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Friction Tensor for a Pair of Brownian Particles: Spurious Finite-Size Effects and Molecular Dynamics Estimates

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In this work, we show that *in any finite system*, the binary friction tensor for two Brownian particles *cannot* be directly estimated from an evaluation of the microscopic Green–Kubo formula, involving the time integral of force–force autocorrelation functions. This pitfall is associated with a subtle inversion of the thermodynamic and long-time limits and leads to spurious results for the estimates of the friction matrix based on molecular dynamics simulations. Starting from a careful analysis of the coupled Langevin equations for two interacting Brownian particles, we derive a method to circumvent these effects and extract the binary friction tensor from the correlation function matrix of the instantaneous forces exerted by the bath particles on the fixed Brownian particles, and from the relaxation of the total momentum of the bath in a *finite* system. The general methodology is applied to the case of two hard or soft Brownian spheres in a bath of light particles. Numerical estimates of the relevant correlation functions and of the resulting self and mutual components of the matrix of friction tensors are obtained by molecular dynamics simulations for various spacings between the Brownian particles.

KEY WORDS: Brownian motion; friction matrix; hydrodynamic predictions; finite-size effects; molecular dynamics simulations.

This paper is dedicated to B. Jancovici on the occasion of his 65th birthday.

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1. INTRODUCTION

Ever since Green–Kubo (GK) formulae have been derived, expressing linear transport coefficients as time integrals of correlation functions of thermally fluctuating dynamical variables, it has been known that particular care must be exercised in evaluating these integrals from correlation functions for finite systems.(1) Strictly speaking, GK formulae yield non-zero results only provided the thermodynamic limit is taken before the upper limit in the GK integral is taken to infinity. To obtain sensible, non-zero results from the integration of correlation functions of finite systems, like those provided by molecular dynamics (MD) simulations of samples of $N \simeq 10^2 - 10^4$ particles, a somewhat arbitrary upper cut-off τ_N must be applied. For most transport coefficients, involving systems of identical or similar particles, the resulting values are not very sensitive to the precise value of τ_N, since it is found that after a time of the order of the initial, fast relaxation of the system under study (typically a picosecond for dense fluids), the integral reaches a "plateau" value, which roughly coincides with the time beyond which the MD-generated correlation function drops below the noise level.

However, the difficulty is less easily overcome when one considers the classic example of the friction coefficient ζ exerted on a heavy Brownian particle by a bath of much lighter particles. ζ is related to the time integral of the autocorrelation function (ACF) of the instantaneous force exerted by the bath particles on the Brownian particle. Recent MD simulations clearly show that no well-defined "plateau" value of the GK integrand is observed in systems involving several hundred bath particles, so that the cut-off time becomes totally arbitrary.(2, 3) In practice, ζ was determined from the relaxation of the total momentum of the fluid, due to the collisions with a fixed Brownian particle of infinite mass M. In this paper, we consider the case of two Brownian particles suspended in a bath of discrete light particles. We show that finite size effects are even more subtle in this system and lead to spurious results for the computed friction tensor. We then present a method to overcome these effects and obtain the correct friction tensor valid in the thermodynamic limit. This is a first step in a statistical (first principles) approach to the hydrodynamic interactions in suspensions; such interactions are traditionnally derived from macroscopic hydrodynamics(4) which ignore the discrete nature of the bath, and are hence expected to fail at nanometric scales, like those explored by modern surface force machines.(5)

2. SPURIOUS FINITE SIZE EFFECTS

Consider two heavy, spherical Brownian particles suspended in a fluid or bath of much lighter atoms or molecules. The friction tensor $\underline{\underline{\zeta}}$ relates the fluctuations of the forces acting on each Brownian particle to the velocities of the two Brownian particles:

$$\begin{aligned}\delta \mathbf{F}_1(t) &= -\underline{\underline{\zeta}}_{11} \mathbf{V}_1(t) - \underline{\underline{\zeta}}_{12} \mathbf{V}_2(t) \\ \delta \mathbf{F}_2(t) &= -\underline{\underline{\zeta}}_{21} \mathbf{V}_1(t) - \underline{\underline{\zeta}}_{22} \mathbf{V}_2(t)\end{aligned} \tag{1}$$

where the 2×2 matrix ζ_{ab} of friction tensors is a complicated function of the relative position $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$ of the two Brownian particles.

The evaluation of this tensor is a classic problem in macroscopic hydrodynamics which has been given a complete solution quite recently.[4] Conservation laws inside the bath lead to long range hydrodynamic interaction effects between the suspended particles, which decrease like $1/|\mathbf{R}|$:

$$\begin{aligned}\underline{\underline{\zeta}}_{11}^{\parallel/\perp} = \underline{\underline{\zeta}}_{22}^{\parallel/\perp} &\simeq \zeta_0 \left\{1 + \left(\alpha_{\parallel/\perp} \frac{3\Sigma}{8|\mathbf{R}|}\right) + \mathcal{O}[(\Sigma/|\mathbf{R}|)^3]\right\} \\ \underline{\underline{\zeta}}_{12}^{\parallel/\perp} = \underline{\underline{\zeta}}_{21}^{\parallel/\perp} &\simeq \zeta_0 \alpha_{\parallel/\perp} \frac{3\Sigma}{8|\mathbf{R}|} \left\{1 + \mathcal{O}[(\Sigma/|\mathbf{R}|)^3]\right\}\end{aligned} \tag{2}$$

Σ is the diameter of the Brownian particles, $\zeta_0 = 3\pi\eta\Sigma$ is the Stokes estimate of the friction coefficient for a single sphere in the fluid (of shear viscosity η) and the index $\parallel(\perp)$ refers to the direction parallel (perpendicular) to $\mathbf{R}$. The numerical constants $\alpha_{\parallel/\perp}$ are $\alpha_\perp = 1$ and $\alpha_\parallel = 2$. Note that these estimates are valid in the limit where the distance between the spheres is much larger than their radius. In the opposite limit $|\mathbf{R}|/\Sigma \to 1$ (lubrication limit), the main contribution to friction stems from the parallel component of the friction tensor, which is shown to diverge like $1/h_{ab}$, with h_{ab} the minimal distance between the two spheres.[6]

However the macroscopic description completely neglects the molecular nature of the suspending bath, which is treated as a continuum. Therefore, the validity of the hydrodynamic results becomes dubious when the diameter, σ, of the fluid particles and that of the suspended Brownian spheres are comparable or when the minimal distance between the surfaces of the Brownian spheres becomes of the order of σ. In particular, one expects the discrete nature of the bath to remove the divergence of friction in the lubrication limit. Even more questionable is the validity of the long-range character of the hydrodynamic interactions between the Brownian particles in this case.

In this paper, we use numerical simulations to compute the friction tensors for various geometries in the case where σ/Σ is of the order of unity. Our starting point is a microscopic expression for the friction tensor,

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relating the latter to equilibrium force–force correlation functions, in the form of a Green–Kubo formula:[7]

$$\underline{\underline{\zeta}}_{ab} = \frac{1}{k_B T} \int_0^\infty d\tau \langle \delta \mathbf{F}(\mathbf{R}_a; 0)\, \delta \mathbf{F}(\mathbf{R}_b; -\tau) \rangle_{(eq \mid \mathbf{R}_1, \mathbf{R}_2)} \tag{3}$$

where $\delta \mathbf{F}(\mathbf{R}_a; t) = \mathbf{F}(\mathbf{R}_a; t) - \langle \mathbf{F}(\mathbf{R}_a) \rangle_{(eq \mid \mathbf{R}_1, \mathbf{R}_2)}$ is the fluctuation of the force experienced by the Brownian particle a resulting from collisions with fluid particles. The notation $(eq \mid \mathbf{R}_1, \mathbf{R}_2)$ refers to an equilibrium average over the fluid variables in the field of the two fixed Brownian particles, located at $\mathbf{R}_1$ and $\mathbf{R}_2$. This expression (3) has been derived in a variety of ways[8, 9, 10, 11] but recently, we proposed a rigorous and systematic approach for a hard-sphere mixture, using a multiple time-scale analysis,[12] which avoids any "ad hoc" assumptions concerning the separation of time scales. For hard spheres, the fluctuating force reduces to the rate of transfer of momentum from the bath to Brownian particles in the course of instantaneous elastic collisions, as one might have intuitively expected.[13] The average force, on the other hand, which will henceforth be denoted by $\bar{\mathbf{F}}_a$ for brevity, may be identified with the familiar entropic depletion force acting between sterically stabilized colloidal particles.[14]

To obtain a quantitative estimate of the friction tensor, one can in principle compute the force autocorrelation function (FACF) occuring in the r.h.s. of (3) in a numerical experiment, such as in molecular dynamics (MD) simulations, to obtain the friction coefficient after integration. We might expect that such an estimate, obtained for a finite system, would differ from the thermodynamic limit value only by a factor of order of the inverse system size. However, we shall show below that this is not the case, due to a delicate problem associated with the order of thermodynamic and infinite-time (or equivalently infinite mass) limits. We then present a way of extracting the exact (infinite size) friction tensors from the dynamics of a finite system.

Let us first try to understand physically why such a spurious behaviour should be expected in a finite system. We first recall the situation when one attempts to compute the friction coefficient experienced by a single Brownian particle, as discussed in refs. 3 and 2. The scalar friction coefficient is then defined by

$$\zeta = \frac{1}{3k_B T} \int_0^\infty d\tau \langle \mathbf{F}(0) \cdot \mathbf{F}(-\tau) \rangle_{(eq \mid \mathbf{R})} \tag{4}$$

where $\mathbf{F}$ is the instantaneous force acting on the Brownian particle fixed at $\mathbf{R}$. If we consider a finite system, then this force can be expressed as the time-derivative of the total momentum $\mathbf{P}(t)$ of the fluid particles. The integration on the r.h.s. of (4) can be done explicitly yielding

$$\int_0^{\infty} \langle \mathbf{F}(0) \cdot \mathbf{F}(-\tau) \rangle_N \, d\tau = -\lim_{t \to \infty} \langle \dot{\mathbf{P}}(t) \cdot \mathbf{P}(0) \rangle_N = 0 \tag{5}$$

On the contrary, if the thermodynamic limit is taken first in the FACF of Eq. (4), before taking time to infinity, then the momentum gained by the fluid can be carried off to infinity and the r.h.s. of Eq. (5), with $N = \infty$, does not vanish. Now let us return to the case of two fixed Brownian particles in the presence of N fluid particles. In this case, the time derivative of the total fluid momentum can be identified with the sum of the forces acting on the two Brownian spheres:

$$\dot{\mathbf{P}}(t) = \delta \mathbf{F}(\mathbf{R}_1; t) + \delta \mathbf{F}(\mathbf{R}_2; t) \tag{6}$$

Therefore, using similar arguments asking the single Brownian particle case, we find that the sum of the self and mutual contributions of the friction tensor vanishes in any finite system:

$$\begin{aligned} \underline{\underline{\zeta}}^N_{1a} + \underline{\underline{\zeta}}^N_{2a} &= \frac{1}{k_B T} \int_0^{\infty} d\tau \langle [\delta \mathbf{F}(\mathbf{R}_1; \tau) + \delta \mathbf{F}(\mathbf{R}_2, \tau)] \, \delta \mathbf{F}(\mathbf{R}_a; 0) \rangle_N \\ &= \frac{1}{k_B T} \int_0^{\infty} d\tau \langle \dot{\mathbf{P}}(\tau) \, \delta \mathbf{F}(\mathbf{R}_a; 0) \rangle_N = 0 \end{aligned} \tag{7}$$

Since there is no reason why this relation should hold, the spurious result (7) must be regarded as a consequence of the finite size of the system. On the contrary, if the thermodynamic limit is taken first in the force–force correlation function of Eq. (3), before letting time go to infinity, then the momentum gained by the fluid can once more be carried off to infinity and the r.h.s. of Eq. (7) with $N = \infty$ does not vanish.

Clearly, this argument shows that the computation of the friction tensor in any finite size simulation cannot be an estimate of its $N = \infty$ value. However, some information can be extracted from this relation and we shall show that for any finite system the following relations hold:

$$\underline{\underline{\zeta}}^N_{11} = -\underline{\underline{\zeta}}^N_{12} = \underline{\underline{\zeta}}^N_{22} = -\underline{\underline{\zeta}}^N_{21} = \frac{\underline{\underline{\zeta}}^{N=\infty}_{11} - \underline{\underline{\zeta}}^{N=\infty}_{12}}{2} + \mathcal{O}\left(\frac{1}{N}\right) \tag{8}$$

Let us stress the fact that contrary to the case of a single Brownian particle (see discussion above), we expect each term $\underline{\underline{\zeta}}^N_{11}$ and $\underline{\underline{\zeta}}^N_{12}$

individually to be non-vanishing in the case of two Brownian particles in the presence of a finite number of fluid particles. This is related to the fact that part of the momentum gained by the fluid due to collisions with one Brownian particle can be absorbed by the other Brownian particle.

3. A PHENOMENOLOGICAL LANGEVIN ANALYSIS

To derive the result (8), we first reconsider the equations of motion of two Brownian particles, cast in the form of phenomenological Langevin equations:

$$\begin{aligned}\dot{\mathbf{P}}_1 &= \bar{\mathbf{F}}_1(t) - \int_0^t d\tau\, \underline{\underline{M}}_{11}(t-\tau)\cdot\mathbf{P}_1(\tau) - \int_0^t d\tau\, \underline{\underline{M}}_{12}(t-\tau)\cdot\mathbf{P}_2(\tau) + \delta\mathbf{F}_1^+(t)\\ \dot{\mathbf{P}}_2 &= \bar{\mathbf{F}}_2(t) - \int_0^t d\tau\, \underline{\underline{M}}_{12}(t-\tau)\cdot\mathbf{P}_1(\tau) - \int_0^t d\tau\, \underline{\underline{M}}_{22}(t-\tau)\cdot\mathbf{P}_2(\tau) + \delta\mathbf{F}_2^+(t)\end{aligned} \tag{9}$$

where $\mathbf{P}_a$ denotes the momentum of the Brownian particle a of mass M, $\underline{\underline{M}}_{ab}$ the memory matrix, $\bar{\mathbf{F}}_a(t)$ the mean (depletion) force exerted on the suspended sphere a by the bath in the presence of the other Brownian particle, and $\delta\mathbf{F}_a^+$ the "random" part of the force acting on the Brownian particle due to individual collisions with fluid particles impinging on the suspended sphere. This phenomenological separation of the force into three terms is physically reasonable but it relies on the assumption of a clear separation between time-scales associated with the fluid and Brownian particles; such a separation can be rigorously proven through the multiple time-scale analysis used in ref. 12.

The properties of the random force $\delta\mathbf{F}_a^+$ are specified as usual: it is assumed to vanish in the mean, to be uncorrelated with the momentum $\mathbf{P}_a$ of each Brownian sphere and with the mean force $\bar{\mathbf{F}} = \bar{\mathbf{F}}_1 = -\bar{\mathbf{F}}_2$ and to have an infinitesimally short correlation time:

$$\begin{aligned}\langle\delta\mathbf{F}_a^+(t)\rangle &= 0\\ \langle\delta\mathbf{F}_a^+(t)\,\mathbf{P}_b(t')\rangle &= 0\\ \langle\delta\mathbf{F}_a^+(t)\,\bar{\mathbf{F}}(t')\rangle &= 0\\ \langle\delta\mathbf{F}_a^+(t)\,\delta\mathbf{F}_b^+(t')\rangle &= 2\left\{\int_0^\infty d\tau\langle\delta\mathbf{F}_a^+(\tau)\,\delta\mathbf{F}_b^+(0)\rangle\right\}\delta(t-t')\end{aligned} \tag{10}$$

for any $t \geqslant t'$. This last assumption amounts to ignoring memory effects, so that the convolution terms on the r.h.s. of Eq. (9) are replaced by instantaneous friction terms acting on each suspended sphere:

$$\int_0^t d\tau \, \underline{\underline{M}}_{ab}(t-\tau) \cdot \mathbf{P}_b(\tau) \simeq \left\{ \int_0^{\infty} d\tau \, \underline{\underline{M}}_{ab}(\tau) \right\} \cdot \mathbf{P}_b(t) \tag{11}$$

This relation relies on a Markovian approximation of the memory matrix $\underline{\underline{\mathscr{M}}}$ (or equivalently of the random force), which is assumed to relax much faster than the momentum of the Brownian particles. This assumption is valid in the limit where the Brownian particles are much heavier than the fluid particles, independently of all other quantities (such as the diameters of the two species). This limit hence implies an infinite mass density, M/Σ^3, of the Brownian particles compared to that of the fluid. Indeed, the correlation time τ_f of the memory matrix can be estimated as a typical hydrodynamic time scale inside the fluid, of order Σ^2/v, where Σ is the diameter of the Brownian particle and $v = \eta/nm$ is the kinematic viscosity of the fluid with number density n. On the other hand, the momentum of the Brownian particles relaxes on a time scale τ_M of order M/ζ, where a typical value for the friction coefficient ζ is given by Stokes' law $\zeta \sim 3\pi\eta\Sigma$. It is then easily verified that the ratio τ_f/τ_M vanishes in the $M \to \infty$ limit (the diameter Σ being fixed), which corresponds to the infinite mass density limit $M/\Sigma^3 \to \infty$ for the Brownian particles. This argument validates therefore the Markovian approximation in our case.

Using matrix notations,

$$\mathscr{P} = \begin{pmatrix} \mathbf{P}_1 \\ \mathbf{P}_2 \end{pmatrix}; \qquad \bar{\mathscr{F}} = \begin{pmatrix} \bar{\mathbf{F}}_1 \\ \bar{\mathbf{F}}_2 \end{pmatrix}; \qquad \delta\mathscr{F}^+ = \begin{pmatrix} \delta\mathbf{F}_1^+ \\ \delta\mathbf{F}_2^+ \end{pmatrix} \tag{12}$$

and

$$\underline{\underline{\bar{\mathscr{M}}}} = \int_0^{\infty} d\tau \, \underline{\underline{\mathscr{M}}}(\tau), \qquad \underline{\underline{\mathscr{M}}} = \begin{pmatrix} \underline{\underline{M}}_{11} & \underline{\underline{M}}_{12} \\ \underline{\underline{M}}_{21} & \underline{\underline{M}}_{22} \end{pmatrix} \tag{13}$$

the Langevin Eq. (9) can be cast in the following compact form

$$\dot{\mathscr{P}}(t) = \bar{\mathscr{F}}(t) - \underline{\underline{\bar{\mathscr{M}}}} \cdot \mathscr{P}(t) + \delta\mathscr{F}^+(t) \tag{14}$$

The friction matrix $\underline{\underline{\bar{\mathscr{M}}}}$ is related to the fluctuating force autocorrelation function via the fluctuation-dissipation theorem

$$\underline{\underline{\bar{\mathscr{M}}}} = \underline{\underline{\Gamma}} \cdot \langle \mathscr{P}\mathscr{P} \rangle^{-1} = \int_0^{\infty} d\tau \langle \delta\mathscr{F}^+(0) \, \delta\mathscr{F}^+(\tau) \rangle \cdot \langle \mathscr{P}\mathscr{P} \rangle^{-1} \tag{15}$$

The friction tensor $\underline{\underline{\zeta}}$ on the other hand is defined in terms of the time-integral of the autocorrelation function of the fluctuation of the "bare" force acting on the Brownian particles, defined as $\delta\mathscr{F}(t)=\dot{\mathscr{P}}(t)-\bar{\mathscr{F}}(t)$. As shown in the appendix, the Laplace transform of this FACF, denoted by $\langle \delta\tilde{\mathscr{F}}(s)\,\delta\mathscr{F}\rangle$, can be expressed in terms of the FACF of the random force $\langle \delta\tilde{\mathscr{F}}^{+}(s)\,\delta\mathscr{F}^{+}(0)\rangle$ via:

$$\langle \delta\tilde{\mathscr{F}}(s)\,\delta\mathscr{F}\rangle=\left(\underline{\underline{1}}+\frac{\underline{\underline{\tilde{\mathscr{M}}}}}{s}\right)^{-1}\cdot\langle \delta\tilde{\mathscr{F}}^{+}(s=0)\,\delta\mathscr{F}^{+}(0)\rangle \tag{16}$$

where the tilda denotes a Laplace transform and s is the Laplace frequency. Note that, because of the Markovian assumption, $\langle \delta\tilde{\mathscr{F}}^{+}(s)\,\delta\mathscr{F}^{+}(0)\rangle = \langle \delta\tilde{\mathscr{F}}(s=0)\,\delta\mathscr{F}^{+}(0)\rangle$ and the memory matrix $\underline{\underline{\tilde{\mathscr{M}}}}$ does not depend on the Laplace frequency either.

It is important to specify the ensemble over which the averages $\langle ... \rangle$ are taken. In order to compare with simulation data, we choose a "modified" microcanonical ensemble, in which the energy and momentum associated with the complete system (composed of N fluid particles of mass m evolving in the presence of two Brownian particles of mass M) are constant, but in which the position of the two Brownian particles are frozen. Note however that their momentum will still fluctuate, since momentum can be exchanged between the two Brownian particles and the fluid. Therefore the total momentum of the fluid alone is not a conserved quantity anymore (as in "standard" microcanonical ensembles). In such an ensemble, the mass M of the Brownian particles just acts as a control parameter for the amplitude of fluctuations of the total momentum of the fluid.

The choice of this ensemble is justified in the limit where the masses of the Brownian particles become very large, since a wide time-scale separation is expected to occur in this limit.[3]

In the $M\to\infty$ limit, this "conditional" ensemble is expected to be the equilibrium ensemble associated with a simulated system, in which N fluid particles evolve in the presence of two Brownian particles of infinite mass, according to Newton's equations of motions. These equations of motion conserve the total energy of the system.

Español and Zuñiga[2] obtained the following relation for the momentum correlation matrix in a system composed of particles of different masses m_i, valid in a microcanonical ensemble with fixed total energy and momentum:

$$\langle p_i^{\alpha}\cdot p_j^{\beta}\rangle = k_B T(m_i m_j)^{1/2}\,\delta_{\alpha\beta}\left(\delta_{ij}-\frac{(m_i m_j)^{1/2}}{\sum_k m_k}\right) \tag{17}$$

where δ denotes the Kronecker symbol and $\{\alpha, \beta\} = x, y, z$. Equation (17) still applies to our "modified" microcanonical ensemble in which the positions of the two Brownian particles are frozen, since the result relies essentially on the conservation of the total momentum of the system.

Using this equation, we obtain the following result for the static correlation matrix $\langle \mathscr{P}\mathscr{P} \rangle$ of the momentum of two Brownian particles suspended in a bath of N fluid particles:

$$\langle \mathscr{P}\mathscr{P} \rangle = Mk_B T \begin{pmatrix} (1-\lambda)\,\underline{\underline{1}} & -\lambda \underline{\underline{1}} \\ -\lambda \underline{\underline{1}} & (1-\lambda)\,\underline{\underline{1}} \end{pmatrix} \tag{18}$$

with $\lambda = M/(2M + Nm)$. In the following, we will need the inverse of this matrix which is easily calculated to be:

$$\langle \mathscr{P}\mathscr{P} \rangle = Mk_B T \begin{pmatrix} \dfrac{1-\lambda}{1-2\lambda}\underline{\underline{1}} & \dfrac{\lambda}{1-2\lambda}\underline{\underline{1}} \\ \dfrac{\lambda}{1-2\lambda}\underline{\underline{1}} & \dfrac{1-\lambda}{1-2\lambda}\underline{\underline{1}} \end{pmatrix} \tag{19}$$

To summarize, in the previous considerations, we were led to consider three different friction tensors, for which we recall the definitions.

First, in Eq. (1), we introduced the "standard" friction tensor defined in Eq. (3) as:

$$\underline{\underline{\zeta}} = \frac{1}{k_B T} \int_0^\infty dt \langle \delta\mathscr{F}(t)\, \delta\mathscr{F} \rangle_{N=\infty} \equiv \underline{\underline{\zeta}}^{N=\infty} \tag{20}$$

where the equilibrium average is taken in a system composed of an infinite number of fluid particles (i.e., in the thermodynamic limit), evolving in the presence of two fixed Brownian particles. In the rest of the paper, we shall refer to this friction tensor as the "physical" friction tensor (to distinguish it from the numerically computed one, defined below).

Similarly, the friction tensor computed in a finite system (like those simulated in molecular dynamics simulations) is defined as

$$\underline{\underline{\zeta}}^N = \frac{1}{k_B T} \int_0^\infty dt \langle \delta\mathscr{F}(t)\, \delta\mathscr{F} \rangle_N \tag{21}$$

where the average is now taken in a system of two fixed Brownian particles and a finite number N of fluid particles.

Our aim is to relate this estimate, $\underline{\underline{\zeta}}^N$, made in finite systems, to its physical value $\underline{\underline{\zeta}} = \underline{\underline{\zeta}}^{N=\infty}$, defined in Eq. (20). As already discussed in the introduction, the connection between these two estimates is not obvious due to spurious finite size effects, so that $\underline{\underline{\zeta}}^{N=\infty} \neq \lim_{N\to\infty} \underline{\underline{\zeta}}^{N}$.

The connection will be achieved via the use of a third estimate of the friction tensor, defined in terms of the random force autocorrelation function:

$$\underline{\underline{\zeta}}^{N,+} = \frac{1}{k_B T} \int_0^\infty dt \langle \delta \mathscr{F}^+(t)\, \delta \mathscr{F}^+(0) \rangle_N \tag{22}$$

As will be argued in the next section, the latter does not present any singularity when going to the thermodynamic limit, so that $\underline{\underline{\zeta}}^{N=\infty,+} = \lim_{N\to\infty} \underline{\underline{\zeta}}^{N,+}$, in contradistinction to $\underline{\underline{\zeta}}^{N}$. This last estimate of the friction tensor, $\underline{\underline{\zeta}}^{N,+}$ can be related to $\underline{\underline{\zeta}}^{N}$ by taking the zero Laplace-frequency limit in Eq. (16), leading to

$$\underline{\underline{\zeta}}^{N} = \left\{ \lim_{s\to 0} \left(\underline{\underline{1}} + \frac{\underline{\underline{\mathscr{M}}}}{s} \right)^{-1} \right\} \cdot \underline{\underline{\zeta}}^{N,+} \tag{23}$$

4. RELATING THE FRICTION TENSORS IN FINITE AND INFINITE SYSTEMS

The microscopic formulae (3) for the friction tensor involve an average over the fluid configurations, in the presence of two fixed (i.e. infinitely heavy) Brownian particles. However the thermodynamic limit for the bath is implicitly assumed, which is out of reach of computer simulations. We show below that the order of limits between the thermodynamic limit ($N \to \infty$), and the infinite mass limit ($M \to \infty$) plays a fundamental role and leads to some pathological behavior of the correlation functions in a finite system.

4.a. Infinite Systems

Let us first consider the case where the thermodynamic limit is taken first, i.e., we have to take first the $N \to \infty$ limit followed by the $M \to \infty$ limit. In this case, the inverse of the momentum matrix, $\langle \mathscr{P}\mathscr{P} \rangle^{-1}$, is proportional to the unit tensor, with a proportionality constant $(Mk_B T)^{-1}$. Using Eq. (15), we thus obtain $\underline{\underline{\mathscr{M}}} \sim 1/M \to 0$ as $M \to \infty$. Relation (16) shows that the force autocorrelation function can be identified with the random force autocorrelation function, with null memory effects. This shows that, in this limit, the friction tensor $\underline{\underline{\zeta}}^{+}$, defined as the time integral of the random force correlation function, can be identified with the standard result (3), involving the time integral of the "bare" force autocorrelation function, i.e.:

$$\underline{\underline{\zeta}}^{+} = \frac{1}{k_B T} \int_0^{\infty} \langle \delta\mathscr{F}^{+}(0)\, \delta\mathscr{F}^{+}(\tau) \rangle \, d\tau \equiv \underline{\underline{\zeta}}^{N=\infty} \tag{24}$$

Moreover, we expect that the estimate (24) of the friction tensor will not exhibit any singularity when inverting the two previous limits. Indeed, as discussed in Section 2, the troubles when inverting these two limits in the bare force correlation function stem from the conservation of the total momentum of the system, so that the sum of the forces acting on the two Brownian particles is equal to the time derivative of the momentum of the fluid. Except in the thermodynamic limit, this symmetry leads to spurious relations such as Eq. (7). On the contrary, the random force is not affected by the total momentum conservation, since all the slowly varying variables have been eliminated when projecting onto the fluid variables. Hence, the thermodynamic limit of the friction tensor will only differ from the result (24) in the $\{M=\infty, N \text{ finite}\}$ case, by a term of order $1/N$:

$$\underline{\underline{\zeta}}^{N=\infty} = \underline{\underline{\zeta}}^{N,+} + \mathcal{O}\left(\frac{1}{N}\right) \tag{25}$$

However, the projected forces cannot be computed from the dynamical trajectories generated in a MD simulation, and we now have to link the estimate (24) of $\underline{\underline{\zeta}}^{N,+}$ to the estimate of the friction tensor, obtained by integrating the bare force correlation functions in a finite system with two fixed Brownian particles, i.e., with $M=\infty$.

To simplify notations, we shall discard in the following the superscript N for the tensor $\underline{\underline{\zeta}}^{+}$.

4.b. Finite Systems

We now consider the limit where the mass M of the Brownian particles becomes infinite, while the number N of fluid particles is kept finite. This will be precisely the situation in computer simulations, where N fluid particles evolve in the presence of two fixed Brownian particles. The first step to investigate this limit will be to relate the force autocorrelation matrix $\langle \delta\mathscr{F}(t)\, \delta\mathscr{F} \rangle$ to the force autocorrelation matrix of the random force via Eq. (16). As we shall see, the structure of the friction matrix defined in Eq. (15) will be of crucial importance to obtain the long-time behavior of $\langle \delta\mathscr{F}(t)\,\delta\mathscr{F}\rangle$.

The inverse static correlation matrix of the momenta of the two Brownian particles can be computed by taking the $M \to \infty$ limit in Eq. (19), yielding:

$$\langle \mathscr{P}\mathscr{P}\rangle^{-1} = \frac{1}{Nmk_BT}\begin{pmatrix} \underline{\underline{1}} & \underline{\underline{1}} \\ \underline{\underline{1}} & \underline{\underline{1}} \end{pmatrix} \tag{26}$$

and using the fluctuation-dissipation relation (15), the friction matrix can be cast in the form:

$$\underline{\underline{\tilde{\mathscr{M}}}} = \frac{1}{Nm}\begin{pmatrix} \underline{\underline{\zeta}}_{11}^{+} + \underline{\underline{\zeta}}_{12}^{+} & \underline{\underline{\zeta}}_{11}^{+} + \underline{\underline{\zeta}}_{12}^{+} \\ \underline{\underline{\zeta}}_{11}^{+} + \underline{\underline{\zeta}}_{21}^{+} & \underline{\underline{\zeta}}_{11}^{+} + \underline{\underline{\zeta}}_{21}^{+} \end{pmatrix} \tag{27}$$

Note that in the limit $\{M \to \infty,\ N \text{ finite}\}$, the inverse matrix $\langle \mathscr{P}\mathscr{P}\rangle^{-1}$ converges towards a finite value, given in Eq. (26), while the infinite mass limit of the matrix $\langle \mathscr{P}\mathscr{P}\rangle$ is undefined, as can be checked using Eq. (18).

Symmetry considerations imply that the tensors $\underline{\underline{\zeta}}_{ab}^{+}$ are diagonal, of the form

$$\underline{\underline{\zeta}}_{11}^{+} = \underline{\underline{\zeta}}_{22}^{+} = \begin{pmatrix} \zeta_{s\perp}^{+} & & 0 \\ & \zeta_{s\perp}^{+} & \\ 0 & & \zeta_{s\parallel}^{+} \end{pmatrix} \tag{28.a}$$

$$\underline{\underline{\zeta}}_{12}^{+} = \underline{\underline{\zeta}}_{21}^{+} = \begin{pmatrix} \zeta_{m\perp}^{+} & & 0 \\ & \zeta_{m\perp}^{+} & \\ 0 & & \zeta_{m\parallel}^{+} \end{pmatrix} \tag{28.b}$$

The subscripts s and m stand respectively for "self" and "mutual" friction coefficient and the Oz axis has been chosen along $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$; the orthogonal components along the x and y axes are clearly equivalent.

The matrix $\underline{\underline{\mathscr{M}}}$ enters Eq. (16) through the combination $(\underline{\underline{1}} + \tilde{\mathscr{M}}/s)^{-1}$. With the simplifications embodied in Eq. (28), the latter can be computed in a straightforward way, with the result

$$\left(\underline{\underline{1}} + \frac{\underline{\underline{\tilde{\mathscr{M}}}}}{s}\right)^{-1} = \begin{pmatrix} \underline{\underline{\mathscr{A}}} & \underline{\underline{\mathscr{B}}} \\ \underline{\underline{\mathscr{B}}} & \underline{\underline{\mathscr{A}}} \end{pmatrix} \tag{29}$$

where $\underline{\underline{\mathscr{A}}}$ is a diagonal matrix given by

$$\underline{\underline{\mathscr{A}}} = \begin{pmatrix} \frac{1+\alpha_\perp}{1+2\alpha_\perp} & & 0 \\ & \frac{1+\alpha_\perp}{1+2\alpha_\perp} & \\ 0 & & \frac{1+\alpha_\parallel}{1+2\alpha_\parallel} \end{pmatrix} \tag{30.a}$$

with

$$\alpha_{\perp/\parallel} = \frac{1}{s} \frac{\zeta^{+}_{s,\perp/\parallel} + \zeta^{+}_{m,\perp/\parallel}}{Nmk_B T} \tag{30.b}$$

and $\underline{\underline{\mathscr{B}}} = \underline{\underline{\mathscr{A}}} - \underline{\underline{1}}$.

Collecting Eqs. (30), (29) and (16), we obtain an explicit expression for the Laplace transform of the bare force autocorrelation function $\langle \delta\tilde{\mathscr{F}}(s)\, \delta\mathscr{F} \rangle$ as a function of the Laplace frequency s.

As s goes to zero, the terms $\alpha_{\perp/\parallel}$ defined in Eq. (30.b) grow to infinity like $1/s$ and the matrix $(\underline{\underline{1}} + \frac{\tilde{\underline{\underline{\mathscr{M}}}}}{s})^{-1}$ converges accordingly towards a finite value

$$\left(\underline{\underline{1}} + \frac{\tilde{\underline{\underline{\mathscr{M}}}}}{s}\right)^{-1} (s=0) = \frac{1}{2} \begin{pmatrix} \underline{\underline{1}} & -\underline{\underline{1}} \\ -\underline{\underline{1}} & \underline{\underline{1}} \end{pmatrix} \tag{31}$$

Therefore, replacing Eq. (31) into Eq. (23), which relates the two estimates $\underline{\underline{\zeta}}^{N}$ and $\underline{\underline{\zeta}}^{N,+}$, we eventually find:

$$\underline{\underline{\zeta}}^{N} = \frac{1}{2} \begin{pmatrix} (\underline{\underline{\zeta}}^{+}_{11} - \underline{\underline{\zeta}}^{+}_{21}) & -(\underline{\underline{\zeta}}^{+}_{11} - \underline{\underline{\zeta}}^{+}_{21}) \\ -(\underline{\underline{\zeta}}^{+}_{11} - \underline{\underline{\zeta}}^{+}_{21}) & (\underline{\underline{\zeta}}^{+}_{11} - \underline{\underline{\zeta}}^{+}_{21}) \end{pmatrix} \tag{32}$$

where use was made of the symmetry properties $\underline{\underline{\zeta}}^{+}_{11} = \underline{\underline{\zeta}}^{+}_{22}$ and $\underline{\underline{\zeta}}^{+}_{12} = \underline{\underline{\zeta}}^{+}_{21}$. In other words, we obtain

$$\underline{\underline{\zeta}}^{N}_{11} = -\underline{\underline{\zeta}}^{N}_{11} = \frac{(\underline{\underline{\zeta}}^{+}_{11} - \underline{\underline{\zeta}}^{+}_{21})}{2} + \mathcal{O}\left(\frac{1}{N}\right) \tag{33}$$

This surprising prediction will be checked numerically in Section 6.

Equation (33) provides a first relation between the "physical" friction tensor and the computed one, $\underline{\underline{\zeta}}^{N}$, but is clearly not sufficient to extract the whole information. Another relation is needed to determine the self and mutual friction tensors separately from MD simulations, which we shall find by examining the relaxation of fluctuations in the system.

5. RELAXATION OF FLUCTUATIONS

5.a. Relaxation of the Time-Dependent Friction

First, we analyse the relaxation of the time-dependent friction tensor, defined by

$$\underline{\underline{\zeta}}^N(t) = \frac{1}{k_B T} \int_0^t d\tau \langle \delta\mathscr{F}(0)\, \delta\mathscr{F}(\tau) \rangle, \tag{34}$$

towards its asymptotic value given in Eq. (32). The Laplace transform of $\underline{\underline{\zeta}}^N(t)$ can be written in terms of the Laplace transform of the force–force correlation function according to

$$\tilde{\underline{\underline{\zeta}}}^N(s) = \frac{1}{s} \langle \delta\tilde{\mathscr{F}}(s)\, \delta\mathscr{F} \rangle = \frac{1}{s} \left(\underline{\underline{1}} + \frac{\underline{\underline{\mathscr{M}}}}{s} \right)^{-1} \cdot \langle \delta\tilde{\mathscr{F}}^+(s=0)\, \delta\mathscr{F}^+(0) \rangle \tag{35}$$

where the expression of the inverse matrix $(\underline{\underline{1}} + \frac{\underline{\underline{\mathscr{M}}}}{s})^{-1}$ is given in Eqs. (29)–(30). According to (30), this matrix exhibits three poles (two of which are equal) on the real-axis, located at the frequencies:

$$\omega_{\perp/\parallel} = -\frac{2(\zeta^+_{s,\perp/\parallel} + \zeta^+_{m,\perp/\parallel})}{Nmk_B T} \tag{36}$$

depending on the component of the matrix under consideration, parallel or perpendicular to the vector **R**. This shows that $\underline{\underline{\zeta}}^N(t)$ relaxes exponentially towards its infinite time value, with a relaxation time given by

$$\tau_{\perp/\parallel} = -\omega^{-1}_{\perp/\parallel} \tag{37}$$

Since the relation $\underline{\underline{\zeta}}^N_{11}(t=\infty) = -\underline{\underline{\zeta}}^N_{12}(t=\infty)$ holds in a finite system (see Eq. (33)),[3] we eventually obtain

$$\log S_\alpha(t) \equiv \log \left(\frac{(\underline{\underline{\zeta}}^N_{11} + \underline{\underline{\zeta}}^N_{12})(t)}{(\underline{\underline{\zeta}}^N_{11} + \underline{\underline{\zeta}}^N_{12}(t=0^+))} \right) = -2\, \frac{\zeta^+_{s,\alpha} + \zeta^+_{m,\alpha}}{Nmk_B T} \cdot t \tag{38}$$

with $\alpha = \{\parallel, \perp\}$, where the first equality defines $S_\alpha(t)$. Therefore a measure of the slope of $\log S_\alpha(t)$ provides the second relation which, with Eq. (33) allows a separate evaluation of $\underline{\underline{\zeta}}^+_{11}$ and $\underline{\underline{\zeta}}^+_{12}$.

[3] Let us stress the fact that this relation only holds in the infinite time limit, i.e., null Laplace frequency $s = 0$, but not for any time, i.e. $s \neq 0$.

However, this analysis shows that the relaxation of $\underline{\underline{\zeta}}^N(t)$ towards its infinite time value, which determines, thanks to Eq. (33), the other combination of friction tensors $\underline{\underline{\zeta}}_{11}^+ - \underline{\underline{\zeta}}_{12}^+$ is rather slow since, according to (37), the relaxation times $\tau_{\perp/\parallel}$ are proportional to the system size N. This behavior could spoil the estimation of $\underline{\underline{\zeta}}_{11}^+ - \underline{\underline{\zeta}}_{21}^+$, based on a measure of the asymptotic value of $\underline{\underline{\zeta}}^N(t)$. Fortunately, one can check that the difference between the time integrals of the self and mutual FACF also relaxes towards $\underline{\underline{\zeta}}_{11}^+ - \underline{\underline{\zeta}}_{21}^+$ (according to Eq. (33)), but on a much shorter timescale, of the order of the correlation time of the random force. This fast relaxation is due to a compensation between the slow decays of $\underline{\underline{\zeta}}_{11}^N$ and $\underline{\underline{\zeta}}_{12}^N$ as can be easily verified by replacing the expression (30) of the matrix $(\underline{1} + \frac{\underline{\underline{\mathscr{M}}}}{s})^{-1}$ into Eq. (35). This property will prove very useful to obtain accurate estimates of $\underline{\underline{\zeta}}_{11}^+ - \underline{\underline{\zeta}}_{21}^+$ from MD simulations (see Section 6).

5.b. Momentum Relaxation

Another quantity of interest is the total momentum $\mathbf{P}(t)$ of the N fluid particles. Because of the presence of the two infinitely massive Brownian particles, $\mathbf{P}$ fluctuates, defining a correlation time which is intimately connected with the friction properties. Due to the conservation of total momentum (fluid plus Brownian particles), the momentum of the fluid $\mathbf{P}(t)$ can be identified with minus the sum of the momenta of the Brownian particles, i.e., $\mathbf{P} = -\mathbf{P}_1 - \mathbf{P}_2$. The latter obey the Langevin equations (9) (written in the Markovian approximation (11)). In the $\{M \to \infty, N \text{ finite limit}\}$, the memory matrix $\underline{\underline{\mathscr{M}}}$ takes the previously derived form (27), so that we finally obtain, after summing the two Langevin equations (9) for $\mathbf{P}_1$ and $\mathbf{P}_2$ and noting that $\bar{\mathbf{F}}_1 = -\bar{\mathbf{F}}_2$,:

$$\dot{\mathbf{P}}(t) = -2\{\underline{\underline{\zeta}}_{11}^+ + \underline{\underline{\zeta}}_{12}^+\} \frac{\mathbf{P}(t)}{mN} + \delta\mathbf{F}^+(t) \tag{39}$$

where $\delta\mathbf{F}^+ = \delta\mathbf{F}_1^+ + \delta\mathbf{F}_2^+$ is the total random force acting on the Brownian particles and the symmetry relations $\underline{\underline{\zeta}}_{11}^+ = \underline{\underline{\zeta}}_{22}^+$ and $\underline{\underline{\zeta}}_{12}^+ = \underline{\underline{\zeta}}_{21}^+$ have been used.

Since the momenta are uncorrelated with the random forces (see Eq. (10)), we conclude that the components of the fluid momentum relax exponentially, on time scales identical to those of the integrated FACF, given in Eq. (37).

The equation of motion (39) can be given a simple interpretation. Indeed, according to Onsager's principle, the regression of a fluctuation of the momentum of the bath will be governed by the equations of motion of macroscopic hydrodynamics. In this description, the force exerted by the flowing fluid is proportional to the "unperturbed" velocity field computed at the positions of the suspended spheres, as given in Eq. (1). In the case of equilibrium fluctuations, this velocity can be identified with the center-of-mass velocity of the fluid, $\mathbf{v} = \mathbf{P}(t)/mN$, yielding:

$$\delta \mathbf{F}_a(t) = -\underline{\underline{\zeta}}_{a1}\mathbf{v}(t) - \underline{\underline{\zeta}}_{a2}\mathbf{v}(t) = -\{\underline{\underline{\zeta}}_{11} + \underline{\underline{\zeta}}_{12}\}\frac{\mathbf{P}(t)}{mN}; \qquad a = 1, 2 \tag{40}$$

This leads to the evolution equation of the total momentum of the fluid

$$\dot{\mathbf{P}}(t) = \delta\mathbf{F}_1(t) + \delta\mathbf{F}_2(t) = -2\{\underline{\underline{\zeta}}_{11} + \underline{\underline{\zeta}}_{12}\}\frac{\mathbf{P}(t)}{mN} \tag{41}$$

which is equivalent to (39). Note that in Eqs. (40) and (41), the friction tensors $\underline{\underline{\zeta}}_{ab}$ refer the physical friction tensors (at least, within an error of order $\mathcal{O}(1/N)$).

The normalized momentum ACF can thus be expressed as:

$$\log F_\alpha(t) \equiv \log\left[\frac{\langle P_\alpha(t)\cdot P_\alpha(0)\rangle_N}{Nmk_BT}\right] = -2\,\frac{\zeta^+_{s,\alpha} + \zeta^+_{m,\alpha}}{Nmk_BT}\cdot t \tag{42}$$

where $\alpha = \{\parallel, \perp\}$ is either a longitudinal or transverse component.

As expected, the decay of momentum fluctuations behaves exactly as the relaxation of the time-dependent friction towards its infinite time-value, as embodied in Eq. (38). Both are characterized by the same correlation time, which is proportional to the combination $(\zeta^+_{s,\alpha} + \zeta^+_{m,\alpha})(\alpha = \{\parallel, \perp\})$ of the "physical" friction coefficients.

The strategy to compute the friction tensors is now clear. We consider a system composed of N fluid particles evolving in the presence of two fixed Brownian particles. First, we compute the infinite time limit of the correlation function integral. This gives an estimate of the difference between the physical self and mutual friction tensors (see Eq. (33)). On the other hand, the sum of these tensors is obtained by analysing the relaxation of fluctuations in the system (see Eqs. (38, 42)). These two combinations yield the desired "physical" friction matrix, as defined in Eq. (3).

6. MOLECULAR DYNAMICS ESTIMATES

In order to check the predictions of the phenomenological Langevin analysis, we performed molecular dynamics simulations on systems of N fluid particles evolving in a periodic box in the presence of two fixed Brownian particles. Two types of systems were examined, one involving soft interactions between particles and the other with purely hard-sphere interactions.

6.a. Microscopic models

In the soft interaction case, the fluid particles were assumed to interact through a pairwise soft-sphere potential

$$v(r) = \varepsilon\left(\frac{\sigma}{r}\right)^{12} \tag{43}$$

while the interaction between the fluid particles and the fixed Brownian spheres was chosen to be a "modified" soft-sphere potential, containing a hard core

$$v_B(r) = \begin{cases} \varepsilon\left(\dfrac{\sigma}{r - r_0}\right)^{12} & \text{if } r > r_0 \\ \infty & \text{if } r < r_0 \end{cases} \tag{44}$$

In the results described below, the value $r_0 = \sigma/2$ was chosen. The distance between the two Brownian particles is held fixed in the simulations.

The equations of motion were solved numerically with the standard Verlet algorithm, which ensures a good conservation of the total energy of the system. The time-step was taken to be $\delta t = 0.005(m\sigma^2/\varepsilon)^{1/2}$. The density of the suspending fluid was fixed at $\rho\sigma^3 = 0.47$ and the temperature at $k_B T = 1.0\varepsilon$. The methods presented in refs. 2 and 3 were used to compute the friction coefficient on a single Brownian particle. In the system defined above, the latter is found to be $\zeta_0 \simeq 6.5\sqrt{mk_B T/\sigma^2}$. Of course, in the case of two Brownian particles separated by a distance $\mathbf{R}$, we expect this value to be recovered in the $|\mathbf{R}| \to \infty$ limit. The hydrodynamic diameter of the Brownian particles, d_h, can be defined by assuming the (stick) Stokes' law for the friction coefficient, $\zeta_0 = 3\pi\eta d_h$. For the system under consideration, this leads to the value $d_h = 1.95\sigma$.

In the case of purely hard-sphere interactions, MD simulations yield exact phase space trajectories, up to computer round-off errors. The microscopic formula (3) can be extended to the hard-sphere case by replacing the continuous force $\mathbf{F}(t)$ by the momentum transferred from the fluid spheres to the infinitely massive Brownian spheres during instantaneous collisions:[3, 12]

$$\mathbf{F}_a(t) = \sum_{(c),\, a} \delta\mathbf{p}_c^a \delta(t - t_c) \tag{45}$$

where the sum is over all collisions between the fluid particles and the fixed Brownian particle a and $\delta\mathbf{p}_c^a = -2m(\mathbf{v}_{c,a} \cdot \hat{\mathbf{r}}_{c,a})\, \hat{\mathbf{r}}_{c,a}$ stands for the momentum transferred from the fluid particle during collision c; $\mathbf{v}_{c,a}$ is the velocity of the colliding bath particle just before the collision and $\hat{\mathbf{r}}_{c,a}$ denotes the unit vector defining the relative position of the bath particle with respect to the centre of the Brownian particle. This yields the following expression for the friction tensor in the hard-sphere case

$$\underline{\underline{\zeta}}^N_{ab} = \frac{\nu\delta_{a,b}}{k_BT}\frac{\langle \delta\mathbf{p}^a_c\,\delta\mathbf{p}^a_c\rangle_{c,a}}{2} + \frac{\nu}{k_BT}\sum_{k=1}^{\infty}\langle(\delta\mathbf{p}^a_c - \langle\delta\mathbf{p}^a_c\rangle_{c,a})(\delta\mathbf{p}^b_{c+k} - \langle\delta\mathbf{p}^b_c\rangle_{c,b})\rangle_{c,a} \tag{46}$$

The notation $\langle ...\rangle_{c,a}$ denotes a statistical average over fluid/Brownian particle a collisions and ν is the corresponding collision frequency. Note that in the first term on the r.h.s. of (46), the mean value $\langle\delta\mathbf{p}^a_c\rangle_{c,a}$ of the momentum transfer is not substracted, in view of the instantaneous character of the collisions.

In the results presented below, the diameter of the Brownian particles is $\Sigma = 2\sigma$, and a packing fraction $\eta_f = \pi/6n\sigma^3 = 0.2468$ was chosen for the suspending bath (with number density n). With these parameters, the value of the friction coefficient on a single Brownian particle was calculated in our previous work[3] to be $\zeta_0 = 10.10\sqrt{mk_BT/\sigma^2}$. Using the previous definition of the hydrodynamic diameter of the Brownian particles, we obtain $d_h = 2.08\sigma$.

In both cases (soft and hard sphere interactions), the simulation cell was chosen to be rectangular, of dimensions $L \times L \times (L + R_{12})$, with $R_{12} = |\mathbf{R}_1 - \mathbf{R}_2|$ the distance between the two fixed Brownian particles. For a given number N of fluid spheres, the dimension L is computed from the constraint of given packing fraction η_f for the suspending bath. For increasing distance d between the spheres, the number of particles N in the simulation cell was increased, in order to ensure that the distance L between two periodic images was significantly larger than the diameter Σ of the fixed spheres ($L \gtrsim 4\Sigma$ at least) and the distance between the spheres (at least $L \gtrsim 1.5R_{12}$ for the largest R_{12}). A study of the size dependence of the friction coefficient has been made for a particular distance $R_{12} = 5\sigma$ between the two Brownian particles, in order to ensure that the numerical results are not affected by any dramatic finite size effect. As seen on Fig. 3, the friction coefficients depend only weakly on the number of fluid particles which justifies the use of rather small systems for the numerical estimates.

6.b. Test of the Phenomenological Analysis

We begin by testing the phenomenological analysis of Section 5, through a comparison of the predictions of the latter with the results of the molecular dynamics simulations.

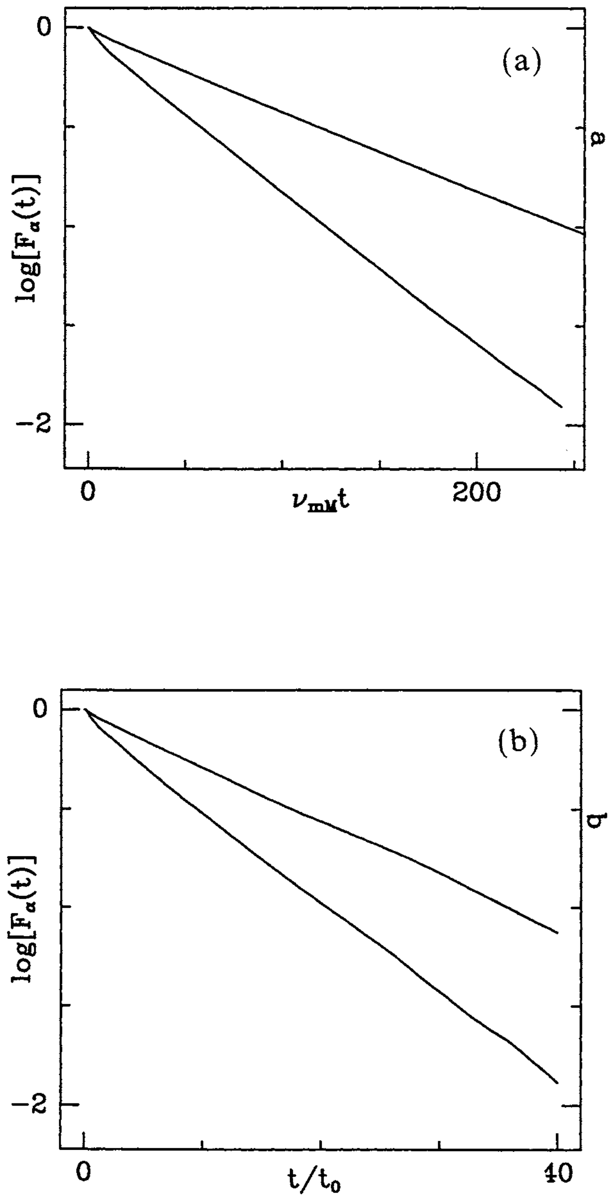


Fig. 1. Logarithmic plot of the normalized momentum ACF, $F_\alpha(t)$, of the total fluid momentum versus reduced time for various system sizes and distances between the two (fixed) Brownian spheres: (a) in the case of hard spheres; ν_{mM} is the collision frequency between the bath and the Brownian particles; (b) in the case of soft interactions; $t_0 = (m\sigma^2/k_B T)^{1/2}$. The exponential decay of the momentum ACF is clearly confirmed by these plots.

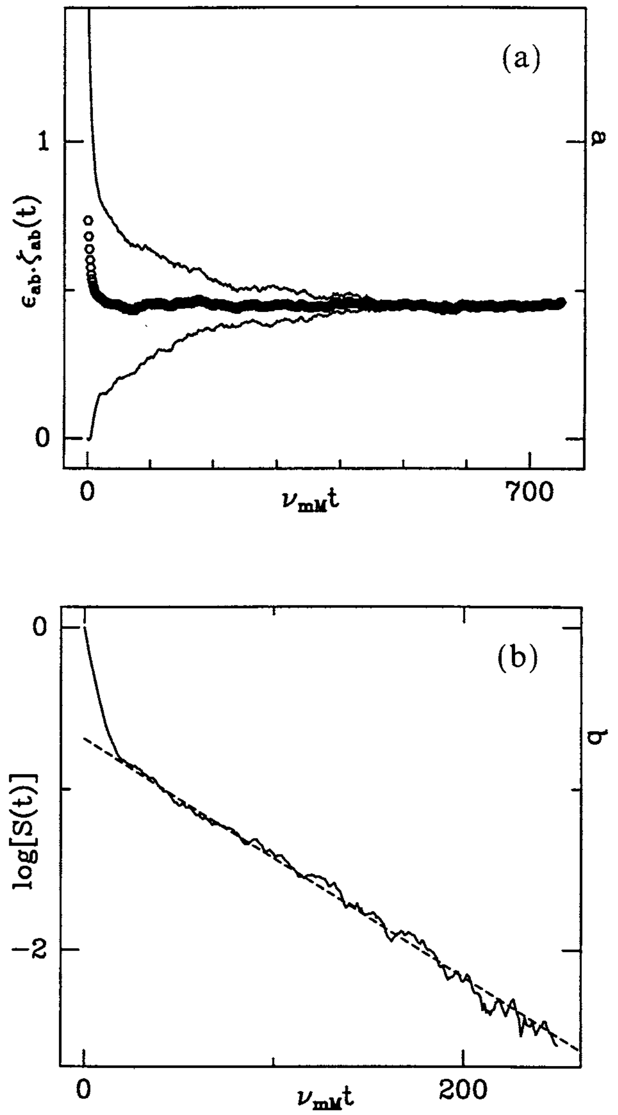


Fig. 2. (a) Time-dependence of the reduced self (upper curve) and mutual (lower curve) friction coefficient, with appropriate sign ($\varepsilon_{ab} = +1$ if $a = b$ and -1 if $a \neq b$). $\zeta^N_{ab}(t)$ (in units of $\sqrt{mk_B T/\sigma^2}$) is defined as the integral of the corresponding force ACF in a finite system, up to time t (see Eq. (47)). The half difference between the two previous estimates (open circles), is shown to converge towards the same asymptotic value on a much faster time-scale, of the order of a few collision times inside the fluid. (b) Logarithmic plot of the normalized sum of time-dependent friction coefficients in a finite system, $S_\alpha(t)$, versus reduced time, confirming the exponential decay of the friction coefficients towards their infinite-time values.

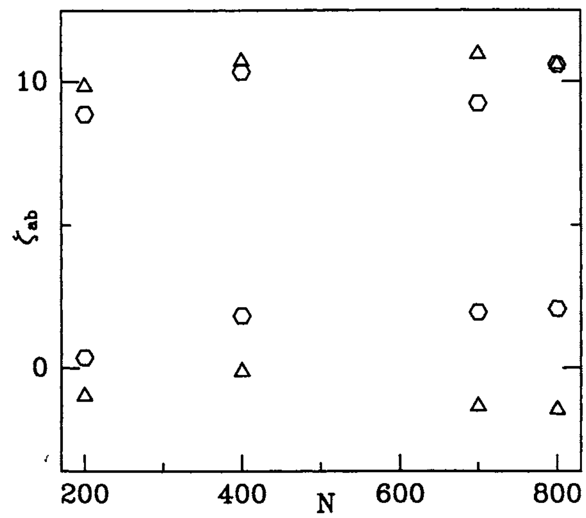


Fig. 3. Dependence of the components of the "physical" estimation of the friction tensor $\underline{\underline{\zeta}}$ on the size of the system. The particles are hard spheres. The two Brownian particles, of diameter $\Sigma = 2\sigma$, are separated by a distance $R_{12} = 5\sigma$. N is the number of fluid particles. The friction coefficients are measured in units of $\sqrt{mk_BT/\sigma^2}$. The circles (resp. triangles) represent the components of the friction tensors perpendicular (resp. parallel) to the line joining the centres of the Brownian particles.

We compute first the momentum ACF, which according to Eq. (42), may be expected to decay exponentially. Logarithmic plots of the ACF should hence yield straight lines, the negative slopes of which are directly proportional to the sums $\zeta_{s,\alpha} + \zeta_{m,\alpha}$ (with $\alpha \in \{\|, \perp\}$ depending on the component considered and the subscripts s and m stand for "self" and "mutual" friction coefficients). Example of such plots are shown in Fig. 1a in the case of hard spheres and in Fig. 1b in the case of soft interactions, which both confirm the predicted behavior.

We now procede to the main test of the Langevin analysis. In Fig. 2a., we present an example of our numerical results. The two continuous curves represent respectively the self and mutual parts of the time integral of the FACF:

$$\begin{aligned} \zeta_s^\alpha(t) &= \frac{1}{k_BT} \int_0^t d\tau \langle \delta\mathscr{F}_1^\alpha(\tau)\, \delta\mathscr{F}_1^\alpha(0) \rangle_N \\ \zeta_m^\alpha(t) &= \frac{1}{k_BT} \int_0^t d\tau \langle \delta\mathscr{F}_1^\alpha(\tau)\, \delta\mathscr{F}_2^\alpha(0) \rangle_N \end{aligned} \tag{47}$$

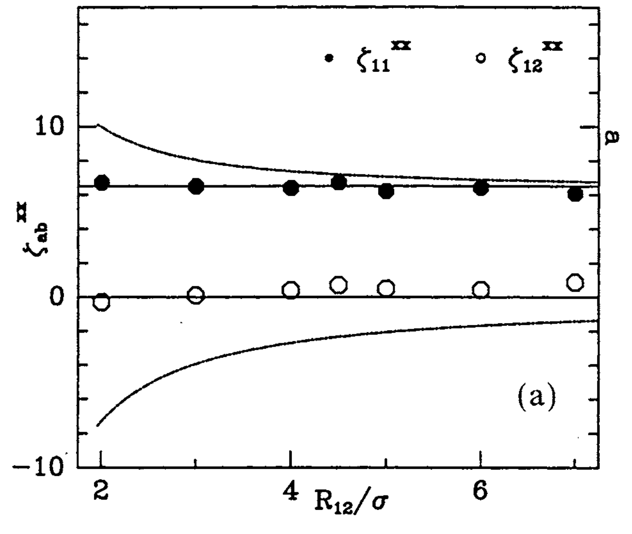
where $\alpha \in \{\parallel, \perp\}$. Both curves are seen to relax slowly to the same constant value (with a minus sign for the mutual contribution), as predicted by the theoretical analysis. The circles represent the difference between these contributions, which is found to relax much faster towards the infinite time value of the two previous contributions. This is in complete agreement with the Langevin analysis of Section 5. Moreover, according to Eq. (38), the sum of the two contributions (47), $S_\alpha(t)$, should relax exponentially towards zero. This prediction is checked in Fig. 2b., where we plot the logarithm of $S_\alpha(t)$ as a function of time. This plot yields another estimate of the sum $\zeta^+_{s,\alpha} + \zeta^+_{m,\alpha}$, which is found to coincide within statistical errors with the estimate of this quantity based on the momentum ACF.

7. RESULTS AND DISCUSSION

The previously described procedure has been used to estimate the value of the physical friction tensors for various distances between the two Brownian particles.[4] The two microscopic models have been investigated. The results are plotted in Figs. 4 and 5 as a function of the distance between the two Brownian particles. A typical error bar for the friction coefficients is estimated to be of the order of $\pm 10\%$ from comparison of several numerical estimates of the coefficients using different methods of evaluation, independent runs and different system sizes (from $N = 200$ to $N = 800$).

Some interesting results emerge from these plots. First, the divergence of the friction tensors as the two Brownian particles approach each other (lubrication limit), is removed. As mentioned in the introduction, this is not unexpected since this singularity stems from the description of the fluid as a hydrodynamic continuum. More surprising is that, for the models under consideration, not even a sharp increase of these friction tensors is observed in this limit. The second interesting point concerns the striking behavior of ζ^{xx}_{ab} around the value $R_{12} = \Sigma + \sigma$ for the hard sphere system. As shown in Fig. 5b, an important increase of the absolute value of ζ^{zz}_{ab} is measured at this point, which corresponds geometrically to the situation where one fluid particle separates the two Brownian spheres. This finding agrees qualitatively with an Enskog-like kinetic calculation, which accounts only for static correlations.[15] A possible explanation for such an increase is that in this "confined" geometry, the two Brownian particles can suffer many correlated recollisions with a single fluid particle. The corresponding transfers of momentum are mainly in the z direction, and nothing special

[4] In this last section, the estimation of the friction tensor always refer to the desired "physical" friction tensor, as defined in Eq. (20).



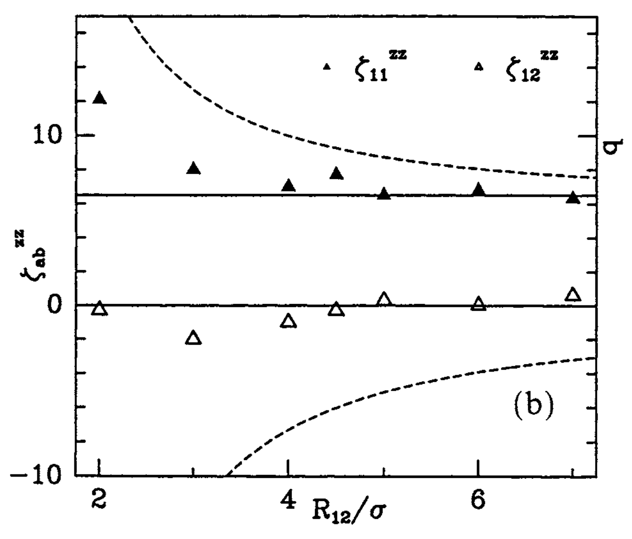


Fig. 4. (a) Estimation of the x-component (perpendicular to the line joining the centres of the Brownian particles) of the self (ζ_{11}^{xx}) and mutual (ζ_{12}^{xx}) physical friction tensors, as a function of the distance R_{12}/σ. The particles interact through the soft interaction potential. The friction coefficients are measured in units of $\sqrt{mk_BT/\sigma^2}$. The solid lines indicate the expected asymptotic values of the friction coefficients in the limit $R_{12} \rightarrow \infty$. (b) Same as Fig. 3a but for the z-component (parallel to the line joining the centres of each Brownian particle) of the friction tensors.

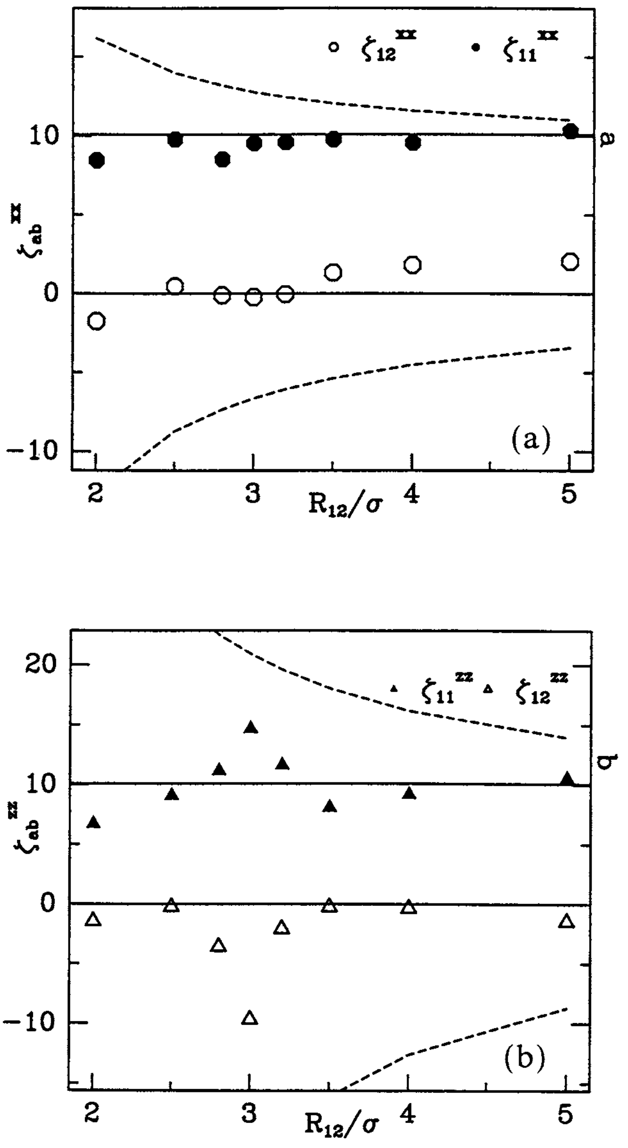


Fig. 5. (a) Estimation of the x-component (perpendicular to the line joining the centres of the Brownian particles) of the self (ζ_{11}^{xx}) and mutual (ζ_{12}^{xx}) physical friction tensors, as a function of the distance R_{12}/σ. The particles interact through the hard sphere interaction potential. The friction coefficients are measured in units of $\sqrt{mk_BT/\sigma^2}$. The solid lines indicate the expected asymptotic values of the friction coefficients in the limit $R_{12} \to \infty$. (b) Same as Fig. 5a but for the z-component (parallel to the line joining the centres of each Brownian particle) of the friction tensors.

should therefore occur for the x component. This expectation is in full agreement with the numerical results of Figs. 5a and 5b. Finally we compare our results with the hydrodynamic predictions for the friction coefficients in the $R_{12} \to \infty$ limit, as displayed in Eq. (2). As is clearly observed on Figs. 4 and 5, the hydrodynamic estimates break down for the distances and length scales considered here. This discrepancy is certainly a consequence of the small diameter ratio $\Sigma/\sigma = 2$ between the Brownian and fluid particles and the rather short distances considered in our study. However more extensive numerical work needs to be done in order to confirm these predictions using much bigger systems. Another open question concerns the behavior of the friction coefficients as the diameter ratio Σ/σ is increased, and will require considerably more numerical work, going beyond the stage of this preliminary study.

APPENDIX

In this appendix, we give some details of the derivation of Eq. (16).

First, by noting that $\delta\mathscr{F}(t) = \dot{\mathscr{P}}(t) - \bar{\mathscr{F}}(t)$, the generalized Langevin equation (9) can be cast in the form

$$\delta\mathscr{F}(t) = -\int_0^t d\tau\, \underline{\underline{\mathscr{M}}}(t-\tau) \cdot \mathscr{P}(\tau) + \delta\mathscr{F}^+(t) \tag{A.1}$$

the Laplace transform of which reads:

$$\delta\tilde{\mathscr{F}}(s) = -\underline{\underline{\tilde{\mathscr{M}}}}(s) \cdot \tilde{\mathscr{P}}(s) + \delta\tilde{\mathscr{F}}^+(s) \tag{A.2}$$

where s is the Laplace frequency. On the other hand, $\tilde{\mathscr{P}}(s)$ is related to $\delta\tilde{\mathscr{F}}(s)$ by

$$\tilde{\mathscr{P}}(s) = \frac{1}{s}\left(\delta\tilde{\mathscr{F}}(s) + \tilde{\bar{\mathscr{F}}}(s) + \mathscr{P}(t=0)\right) \tag{A.3}$$

Substituting Eq. (A.3) into Eq. (A.2), we obtain after some rearrangements

$$\begin{aligned}\delta\tilde{\mathscr{F}}(s) = &-\left(\underline{\underline{1}} + \frac{\underline{\underline{\tilde{\mathscr{M}}}}(s)}{s}\right)^{-1} \cdot \frac{\underline{\underline{\tilde{\mathscr{M}}}}(s)}{s} \cdot \left(\tilde{\bar{\mathscr{F}}}(s) + \mathscr{P}(t=0)\right)\\ &+\left(\underline{\underline{1}} + \frac{\underline{\underline{\tilde{\mathscr{M}}}}(s)}{s}\right)^{-1} \cdot \delta\tilde{\mathscr{F}}^+(s)\end{aligned} \tag{A.4}$$

Then by multiplying both sides of this equation by $\delta\mathscr{F}(t=0)$, averaging and using the statistical properties (10), we obtain the desired equation:

$$\langle \delta\tilde{\mathscr{F}}(s)\, \delta\mathscr{F} \rangle = \left(\underline{\underline{1}} + \frac{\tilde{\underline{\underline{\mathscr{M}}}}(s)}{s}\right)^{-1} \cdot \langle \delta\tilde{\mathscr{F}}^{+}(s)\, \delta\mathscr{F}^{+}(0) \rangle \qquad \text{(A.5)}$$

where the relation $\delta\mathscr{F}^{+}(t=0) = \delta\mathscr{F}(t=0)$ has been used, which can be viewed as a consequence of the generalized Langevin equations (A.1). Within the Markovian approximation, the memory matrix and the random force autocorrelation function can be both replaced by their values at null frequency: $\tilde{\underline{\underline{\mathscr{M}}}}(s) \simeq \tilde{\underline{\underline{\mathscr{M}}}}(s=0)$ and $\langle \delta\tilde{\mathscr{F}}^{+}(s)\, \delta\mathscr{F}^{+}(0) \rangle \simeq \langle \delta\tilde{\mathscr{F}}^{+}(s=0)\, \delta\mathscr{F}^{+}(0) \rangle$. Under these simplifications, Eq. (A.5) reduces to Eq. (16) of the main text.

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