Vol. 29 (1998) *ACTA PHYSICA POLONICA B* No 6

FROM A STOCHASTIC TO A MICROSCOPIC APPROACH TO BROWNIAN MOTION*

L. Bocquet

Laboratoire de Physique (URA CNRS 1325)
Ecole Normale Supérieure de Lyon
46 Allée d'Italie, 69007 Lyon, France
e-mail: `lbocquet@physique.ens-lyon.fr`

(Received September 17, 1997)

In this lecture, we examine the dynamics of suspensions of mesoscopic (Brownian) particles in a molecular fluid, starting from first principles. We introduce the technique of multiple time-scales to derive the Fokker–Planck equation for a single, or for a set of interacting Brownian particles, starting from the Liouville equation for the full system (Brownian particles and discrete bath). The limitations of the Fokker–Planck equation will then be emphasized. In particular, we shall point out that under "standard" experimental conditions, the Fokker–Planck description cannot be correct and that non-Markovian effects are expected. A microscopic description in the true experimental limit confirms this breakdown and leads to a "generalized" (non-Markovian and non-local in velocity space) Fokker–Planck equation, which describes the thermalization of the Brownian particle.

PACS numbers: 05.40. +j, 05.20. Dd, 82.70. Dd

1. Stochastic description of Brownian motion

We consider systems involving a wide *time-scale* separation in their dynamical evolution. The canonical example for such situations is the Brownian motion of a large and massive Brownian (B) particle suspended in a bath of much smaller and lighter particles. Two time-scales separate out in the system, one associated with the relaxation of the velocity of the B particle and another linked to the collisions with the fluid particles. Therefore, the force due to the fluid acting on the Brownian particle is assumed to consist of two parts: a systematic friction force and a "random" force, which

---

[*] Presented at the Marian Smoluchowski Symposium on Statistical Physics, Zakopane, Poland, September 1–10, 1997.

stems from individual collisions of fluid particles with B. This leads to the well-known stochastic Langevin equation of motion:

$$M\frac{d\boldsymbol{V}}{dt} = \mathcal{F}(\boldsymbol{R}(t)) - M\zeta\boldsymbol{V}(t) + \tilde{\boldsymbol{F}}(t)\,, \tag{1.1}$$

where $\boldsymbol{V}(t)$ is the velocity of B (of mass M), ζ the friction coefficient and $\mathcal{F}(\boldsymbol{R},t)$ an external force. The random force $\tilde{\boldsymbol{F}}(t)$ obeys the fluctuation-dissipation relation

$$\langle\tilde{\boldsymbol{F}}(t')\cdot\tilde{\boldsymbol{F}}(t)\rangle = 2\,\zeta\,\frac{k_BT}{M}\,\delta(t-t')\,. \tag{1.2}$$

An equivalent description can be given in terms of the distribution function $f(\boldsymbol{R},\boldsymbol{V};t)$ of the position $\boldsymbol{R}$ and velocity $\boldsymbol{V}$ of particle B. Because the fluid evolves on a much shorter time-scale than B, a Markov assumption for particle B variables is usually made. Moreover, because of the large mass ratio, collisions with the fluid particles involve only small transfers of momentum and the transition probability between two states of particle B is accordingly sharply peaked around its mean value (*i.e.* only small jumps occurs). Within these two assumptions, the time evolution of $f(\boldsymbol{R},\boldsymbol{V};t)$ reduces to the Fokker–Planck (or Kramers) equation:

$$\left(\frac{\partial}{\partial t} + \boldsymbol{V}\cdot\frac{\partial}{\partial\boldsymbol{R}} + \frac{\mathcal{F}(\boldsymbol{R})}{M}\right)f(\boldsymbol{R},\boldsymbol{V};t) = \zeta\,\frac{\partial}{\partial\boldsymbol{V}}\cdot\left(\boldsymbol{V} + \frac{k_BT}{M}\frac{\partial}{\partial\boldsymbol{V}}\right)f(\boldsymbol{R},\boldsymbol{V};t)\,. \tag{1.3}$$

Note that in this equation, the fluid enters only through the friction coefficient ζ and the temperature T, *i.e.* the fluid variables have been eliminated. This description was first given by Klein [1] and Kramers [2].

However, another level of description is commonly used. If only the spatial evolution of the particle is considered, one may rather use the Smoluchowski equation, governing the time evolution of the probability density $\rho(\boldsymbol{R},t)$ in configuration space:

$$\frac{\partial}{\partial t}\rho(\boldsymbol{R},t) = \frac{1}{M\zeta}\frac{\partial}{\partial\boldsymbol{R}}\cdot\left\{k_BT\,\frac{\partial}{\partial\boldsymbol{R}} - \mathcal{F}(\boldsymbol{R})\right\}\rho(\boldsymbol{R},t)\,, \tag{1.4}$$

where the Stokes-Einstein relation between the friction coefficient ζ and the diffusion constant D of particle B, has been used:

$$D = \frac{k_BT}{M\zeta}\,. \tag{1.5}$$

The description based on Eq. (1.4), first put forward by Smoluchowski [3], predates that of Kramers and Klein. As was pointed out by Kramers [2], the

Smoluchowski description should be obtained from the Kramers equation in the limit where the friction coefficient ζ is large. This can indeed be intuitively understood: if the friction is high, the velocity relaxes after a short time, of order $1/\zeta$, and the evolution on larger time scales is only determined by the spatial distribution. In this limit, the Smoluchowski equation can therefore be derived from the Kramers equation via a perturbative expansion in powers of $1/\zeta$ [4]. However, because the small parameter $1/\zeta$ multiplies the time derivative, a naive application of the perturbation theory fails in the long time limit and leads to secular divergences. The first rigorous link between the two description was given by Wilemski only in 1976 [5] ! In the next section, we present an alternative approach, based on the multiple time scale analysis, which leads to a uniformly convergent expansion [6]. This derivation will serve us as a pedagogical presentation of this technique, which we will use to adress the more fundamental problem of an "ab-initio" description of Brownian motion presented in Section 4.

2. From Kramers to Smoluchowski: multiple time-scale analysis

Let us first show why a standard perturbative expansion of the Fokker–Planck equation fails in the long-time limit. Such an expansion procedure can be found in van Kampen's reference book [4]. We restrict ourselves to the one-dimensional case to simplify the analysis.

Introducing dimensionless variables

$$\tau = t\,\frac{v_T}{\ell}; \quad V = \frac{v}{v_T}; \quad X = \frac{x}{\ell}; \quad F = \mathcal{F}\frac{\ell}{Mv_T^2}; \quad \zeta_d = \zeta\frac{\ell}{v_T}\,, \tag{2.1}$$

where $v_T = \sqrt{k_B T/M}$ is the thermal velocity and ℓ is a characteristic length scale of the system (such as the Brownian particle diameter), the Fokker–Planck equation can be cast in the form

$$\frac{\partial}{\partial V}\left(V + \frac{\partial}{\partial V}\right) f(X,V;\tau) = \frac{1}{\zeta_d}\left[\frac{\partial}{\partial \tau} + V\frac{\partial}{\partial X} + F(X)\frac{\partial}{\partial V}\right] f(X,V;\tau)\,. \tag{2.2}$$

If we insert into (2.2) the "naive" expansion

$$f = f^{(0)} \;+\; \zeta_d^{-1}\, f^{(1)} \;+\; \zeta_d^{-2}\, f^{(2)} \;+\; \ldots \tag{2.3}$$

and identify terms of the same order, we find the following equations

$$\begin{aligned}
&\mathcal{L}_{FP}\; f^{(0)} = 0\,,\\
&\mathcal{L}_{FP}\; f^{(1)} = \left[\frac{\partial}{\partial \tau} + V\frac{\partial}{\partial X} + F(X)\frac{\partial}{\partial V}\right] f^{(0)}\,,
\end{aligned}$$

$$\begin{aligned}\mathcal{L}_{FP}\ f^{(2)} &= \left[\frac{\partial}{\partial\tau} + V\frac{\partial}{\partial X} + F(X)\frac{\partial}{\partial V}\right] f^{(1)}\,,\\ &\dots\end{aligned} \tag{2.4}$$

where we introduced a "Fokker–Planck" operator $\mathcal{L}_{FP}$ defined as

$$\mathcal{L}_{FP} = \frac{\partial}{\partial V}\left(V + \frac{\partial}{\partial V}\right) \tag{2.5}$$

The zeroth order equation imposes a maxwellian velocity distribution

$$f^{(0)}(X,V;\tau) = \Phi(X;\tau)e^{-1/2V^2} \tag{2.6}$$

and the function Φ has to be determined.

The first order equation then gives

$$\mathcal{L}_{FP}\ f^{(1)} \ = \ \frac{\partial\Phi}{\partial\tau}e^{-1/2V^2} + V\left\{\frac{\partial\Phi}{\partial X} - F\ \Phi\right\}e^{-1/2V^2}\,. \tag{2.7}$$

By integrating both sides over V, one obtains a "solubility condition"

$$\frac{\partial\Phi}{\partial\tau} = 0\,. \tag{2.8}$$

The first order correction can now be obtained from (2.7)

$$f^{(1)}(X,V;\tau) = -V\left\{\frac{\partial\Phi}{\partial X} - F\ \Phi\right\}e^{-1/2V^2} + \Psi(X;\tau)e^{-1/2V^2}\,. \tag{2.9}$$

The function Ψ can be determined by replacing the solution for $f^{(1)}$ in the third equation of the hierarchy (2.4). Integrating both sides over V, this yields again a solubility condition

$$\frac{\partial\Psi}{\partial\tau} - \frac{\partial}{\partial X}\left(\frac{\partial\Phi}{\partial X} - F\ \Phi\right) = 0\,. \tag{2.10}$$

Since the probability density $\rho(X;\tau)$ reads

$$\rho(X;\tau) = \sqrt{2\pi}\left[\Phi(X) + \zeta_d^{-1}\Psi(X;\tau) + \mathcal{O}(\zeta_d^{-2})\right]\,,$$

Eq. (2.10) reduces to the (dimensionless) Smoluchowski equation

$$\frac{\partial\rho(X,\tau)}{\partial\tau} = \frac{1}{\zeta_d}\frac{\partial}{\partial X}\left(\frac{\partial\rho(X,\tau)}{\partial X} - F(X)\ \rho(X,\tau)\right)\,. \tag{2.11}$$

However, this perturbative expansion cannot be valid in the long time limit, *i.e.* $\zeta\, t \gg 1$. Indeed, a careful inspection of Eq. (2.10) shows that Ψ diverges as time goes to infinity, since we showed in Eq. (2.8) that Φ is independent of time. Thus the function Ψ is proportionnal to time τ

$$\Psi(X;\tau) \sim \tau\,. \tag{2.12}$$

The standard expansion (2.3) of the solution thus leads to secular divergences and cannot be correct in the long time limit. In other words, the limit of time going to infinity cannot be inverted with the limit of friction going to infinity, so that taking small corrections in $1/\zeta_d$ into account leads to an upper bound for the time τ. In fact, this procedure implicitly expands time-dependent terms like τ/ζ_d as ζ_d^{-1} terms, and secular divergences appear in the long-time limit.

However this pitfall can be overcome using the multiple time-scale analysis [6]. Indeed, two widely different time-scales separate out in the system: there is first a very short period ($t \sim \zeta^{-1}$) during which the velocity of the Brownian particle thermalizes; thereafter the dynamical evolution is controlled by the time-dependence of the *spatial* distribution on longer time-scales. The multiple time-scale analysis consequently replaces the physical distribution function $f(X,V;\tau)$ by an auxiliary function, $f(X,V;\tau_0,\tau_1,\tau_2,\ldots)$, depending on different time-scales. Accordingly, the time derivative in the physical evolution equation (2.2) is replaced by the sum of time derivatives on each time-scale,

$$\frac{\partial}{\partial\tau} \to \frac{\partial}{\partial\tau_0} \;+\; \zeta_d^{-1}\,\frac{\partial}{\partial\tau_1} \;+\; \zeta_d^{-2}\,\frac{\partial}{\partial\tau_2} + \ldots\,. \tag{2.13}$$

The auxiliary distribution function $f(X,V;\tau_0,\tau_1,\tau_2,\ldots)$ is then expanded in powers of the small parameter ζ_d^{-1} and inserted into the evolution equation, where terms of the same order are identified. The physical solution of the system is eventually obtained by restricting the different time variables to the so-called "physical line"

$$\tau_0 = \tau\ ;\ \tau_1 = \zeta_d^{-1}\,\tau\ ;\ \tau_2 = \zeta_d^{-2}\,\tau\ ;\ \ \ldots\,, \tag{2.14}$$

so that

$$\begin{aligned} f(X,V;\tau) \;=\;& f^{(0)}(X,V;\tau,\zeta_d^{-1}\,\tau,\zeta_d^{-2}\,\tau,\ldots) \\ &+\zeta_d^{-1}\,f^{(1)}(X,V;\tau,\zeta_d^{-1}\,\tau,\zeta_d^{-2}\,\tau,\ldots) \;+\; \ldots \end{aligned} \tag{2.15}$$

will be the solution of the Fokker–Planck equation (2.2). Equation (2.14) indicates that the dependence of the distribution function on τ_n characterizes the evolution on the time-scale $\tau \sim \zeta_d^n$ ($n = 0,1,2,\ldots$). The crucial difference with the standard perturbation method is that outside the physical line (2.14), the auxiliary distribution function has no physical meaning. Therefore appropriate boundary conditions can be imposed to require the expansion to be uniform in the small parameter ζ_d^{-1}. This freedom will be used to eliminate secular divergences.

The identification of different powers of ζ_d^{-1} in the Kramers equation gives the modified hierarchy of relations

$$\begin{aligned}
&\mathcal{L}_{FP}\; f^{(0)} = 0\,,\\
&\mathcal{L}_{FP}\; f^{(1)} = \left[\frac{\partial}{\partial \tau_0} + V\frac{\partial}{\partial X} + F(X)\frac{\partial}{\partial V}\right] f^{(0)}\,,\\
&\mathcal{L}_{FP}\; f^{(2)} \;=\; \left[\frac{\partial}{\partial \tau_0} + V\frac{\partial}{\partial X} + F(X)\frac{\partial}{\partial V}\right] f^{(1)} + \frac{\partial}{\partial \tau_1} f^{(0)}\,,\\
&\dots\;. \qquad (2.16)
\end{aligned}$$

Now, proceeding along the same lines as previously, we obtain the same solutions for $f^{(0)}$ and $f^{(1)}$, as given in Eqs (2.6) and (2.9), but the spatial part of the distribution function, Φ and Ψ, now verify the modified solubility conditions:

$$\begin{aligned}
\frac{\partial \Phi}{\partial \tau_0} &= 0\,,\\
\frac{\partial \Psi}{\partial \tau_0} &= -\left(\frac{\partial \Phi}{\partial \tau_1} - \frac{\partial}{\partial X}\left(\frac{\partial \Phi}{\partial X} - F\;\Phi\right)\right)\,. \qquad (2.17)
\end{aligned}$$

Therefore, Ψ does not evolve on the shortest time-scale τ_0. and the r.h.s. of the second equation in (2.17) does not depend on τ_0 either. One must then impose the condition

$$\frac{\partial \Psi}{\partial \tau_0} = 0 \qquad (2.18)$$

to eliminate the secular divergence as τ_0 grows to infinity. This leads to a *closed* equation for Φ

$$\frac{\partial \Phi}{\partial \tau_1} - \frac{\partial}{\partial X}\left(\frac{\partial \Phi}{\partial X} - F\;\Phi\right) = 0\,. \qquad (2.19)$$

This result has to be compared with Eq. (2.10) of the standard Hilbert procedure, where the time-dependence of the density was only contained in the first order correction (through Ψ). A correct expansion thus modifies the perturbative scheme and leads to different couplings between the successive corrections to the probability distribution.

The physically relevant equation for ρ is now obtained by restricting the different variables τ_i to the physical line (2.14), $\rho(X;\tau) \equiv \rho(X;\tau_0 = \tau, \tau_1 = \tau/\zeta_d, \ldots)$. Using (2.19), one recovers as expected the (dimensionless) Smoluchowski equation (2.11).

3. Brownian motion from first principles

3.1. Multiple time scale derivation of the Fokker–Planck equation

The multiple time-scale analysis will now be used to adress the problem of a "first principles" derivation of the Fokker–Planck equation. In other words, we will show that it is possible to bypass the stochastic assumptions involved in the phenomenological description of Brownian motion as described in Section 1. Starting from the Liouville equation governing the evolution of the phase space density for one heavy Brownian particle of mass M in a bath of small particles of mass m, the fluid variables will be explicitly eliminated via an expansion in powers of the square root of the mass ratio $\sqrt{m/M}$ to eventually obtain the Fokker–Planck equation for particle B only. The following elegant derivation for continuous potentials is due to Cukier and Deutch [7]. The corresponding derivation for the hard sphere potential can be found in [8].

The system is characterized by its phase space distribution function

$$f_{N+1} \equiv f_{N+1}(\boldsymbol{r}_1, \boldsymbol{p}_1, \ldots, \boldsymbol{r}_N, \boldsymbol{p}_N, \boldsymbol{R}, \boldsymbol{P}; t)\,,$$

which evolves according to the Liouville equation

$$\left(\frac{\partial}{\partial t} + \mathcal{L}\right) f_{N+1} = 0\,. \tag{3.1}$$

The notation $\boldsymbol{r}_i, \boldsymbol{p}_i$ stands as usual for position and momentum of particle i. The Liouville operator $\mathcal{L}$ splits into two differential operators involving bath and particle B variables respectively, $\mathcal{L} = \mathcal{L}_b + \mathcal{L}_B$, defined as:

$$\begin{aligned} \mathcal{L}_b &= \sum_i \left(\frac{\boldsymbol{p}_i}{m} \cdot \frac{\partial}{\partial \boldsymbol{r}_i} + \boldsymbol{F}_i \cdot \frac{\partial}{\partial \boldsymbol{p}_i} \right)\,, \\ \mathcal{L}_B &= \frac{\boldsymbol{P}}{M} \cdot \frac{\partial}{\partial \boldsymbol{R}} + \boldsymbol{F} \cdot \frac{\partial}{\partial \boldsymbol{P}}\,, \end{aligned} \tag{3.2}$$

where $\boldsymbol{F}_i$ and $\boldsymbol{F}$ denotes the forces acting on particle i and on particle B respectively. The natural "smallness" parameter in the problem is $\varepsilon = (m/M)^{1/2}$ and the Brownian limit is defined as $\varepsilon \to 0$. Introducing a scaled momentum of particle B as $\boldsymbol{p} = \varepsilon \boldsymbol{P}$, the kinetic energy of the latter becomes $\boldsymbol{P}^2/M = \boldsymbol{p}^2/m$ and the B particle part of the Liouville operator scales as:

$$\mathcal{L}_B = \varepsilon \left(\frac{\boldsymbol{p}}{m} \cdot \frac{\partial}{\partial \boldsymbol{R}} + \boldsymbol{F} \cdot \frac{\partial}{\partial \boldsymbol{p}} \right) \equiv \varepsilon \mathcal{L}'_B \,. \tag{3.3}$$

Our aim is to obtain a closed equation for the B particle distribution function, f_B, which is obtained by integrating the phase-space density over all bath variables:

$$f_B(\boldsymbol{R}, \boldsymbol{p}, t) = \int d\boldsymbol{r}^N d\boldsymbol{p}^N \; f_{N+1}(\boldsymbol{r}_1, \boldsymbol{p}_1, \ldots, \boldsymbol{r}_N, \boldsymbol{p}_N, \boldsymbol{R}, \boldsymbol{p}, t) \,. \tag{3.4}$$

Integrating the Liouville equation (3.1) over bath variables, one arrives at the evolution equation for f_B:

$$\frac{\partial}{\partial t} f_B = -\varepsilon \frac{\boldsymbol{p}}{m} \cdot \frac{\partial}{\partial \boldsymbol{R}} f_B - \varepsilon \int d\boldsymbol{r}^N d\boldsymbol{p}^N \; \boldsymbol{F} \cdot \frac{\partial}{\partial \boldsymbol{p}} f_{N+1} \,. \tag{3.5}$$

If we now apply the multiple time-scale analysis in the $\varepsilon \to 0$ limit, the distribution functions are replaced by auxiliary distributions depending on several time variables $t_0, t_1, t_2, \ldots$ and expanded in powers of ε. The Liouville equation and the reduced equation (3.5) are thus replaced by

$$\left(\frac{\partial}{\partial t_0} + \varepsilon \frac{\partial}{\partial t_1} + \varepsilon^2 \frac{\partial}{\partial t_2} + \ldots \right) f^{\varepsilon}_{N+1} = -\left(\mathcal{L}_b + \varepsilon \, \mathcal{L}'_B \right) f^{\varepsilon}_{N+1} \,, \tag{3.6}$$

$$\left(\frac{\partial}{\partial t_0} + \varepsilon \frac{\partial}{\partial t_1} + \varepsilon^2 \frac{\partial}{\partial t_2} + \ldots \right) f^{\varepsilon}_{B} = -\varepsilon \frac{\boldsymbol{p}}{m} \cdot \frac{\partial}{\partial \boldsymbol{R}} f^{\varepsilon}_B - \varepsilon \int d\boldsymbol{r}^N d\boldsymbol{p}^N \; \boldsymbol{F} \cdot \frac{\partial}{\partial \boldsymbol{p}} f^{\varepsilon}_{N+1} \,. \tag{3.7}$$

To zeroth order, Eq. (3.7) yields

$$\frac{\partial}{\partial t_0} f^{(0)}_B = 0 \,, \tag{3.8}$$

so that $f^{(0)}_B$ is independent of t_0. Now let $f^{eq}_N(1, \ldots, N|\boldsymbol{R})$ denote the equilibrium distribution of the bath in the "external" field of particle B fixed at $\boldsymbol{R}$. The short hand notation $i \equiv (\boldsymbol{r}_i, \boldsymbol{p}_i)$ has been used. By definition, this function verifies $\mathcal{L}_b \, f^{eq}_N = 0$, so that a solution of Eq. (3.6) to zeroth order,

$$\left(\frac{\partial}{\partial t_0} + \mathcal{L}_b \right) f^{(0)}_{N+1} = 0 \tag{3.9}$$

is simply

$$f^{(0)}_{N+1}(1, \ldots, N, \{\boldsymbol{R}, \boldsymbol{p}\}; t_1, t_2) = f^{(0)}_B(\boldsymbol{R}, \boldsymbol{p}; t_1, t_2) \cdot f^{eq}_N(1, \ldots, N|\boldsymbol{R}) \,. \tag{3.10}$$

Now we shall assume that the initial condition is entirely contained in the zero order terms:

$$\begin{aligned} f_B(\boldsymbol{R},\boldsymbol{p};t_0=0,t_1,t_2) &= f_B^{(0)}(\boldsymbol{R},\boldsymbol{p};t_1,t_2)\,, \\ f_B^{(k)}(\boldsymbol{R},\boldsymbol{p};t_0 &= 0,t_1,t_2)=0, \quad k\geq 1\,. \end{aligned} \tag{3.11}$$

To first order, Eqs (3.6), (3.7) reduce to

$$\begin{aligned} \frac{\partial}{\partial t_0} f_{N+1}^{(1)} &+ \frac{\partial}{\partial t_1} f_{N+1}^{(0)} + \mathcal{L}_b f_{N+1}^{(1)} + \mathcal{L}'_B f_{N+1}^{(0)} = 0\,, \\ \frac{\partial}{\partial t_0} f_B^{(1)} &+ \frac{\partial}{\partial t_1} f_B^{(0)} = -\int d\boldsymbol{r}^N d\boldsymbol{p}^N \; \mathcal{L}'_B f_{N+1}^{(0)}\,. \end{aligned} \tag{3.12}$$

Now according to (3.8) and (3.10), $f_B^{(0)}$ and $f_{N+1}^{(0)}$ are independent of t_0. Hence, in order to eliminate secular growth of $f_B^{(1)}$, one must impose

$$\frac{\partial}{\partial t_1} f_B^{(0)} + \int d\boldsymbol{r}^N d\boldsymbol{p}^N \; \mathcal{L}'_B f_{N+1}^{(0)} = 0\,, \tag{3.13}$$

which implies $\frac{\partial}{\partial t_0} f_B^{(1)} = 0$. According to the initial condition (3.11), we arrive at the conclusion that $f_B^{(1)}$ identically vanishes, $f_B^{(1)} \equiv 0$. Moreover, using Eq. (3.10), (3.13) yields

$$\left(\frac{\partial}{\partial t_1} + \frac{\boldsymbol{p}}{m}\cdot\frac{\partial}{\partial \boldsymbol{R}}\right) f_B^{(0)}(\boldsymbol{R},\boldsymbol{p};t_1,t_2) = 0\,, \tag{3.14}$$

and particle B evolves according to free motion on the t_1 time scale. Dissipation is thus expected to occur on the next time scale, characterized by the t_2 variable.

On the other hand, the first order correction $f_{N+1}^{(1)}$ can be obtained from Eq. (3.12), since

$$\begin{aligned} \left(\frac{\partial}{\partial t_0} + \mathcal{L}_b\right) f_{N+1}^{(1)} &= -\left(\frac{\partial}{\partial t_1} + \mathcal{L}'_B\right) f_{N+1}^{(0)} \\ &= -\boldsymbol{F}\cdot\left\{\frac{\beta \boldsymbol{p}}{m} + \frac{\partial}{\partial \boldsymbol{p}}\right\} f_B^{(0)} f_N^{eq}\,, \end{aligned} \tag{3.15}$$

where Eq. (3.14) has been used to obtain the second equality. This equation can be formally solved to give

$$\begin{aligned} & f_{N+1}^{(1)}(1,\ldots,N,\{\boldsymbol{R},\boldsymbol{p}\};t_0,t_1,t_2) \\ & = -\int_0^{t_0} ds \; \exp\{-s\mathcal{L}_b\} \; \boldsymbol{F}\cdot\left\{\frac{\beta \boldsymbol{p}}{m} + \frac{\partial}{\partial \boldsymbol{p}}\right\} f_B^{(0)} f_N^{eq}\,. \end{aligned} \tag{3.16}$$

To second order, Eq. (3.7) yields

$$\frac{\partial}{\partial t_0} f_B^{(2)} + \frac{\partial}{\partial t_2} f_B^{(0)} = - \int d\boldsymbol{r}^N d\boldsymbol{p}^N \; \mathcal{L}'_B f_{N+1}^{(1)} \,. \tag{3.17}$$

Again, secular growth is avoided provided $\frac{\partial}{\partial t_0} f_B^{(2)} = 0$. Using the expression of $f_{N+1}^{(1)}$ obtained in Eq. (3.16), we are left with a closed equation for $f_B^{(0)}$

$$\begin{aligned} \frac{\partial}{\partial t_2} f_B^{(0)} &= \lim_{t_0 \to \infty} \langle \mathcal{L}'_B \int_0^{t_0} ds \; e^{-s\mathcal{L}_b} \boldsymbol{F} \rangle_{\text{bath}} \cdot \left\{ \frac{\beta \boldsymbol{p}}{m} + \frac{\partial}{\partial \boldsymbol{p}} \right\} f_B^{(0)} \,, \\ &= \frac{1}{3} \int_0^{\infty} ds \; \langle \boldsymbol{F} \cdot \boldsymbol{F}(-s) \rangle_{\text{bath}} \frac{\partial}{\partial \boldsymbol{p}} \cdot \left\{ \frac{\beta \boldsymbol{p}}{m} + \frac{\partial}{\partial \boldsymbol{p}} \right\} f_B^{(0)} \,, \end{aligned} \tag{3.18}$$

where the angular brackets denote an average over the bath variables, in equilibrium with particle B fixed at $\boldsymbol{R}$. In going from the first to the second line, the isotropy of the equilibrium state of the bath has been used.

We can now gather results of order 1 and 2, embodied in Eqs. (3.14) and (3.18). Returning to the original variable $\boldsymbol{P}$ and using

$$\frac{\partial}{\partial t} f_B(\boldsymbol{R}, \boldsymbol{P}; t) = \left(\varepsilon \frac{\partial}{\partial t_1} + \varepsilon^2 \frac{\partial}{\partial t_2} \right) f_B^{(0)}(\boldsymbol{R}, \boldsymbol{P}; t_1, t_2)|_{t_1 = \varepsilon t; t_2 = \varepsilon^2 t} + \mathcal{O}(\varepsilon^3) \tag{3.19}$$

one is left with the familiar Fokker–Planck equation for f_B

$$\left(\frac{\partial}{\partial t} + \frac{\boldsymbol{P}}{M} \cdot \frac{\partial}{\partial \boldsymbol{R}} \right) f_B(\boldsymbol{R}, \boldsymbol{P}; t) = \zeta \, \frac{\partial}{\partial \boldsymbol{P}} \cdot \left(\boldsymbol{P} + M k_B T \frac{\partial}{\partial \boldsymbol{P}} \right) f_B(\boldsymbol{R}, \boldsymbol{P}; t) \,, \tag{3.20}$$

where the friction coefficient is explicitly given by the time integral of the autocorrelation function of the force $\boldsymbol{F}$ exerted by the bath on the fixed B particle:

$$\zeta = \frac{1}{3 M k_B T} \int_0^{\infty} ds \; \langle \boldsymbol{F} \cdot \boldsymbol{F}(-s) \rangle_{\text{bath}} \,. \tag{3.21}$$

3.2. Interacting Brownian particles

This analysis can be generalized to any number n of suspended Brownian particles [9, 10]. This leads to a generalized Fokker–Planck equation, in the form

$$\left(\frac{\partial}{\partial t} + \sum_{a=1}^{n} \left[\boldsymbol{V}_a \cdot \frac{\partial}{\partial \boldsymbol{R}_a} + \frac{1}{M} \left(\langle \boldsymbol{F}(\boldsymbol{R}_a; t) \rangle_{\text{bath}} + \sum_{b=1}^{n} \boldsymbol{F}_{ab} \right) \cdot \frac{\partial}{\partial \boldsymbol{V}_a} \right] \right)$$

$$
\times f_n(\boldsymbol{R}_1, \boldsymbol{V}_1, \ldots, \boldsymbol{R}_n, \boldsymbol{V}_n; t)
= \sum_{a=1}^{n} \sum_{b=1}^{n} \bar{\bar{\boldsymbol{\zeta}}}(a,b) : \frac{\partial}{\partial \boldsymbol{V}_a} \left(\frac{\partial}{\partial \boldsymbol{V}_b} + \frac{k_B T}{M} \boldsymbol{V}_b \right) f_n(\boldsymbol{R}_1, \boldsymbol{V}_1, \ldots, \boldsymbol{R}_n, \boldsymbol{V}_n; t) \,. \tag{3.22}
$$

Compared to (1.3), this equation involves two new ingredients. First, the friction is now characterized by a matrix of tensors $\bar{\bar{\boldsymbol{\zeta}}}(a,b)$, defined as

$$
\bar{\bar{\boldsymbol{\zeta}}}_{\text{dyn}}(a,b) = \frac{1}{M k_B T} \int_0^\infty ds \, \langle \delta \boldsymbol{F}(\boldsymbol{R}_a; 0) \cdot \delta \boldsymbol{F}(\boldsymbol{R}_b; -s) \rangle_{\text{bath}} \,, \tag{3.23}
$$

where $\delta \boldsymbol{F}(\boldsymbol{R}_a; s)$ is the fluctuation of the force acting at time s on particle a, all B particles being fixed at $\boldsymbol{R}_1, \ldots, \boldsymbol{R}_n$. Secondly, apart from any direct interaction force $\boldsymbol{F}_{ab}$, the Brownian particles interact through a fluid induced depletion force, $\langle \boldsymbol{F}(\boldsymbol{R}_a; t) \rangle_{\text{bath}}$, occuring because of the anisotropy of the inhomogeous fluid density around the B particles. The multiple time-scale analysis leads very naturally to these depletion effects [10], which are traditionnally introduced on the basis of thermodynamic, entropic arguments [11]. In this analysis, these effects are shown to be the driving force of Brownian particles' motion, on a specific time scale $t \sim \Sigma / \sqrt{k_B T / M}$ (corresponding to the t_1 variable of the previous analysis). In the case of hard spheres, an explicit expression for the depletion force can be found in Ref. [10].

4. Is Brownian motion a markov process ?

This question may sound quite iconoclastic in view of one century of success of the stochastic description. Moreover, we have shown in the previous section that such a description can be derived from first principles in the limit where the Brownian particle is much heavier than the fluid particles. However, an interesting question is: is this the correct limit to describe the motion of suspended particles as observed by Brown and Perrin ? In other words, is the time-scale separation, which is crucial to validate the markov property, correct for suspensions of Brownian particles ?

The answer is in fact negative for typical experimental systems, as already pointed out by many authors [12–15], but already by Lorentz in 1921 [16]. A straightforward calculation shows indeed that the criterium of two widely separated time scales between the relaxation process of the fluid variables and that of the B particle variables, is not met for systems of *suspended* particles. Let us recall shortly the argument. As noticed above, the velocity of particle B relaxes on a time-scale $\tau_V \sim \zeta^{-1}$. If Stokes' law is assumed, this leads to $\tau_V \sim M/\eta\Sigma$, where η is the viscosity of the fluid, and Σ the B particle diameter. On the other hand, a typical hydrodynamic time of the fluid is of order $\tau_f \sim \Sigma^2/(\eta/\rho)$, which is the time for a shear perturbation to propagate over the distance Σ. These rough estimates give $\tau_f/\tau_V \sim \rho/\rho_B$, so that the assumption of a wide time-scale separation is only justified if this ratio is small. This condition was indeed met in the previous derivation of the Fokker–Planck equation of Section 3, since the small mass ratio limit was taken while at the same time *the diameters of the particles* σ *and* Σ *were kept fixed* (thus corresponding to the $\rho/\rho_B \ll 1$ limit). However, this condition is unfortunately far from the experimental situation, where the mass density ratio ρ/ρ_B is taken rather close to unity to avoid sedimentation of particle B. In this case, the fluid dynamics contains slowly decaying modes, which relax on the same time scale as the velocity of the B particle. In other words, non-Markovian effects are expected and the validity of the Fokker–Planck or Langevin equations becomes doubtful. Note however that the Smoluchowski equation, describing the spatial evolution of the B particle, is *a priori* not affected by these arguments, since the position of the B particle relaxes on a time-scale much longer than the velocity (or fluid) relaxation time [14].

Several attempts have been made to overcome these difficulties and determine the dynamical evolution in the general case, that is for any (finite) ρ/ρ_B [12,13,17]. The main idea underlying all these works is that the slowly decaying fluid modes result from the momentum conservation law for the fluid particles. A correct description should therefore treat both fluid and B particle variables on the same level. This can be done for example by using fluctuating hydrodynamics for the fluid motion, with appropriate boundary conditions on the surface of the suspended B particle [12]. These approaches lead to a non-Markovian Langevin equation, involving the time-dependent friction coefficient $\zeta(t)$:

$$M\frac{d\boldsymbol{V}}{dt} = -M\int_0^t d\tau\ \zeta(t-\tau)\ \boldsymbol{V}(\tau) + \tilde{\boldsymbol{F}}(t)\,. \tag{4.1}$$

Instead, our approach has been done at a fully microscopic description, treating both the B particle and the fluid at the same level. This approach allows to clarify and provide the fundamental basis for the phenomenological descriptions. Starting from a microscopic description of the system in the small mass ratio limit, $\frac{m}{M} \ll 1$, *supplemented by the condition of equivalent mass densities*, $\rho \sim \rho_B$, we have shown that the thermalization of the Brownian particle is indeed not a Markov process and thus not governed by a Fokker–Planck equation.

The results are the following. Two important time-scales emerge from the dynamics:

(1) on the first time scale, $t \sim 1/\zeta$, the Brownian particle "does not move", whereas its velocity distribution relaxes in a thermalization process. A closed equation (*i.e.* free of any fluid variable) controlling the relaxation of the B particle distribution function is found, which does not take the Fokker–Planck form. In contradistinction to the latter, the reduced equation controlling thermalization is found to be non-local both in time and velocity space, owing to correlated recollision events between the fluid and particle B. The latter reads:

$$\frac{\partial}{\partial t} f_B(B;t) = \int\limits_0^t ds\ \zeta(t-s) \frac{\partial}{\partial \boldsymbol{V}} \times \exp\left\{ -\int\limits_s^t ds'\ \mathcal{L}_B(s') \right\} \left(\boldsymbol{V} + \frac{k_B T}{M} \frac{\partial}{\partial \boldsymbol{V}} \right) f_B(B;s) \tag{4.2}$$

with $\mathcal{L}_B = \frac{\partial}{\partial \boldsymbol{V}} \cdot \mathcal{F}(B;t)$, $\mathcal{F}(B;t)$ being the dynamical friction force due to the fluid, acting on the B particle during its relaxation (see Eqs. (65)–(66) of Ref. [18] for a complete definition). In Eq. (4.2), $\zeta(t)$ is the time-dependent friction coefficient, defined as:

$$\zeta(t) = \frac{1}{3 M k_B T} \langle \boldsymbol{F} \cdot \boldsymbol{F}(-t) \rangle_{\mathrm{bath}} \,. \tag{4.3}$$

An important point is that, in spite of this complex dynamical behaviour, the diffusion constant of B is still given by the Stokes-Einstein relation (1.5).

The presence of memory terms in (4.2) result from the building up of the friction force by the reaction of the suspending gas to the motion of B. Indeed, the reaction of the fluid to the motion of the Brownian particle takes a finite time to occur (compared to the relaxation time of the velocity of particle B), and the friction force due to the fluid is accordingly displaced in time and velocity space. Moreover, on can show that this non-markovian effect leads to a "slow" thermalization, algebraic in time, in contradistinction to the exponentially decay predicted by the Langevin equation. This non exponential behaviour is in complete agreement with the predictions of the fluctuating hydrodynamics approaches [12, 17]. Numerical simulations of colloidal suspensions, based on fluctuating Lattice Bolztmann techniques [19], do confirm the presence of the so-called "long-time tails" in the velocity autocorrelation function of the Brownian particles. Moreover these algebraic decays has been observed experimentally in the "short-time" dynamics (*i.e.* on the scale of the relaxation of the velocity of the Brownian particles) of colloidal suspensions, the most recent experiments using Diffusing Wave Spectroscopy (DWS) techniques [20].

(2) on the second time scale, $t \sim \Sigma^2/D$, spatial diffusion takes place and is still described by the Smoluchowski equation, *i.e.* no memory effect appears and the corresponding process is markovian.

In other words, the spatial relaxation of the Brownian particle is a Markov process, while the thermalization of the velocity of the Brownian particle, which occurs on a shorter time scale, is not. We refer to Ref. [18] for further details and comments.

REFERENCES

[1] O. Klein, *Ark. Mat. Astron. och Fysik* **16**(5), 1 (1921).

[2] H.A. Kramers, Physica **7**, 284 (1940).

[3] M. von Smoluchowski, *Ann. Phys.* (Germany) **48**, 1103 (1916).

[4] N.G. van Kampen, *Stochastic Processes in Physics and Chemistry*, North Holland, Amsterdam 1990, 6th ed.

[5] G. Wilemski, *J. Stat. Phys.* **14**, 153 (1976).

[6] L. Bocquet, *Am. J. Phys.* **65**, 140 (1997).

[7] R.I. Cukier, J.M. Deutch, *Phys. Rev.* **177**, 240 (1969).

[8] L. Bocquet, J. Piasecki, J.P. Hansen, *J. Stat. Phys.* **76** 505 and 527 (1994).

[9] R.M. Mazo, *J. Stat. Phys.* **1**, 559 (1969).

[10] J. Piasecki, L. Bocquet, J.P. Hansen, *Physica A* **218**, 125 (1995).

[11] S. Asakura, F. Oosawa, J. Polymer Sci. **33**, 183 (1958); see also A. Vrij, *Pure and Appl. Chem.* **48**, 471 (1976).

[12] E.H. Hauge, A. Martin-Löf, *J. Stat. Phys.* **7**, 259 (1973).

[13] E.J. Hinch, *J. Fluid. Mech.* **72**, 499 (1975).

[14] A.J. Masters, *Mol. Phys.* **57**, 303 (1986).

[15] J.N. Roux, *Physica A* **188**, 526 (1992).

[16] H.A. Lorentz, *Lessen over Theoretische Natuurkunde. Kinetische Problemen*, Vol. V., E.J. Brill, Leiden 1921.

[17] D. Bedeaux, P. Mazur, *Physica A* **76**, 247 (1974).

[18] L. Bocquet, J. Piasecki, *J. Stat. Phys.* **87**, 1005 (1997).

[19] A.J.C. Ladd, *Phys. Rev. Lett.* **70**, 1339 (1993); *J. Fluid Mech.* **271**, 311 (1994).

[20] P.D. Fedele, Y.W. Kim, *Phys. Rev. Lett.* **44**, 691 (1980); J.X. Zhu, D.J. Durian, J. Mueller, D.A. Weitz, D.J. Pine, *Phys. Rev. Lett.* **68**, 2559 (1992).