{m}{2} \int P^{(1)}(u_1 - \vec{v}_B)^2 \, du_1 \]  

(53)

and

\[ \rho_B u^\phi_B = \frac{m}{2} \int P^{(2)} \phi_{12} du_1 du_2 dr_2, \]  

(54)

are the densities of kinetic and potential energies, respectively. Taking the temporal derivative of eq. (53) and using the Fokker-Planck eq. (41), one obtains,
\[
\frac{\partial}{\partial t} \rho_B u^k_B = - \frac{\partial}{\partial r_1} \left( \frac{m}{2} \int (u_1 - v_B)^2 u_1 P^{(1)} \, du_1 + \int \frac{P^{(1)} u_1 \cdot \partial (u_1 - v_B)^2}{\partial r_1} \, du_1 \right)
\]
\[
+ \frac{m}{2} \int (u_1 - v_B)^2 \frac{\partial}{\partial u_1} \beta_{11} \left[ P^{(1)} u_1 + \frac{k T_{eq} \partial P^{(1)}}{m} \right] \, du_1
\]
\[
= - \frac{\partial}{\partial r_1} \left[ \frac{m}{2} \int (u_1 - v_B)^2 (u_1 - v_B) P^{(1)} \, du_1 + \int \frac{(u_1 - v_B)^2 P^{(1)} \, du_1 v_B}{2} \right]
\]
\[
+ \frac{m}{2} \int P^{(1)} u_1 \cdot \frac{\partial}{\partial r_1} (u_1 - v_B)^2 \, du_1
\]
\[
- m \left( \frac{T - T_{eq}}{T} \right) \beta_{11} \int P^{(1)} (u_1 - v_B)^2 \, du_1.
\]

Defining now
\[
J^k_q = \frac{m}{2} \int (u_1 - v_B)^2 (u_1 - v_B) P^{(1)} \, du_1 \quad (55)
\]

the kinetic part of the heat flux, using the definition of the kinetic energy density (53) and the next identity,
\[
\frac{m}{2} \int P^{(1)} u_1 \cdot \frac{\partial}{\partial r_1} (u_1 - v_B)^2 \, du_1 =
\]
\[
= m \int P^{(1)} (u_1 - v_B) : \frac{\partial (u_1 - v_B)}{\partial r_1} \, du_1
\]
\[
= - \left[ m \int P^{(1)} (u_1 - v_B) (u_1 - v_B) \, du_1 \right] : \frac{\partial v_B}{\partial r_1},
\]

we obtain the balance equation for the kinetic part,
\[
\frac{\partial}{\partial t} \rho_B u^k_B = - \frac{\epsilon_B^k}{P_B} \ : \ \frac{\partial v_B}{\partial r_1} - \frac{\partial}{\partial r_1} \cdot \left( J^k_q - \rho_B u^k_B v_B \right)
\]
\[
- m \left( \frac{T - T_{eq}}{T} \right) \beta_{11} \int P^{(1)} (u_1 - v_B)^2 \, du_1. \quad (56)
\]

The derivation of the above balance equation deserves some comments. First of all we have assumed that the friction coefficient is independent of the velocity. This means that we have not taken into account the non-linear friction case. The velocity dependence of the friction coefficient \( \beta_{11}(u_1) \) concerns with
the case in which the Brownian particles are able to take up external energy, which can be stored in an internal energy depot [30]. This phenomenon is the so-called active motion and is of interest in the dynamical analysis of driven physico-chemical [31] and biological systems [32]. If we want to take into account this fact, the above balance equation (56) would include the additional term $-m \int P^{(1)\beta_{11}}(u_1 - v_B) \cdot v_B du_1$. Moreover, the temperature $T$ corresponds to a non-equilibrium distribution of the Brownian particles, which eventually thermalizes to the usual Maxwell velocity distribution function $F_{eq}^{(1)}$ with the equilibrium temperature $T_{eq}$. In this manner, the last term of eq. (56) accounts for the kinetic energy interchange between the Brownian particles and the heat bath.

Using the kinetic energy density definition (53) together with the energy equipartition theorem, namely,

$$\rho_B^k u_{B_{eq}}^k = \frac{3 \rho_B k T_{eq}}{2m},$$

(57)

the last term in the equation (56) can be rewritten as follows,

$$-m \left( \frac{T - T_{eq}}{T} \right) \beta_{11} \int P^{(1)}(u_1 - v_B)^2 du_1 = -2\rho_B^k \beta_{11} \left( u_B^k - u_{B_{eq}}^k \right).$$

(58)

With this expression, we recover the usual kinetic energy balance equation for a dilute suspension of Brownian particles [7],

$$\frac{\partial}{\partial t} \rho_B^k u_B^k = -\nabla_B^k \cdot \nabla_B + \beta_{11} \left( J_{qB}^k - \rho_B^k u_B^k v_B \right) - 2\beta_{11} \rho_B^k \left( u_B^k - u_{B_{eq}}^k \right)$$

(59)

The potential energy balance equation follows from its definition eq. (54). By using the two-particle Fokker-Planck eq. (42) and Newton’s third law $\frac{\partial \phi_{12}}{\partial r_1} = -\frac{\partial \phi_{12}}{\partial r_2}$, we obtain

$$\frac{\partial}{\partial t} \rho_B^k u_{\phi}^k = -\frac{\partial}{\partial r_1} \cdot \left( J_{q\phi}^k + \rho_B^k u_{\phi}^k v_B \right) + \frac{m}{2} \int P^{(2)}(u_1 - u_2) \cdot \frac{\partial \phi_{12}}{\partial r_1} du_1 du_2 dr_2,$$

(60)

in which

$$J_{q\phi}^k(r_1, t) = m \int (u_1 - v_B) \frac{\partial \phi_{12}}{\partial r_1} P^{(2)} du_1 du_2 dr_2,$$

(61)

is the current of potential energy density transport and $\frac{\partial}{\partial r_1} \int P^{(2)}(u_1 - u_2) \cdot \frac{\partial \phi_{12}}{\partial r_1} du_1 du_2 dr_2$ is the production term. After applying the approximate expression (48) one has,

$$\frac{\partial}{\partial t} \rho_B^k u_{\phi}^k = -\frac{\partial}{\partial r_1} \cdot \left( J_{q\phi}^{(1)} + J_{q\phi}^{(2)} + \rho_B^k u_{\phi}^k v_B \right)$$

(62)
\[
\int P(2) \frac{\partial \phi_{12}}{\partial r_1} \cdot u_1 du_1 du_2 dr_2 - \rightarrow \mathcal{P}_B \cdot \frac{\partial \nu_B}{\partial r_1} \tag{62}
\]

where

\[
J^{(2)}_{q\phi}(r_1, t) = -\frac{1}{4} \int_{r_1}^{r_2} \frac{\partial \phi_{12}}{\partial r_1} (u_1 + u_2 - 2v_B) \times \]

\[\times \int_0^1 m P^{(2)} (r_1 - [1 - \alpha] r_1, u_2, r_1 + \alpha r_1, u_1; t) d\alpha du_1 du_2 dr_2 \tag{63}\]

is the potential contribution to the heat transport.

Regarding the term \( \int P(2) \frac{\partial \phi_{12}}{\partial r_1} \cdot u_1 du_1 du_2 dr_2 \), when we neglect the velocity dependence of the pair dynamic correlation function, i.e., \( P^{(2)}(x_1, x_2, t) = P^{(1)}(x_1, t) P^{(1)}(x_2, t) g^{(2)}(r_1, r_2, t) \), we have,

\[
\int P^{(2)} \frac{\partial \phi_{12}}{\partial r_1} \cdot u_1 du_1 du_2 dr_2 = \]

\[= \rho_B(r_1, t) m v_B \cdot \int \rho_B(r_2, t) m g^{(2)}(r_1, r_2, t) \frac{\partial \phi_{12}}{\partial r_1} dr_2 \]

\[= -\rho_B(r_1, t) m v_B \cdot F(r_1, t). \tag{64}\]

Taking into account that the potential contributions to the pressure tensor (eq. 49) and the second part for the heat flux (eq. 63) estimate the short range interactions by means of the approximation described in eq. (48), the force \( F(r_1, t) = -\int \rho_B(r_2, t) g^{(2)}(r_1, r_2, t) \frac{\partial \phi_{12}}{\partial r_1} dr_2 \) accounts for the long range interactions. With these considerations, the potential energy balance takes the conventional macroscopic form \([3]\),

\[
\frac{\partial}{\partial t} \rho_B u_B^\phi = -\frac{\partial}{\partial r_1} \cdot \left( J^{(1)}_{q\phi} + J^{(2)}_{q\phi} + \rho_B u_B v_B \right) - \mathcal{P}_B \cdot \frac{\partial \nu_B}{\partial r_1} - \frac{\rho_B}{m} v_B \cdot F. \tag{65}\]

The balance of internal energy follows just by adding eqs. (59) and (65), i.e,

\[
\frac{\partial}{\partial t} \rho_B u_B + \frac{\partial}{\partial r_1} \cdot \left( J^B_q + \rho_B u_B v_B \right) = -\frac{\rho_B}{m} v_B \cdot F + \mathcal{P}_B \cdot \frac{\partial \nu_B}{\partial r_1} - 2\rho_B \beta_{11} \left( u_{B}^k - u_{Beq}^k \right), \tag{66}\]

where

\[
J^B_q = J_{qk} + J^{(1)}_{q\phi} + J^{(2)}_{q\phi} \tag{67}\]
is the total heat flux, due to the energy interchange of Brownian particles with the solvent. The term \(-\frac{\rho_B v_B \cdot F}{m}\) accounts for the rate at which work is done by a Brownian particle over the solvent due to the static pair effective long range interactions. This term would be useful to account for the active motion mentioned above [30].

In this manner, with the help of two-particle Fokker-Planck eqs. (41) and (42), we have obtained the corresponding balance equations for the suspended particles. The expressions for the pressure tensor (eqs. (47) and (49)), and the heat flux (eqs. (55),(61) and (63)) are of particular interest. Using a suitable interaction potential and a pair correlation function for the interacting Brownian particles, and comparing with Fourier and Newton laws, approximate relationships for the heat conductivity and viscosity can be obtained. Moreover, with the help of the momentum balance eq. (50), we can analyze the diffusion regime. This point will be treated in the next section.

5 Diffusion regime

As follows from the balance equation for the momentum of the Brownian particles, the mobility \(b_{11} = \beta_{11}^{-1}\), introduces a characteristic time scale defining the inertial regime in the dynamics of the Brownian particles. For times such that \(t >> b_{11}\), the particle enters the diffusive regime in which the inertial term on the left hand side of eq.(50) is negligibly small, hence this equation yields,

\[-\frac{\partial}{\partial t} \vec{P}_B = \beta_{11} \rho_B \vec{v}_B.\]  

(68)

For the particular case where no external flow is imposed to the system, the pressure tensor \(\vec{P}_B\) reduces to the osmotic pressure \(\vec{P}_B = \rho_B \vec{U}\), with \(\vec{U}\) being the unit tensor and

\[p_B = \frac{\rho_B kT}{m} - \frac{2\pi}{3} \left(\frac{\rho_B}{m}\right)^2 \int \partial \phi_{12}^{(2)}(r_{12})r_{12}^3 dr_{12};\]  

(69)

the pressure that the set of Brownian particles exerts on the host fluid, recovering the usual virial equation of state. This result agrees with the one obtained by Brady using purely hydrodynamic arguments [33].

Using the definition of the mass current \(J = \rho_B \vec{v}_B\) and the expression of the pressure (69), we obtain from eq. (68) the Fick’s law

\[J = -D_c \frac{\partial \rho_B}{\partial \vec{r}},\]  

(70)

from which we can identify the collective diffusion coefficient.

\[D_c = \frac{kT}{m} \left[1 - \frac{4}{3} \frac{\rho_B}{kTm} \int_0^\infty \frac{r_{12}^3}{\partial r} g_{eq}^{(2)} r_{12}^3 dr_{12}\right] b_{11}.\]  

(71)

For long times, this quantity accounts for the relaxation of the spatial distribution of Brownian particles. In the redistribution of particles, we have included
the influence of the solvent through the additional contribution to the potential interaction per particle. For the particular case in which the effective interactions related to $\phi_{12}$ decay faster than $r_{12}^{-3}$, where $r_{12}$ is the relative separation of two Brownian particles, the diffusion coefficient becomes

$$D_c = \frac{kT}{m} \left[ 1 - 4\pi \rho_B \int_0^\infty \left\{ g_{eq}^{(2)}(r_{12}) - 1 \right\} r_{12}^{-1} dr_{12} \right] b_{11} ,$$

which agrees with the corresponding expression given by Russel [35]. Alternatively, by using the virial equation of state for the Brownian particles (69), we obtain the usual thermodynamic relationship [23], [36], between the macroscopic collective diffusion tensor and the osmotic compressibility,

$$D_c = b_{11} \left( \frac{\partial p_B}{\partial \rho_B} \right)_T ,$$

The ensuing expression relating collective diffusion, mobility and compressibility, deserves some additional comments. First of all, it relates the mass transfer ratio with the isothermal compressibility as the driven force and the hydrodynamic mobility as the response function. The mobility appears in our scheme as a phenomenological coefficient, which may in general depend on time [34]. The explicit expression of this coefficient must be borrowed from hydrodynamics.

At the two-particle level of our description, the appropriate approach is the one given by Batchelor [37]. Moreover, the pressure tensor (51) arising from the momentum balance accounts for the pressure exerted over the solvent, thus the pressure difference between two separate points drives the collective motion of Brownian particles from different sides of the solvent. This fact has been used to interpret light scattering experiments in micellar emulsions [38], [4] and lyophilic silica particles in nonpolar solvents [39] where eq. (71) and the virial form for the pressure were used as a working hypothesis. It has served to test the application of liquid theories to suspensions and to analyze its validity for arbitrary concentrations and for pair continuous interaction potentials [35], [36].

The above relation must be complemented with the functional dependence of $b_{11} (\Phi)$ and $p_B (\Phi)$, on $\Phi = \frac{4}{3} \pi a^3 \rho_B$ the volume fraction of the Brownian particles. The expression for the mobility $b_{11} (\Phi)$ can again be obtained from hydrodynamics. For a hard sphere model with stick boundary conditions in the dilute regime, the result is $b_{11} (\Phi) = (6\pi \eta a)^{-1} (1 - 6.55\Phi)$ [37], with $\eta$ the viscosity of the fluid phase and $a$ the radius of the Brownian particle. An analysis that makes use of a combination of stick and slip boundary conditions [10] helps to fit experimental data [1]. Moreover, for strongly charged spheres at low salinity based on an effective macroion fluid theoretical model, the mobility is well represented by the parametric form $b_{11} (\Phi) = (6\pi \eta a)^{-1} (1 - p\Phi^\alpha)$ [41]. Using a model of effective hard spheres with $\Phi$ -dependent diameter, the values $p \approx 1.8$ and $\alpha = \frac{1}{3}$ can be explained.

The effect of interactions in the Brownian motion, was discussed in a phenomenological manner by Van den Broeck et al [12] through the generalized Einstein expression (73). They use the Batchelor’s expression for the mobility
and the virial form for the osmotic pressure (69), such that for the case when the interaction potential contains in addition to a hard core part a purely attractive interaction the mobility $b_{11}(\Phi)$ increases and both, the compressibility $\left(\frac{\partial p_B}{\partial \rho_B}\right)_T$ and the collective diffusion $D_c$ decrease. The opposite effect occurs when a purely repulsive interaction appears along with the hard repulsive part. These results have been corroborated by experiments [2].

We would like to notice on the fact that although our study has been performed for interacting Brownian particles the obtained collective diffusion coefficient (73) could be used to study sedimentation processes [36]. Moreover, to interpret recent experiments of sedimenting particles [43], the functional form of the osmotic pressure $p_B(\Phi)$ for hard sphere Brownian particles is particularly useful. Our study focused on continuous pair interactions, we then confirm the validity of the relation between collective diffusion, mobility and compressibility (eq. 73) for any pair effective interaction.

6 Concluding Remarks

In this paper we have analyzed the dynamics of a set of interacting Brownian particles by using the method of nonequilibrium thermodynamics. Our approach starts from a previous treatment of simultaneous Brownian motion of colloidal particles, for which the Fokker-Planck equation, describing the evolution of the $N$-particle distribution function, was derived in the framework of mesoscopic nonequilibrium thermodynamics. The evolution equations for the $s$-particle distribution functions are obtained from the continuity equation in phase space. The currents occurring in those equations follow from mesoscopic nonequilibrium thermodynamics. The first two equations are the one- and two-particle Fokker-Planck equations.

The corresponding Fokker-Planck-like equations are analogous to the ones obtained by Mazo [24] and Piascik et al. [25], for the case of hard-sphere macroparticles in a hard-sphere fluid with a multiple time scale which permits the derivation of microscopic expressions for the friction tensors between the macroparticles. The account of the discrete nature of the solvent is very useful to describe, for example, the dynamics of nanocolloids [44].

From the kinetic equations we have discussed the hydrodynamic regime. The balance equations for the conserved quantities are derived from the equations relating those quantities with the moments of the distributions. The momentum balance permits the analysis of the diffusion regime emerging at long times. In this particular level of description, we obtain a generalized Einstein relation for the collective diffusion, mobility and compressibility of the Brownian particles, where the excess chemical potential and the mobility stand for the fit parameters.

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