BINARY FRICTION TENSOR FOR
BROWNIAN PARTICLES: OVERCOMING
SPURIOUS FINITE-SIZE EFFECTS.

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ABSTRACT: Starting from a careful analysis of the coupled Langevin equations for
two interacting Brownian particles, we derive a method for extracting 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, which circumvents the pitfalls
associated with the inversion of the thermodynamic and long time limits, is applied to the
case of two Brownian hard spheres in a bath of light spheres.

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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 $\tau_N$ 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 $\tau_N$, 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 $\zeta$ exerted on a heavy Brownian particle by a bath of much lighter particles. $\zeta$ 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 $\zeta$ 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 letter, we will consider the case of two Brownian particles suspended in a bath of discrete light particles. We will show that finite size effects are even more subtle in this system and lead to spurious results for the computed friction tensor. We will then present a method to overcome these effects and obtain the correct friction tensor. 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].

The friction tensor $\zeta$ relates the fluctuations of the forces acting on each suspended Brownian particle to the velocities of these particles:

$$\delta F_a(t) = -\zeta_{a1} V_1(t) - \zeta_{a2} V_2(t); \quad a = 1, 2 \quad (1)$$

where the $2 \times 2$ matrix $\zeta_{ab}$ of friction tensors is a function of the relative position $R = R_1 - R_2$ of the two Brownian particles. The tensor occurs naturally in the two-particle Fokker-Planck equation, describing the dynamical evolution of two massive particles in a bath of much lighter particles [6,7,8]. The resulting microscopic expression for the friction tensor reads:

$$\zeta_{ab} = \frac{1}{k_B T} \int_0^\infty d\tau \langle \delta F(R_a; 0) \cdot \delta F(R_b; \tau) \rangle_{(eq|R_1,R_2)} \quad (2)$$

where the notation $(eq|R_1,R_2)$ refers to an equilibrium average over the fluid variables in the presence of two fixed Brownian particles located at $R_1$ and $R_2$; $\delta F(R_a; t) = F(R_a; t) - \langle F(R_a) \rangle_{(eq|R_1,R_2)}$ is the fluctuation of the force experienced by the Brownian particle at $R_a$ due to collisions with fluid particles. Due to the presence of the other Brownian particle, the average force experienced by particle $a$ does not vanish, and is substracted from the instantaneous force, to yield the fluctuating force for a given configuration of the Brownian particles. Recently we have provided a rigorous derivation of the two-particle Fokker-Planck equation for a system of two Brownian spheres of diameter $\Sigma$ in a fluid of $N$ smaller spheres of diameter $\sigma$ [9]. Use of the multiple time-scale analysis, previously applied to derive the Fokker-Planck equation for a single Brownian particle [10,3], 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 [11]. The average force, on the other hand, which will henceforth be denoted by \( \bar{F}_a \) for brevity, may be identified with the familiar entropic depletion force acting between sterically stabilized colloidal particles [12].

The difficulties encountered in attempting to evaluate the friction tensor from eq. (2) for a finite system are immediately apparent if one notes that for a system of \( N \) fluid particles in the presence of two Brownian particles, the time derivative of the total fluid momentum may be identified with the sum of the forces acting on the two Brownian particles. It follows from this observation that for a finite system:

\[
\zeta_{1a} + \zeta_{2a} = \frac{1}{k_B T} \int_0^\infty d\tau \langle [\delta F(R_1; \tau) + \delta F(R_2; \tau)] \cdot \delta F(R_a; 0) \rangle_{(eq|R_1,R_2)}
\]

where \( P \) is the total fluid momentum. Since there is no reason why the diagonal and off-diagonal (or mutual) friction tensors should be exactly opposite, the spurious result (3) must be regarded as a consequence of the finite size of the system.

In order to see how sensible results may be extracted from dynamical trajectories of finite systems, we consider the coupled evolution equations of the momenta \( P_a \) of the two Brownian particles, in the form of generalized Langevin equations, namely:

\[
\dot{P}_a = \bar{F}_a(t) + \sum_{b=1,2} \int_0^t d\tau \, M_{ab}(t-\tau) \cdot P_b(\tau) + \delta F^+_a(t)
\]

where \( M_{ab} \) is the matrix of memory functions, and \( \delta F^+_a(t) \) is the fluctuating “random” force, associated with the “fast” fluid variables; it satisfies the following constraints:

\[
\langle \delta F^+_a(t) \rangle = 0, \langle \delta F^+_a(t) P_b(t') \rangle = 0, \langle \delta F^+_a(t) \bar{F}_b(t') \rangle = 0
\]

Note that the mean forces \( \bar{F}_b \) depend on time through the slowly varying Brownian particle positions. The clear separation of time scales associated with the heavy Brownian
particles (slow variables), and with the light fluid particles (fast variables), justifies the usual Markovian assumption, namely

$$\langle \delta F^+_a(t) \delta F^+_b(t') \rangle = 2 \Gamma_{a,b} \delta(t-t') \equiv 2 \left\{ \int_0^\infty d\tau \, \langle \delta F^+_a(\tau) \delta F^+_b(0) \rangle \right\} \delta(t-t') \quad (6)$$

which amounts to neglecting memory effects, so that the coupled generalized Langevin equations (4) reduce to the phenomenological local Langevin equations. Using matrix notations (e.g. $\mathcal{P} = (P_1, P_2)$ etc.), they can be cast in the form

$$\dot{\mathcal{P}}(t) = \tilde{F}(t) + \tilde{M} \cdot \mathcal{P}(t) + \delta F^+(t) \quad (7)$$

where the t-independent matrix $\tilde{M}$ is related to the ACF matrix of the random force via the fluctuation-dissipation theorem:

$$\tilde{M} = \Gamma \cdot \langle PP \rangle^{-1} \quad (8)$$

Taking the Laplace transform of the Langevin eq. (7), and projecting onto $\delta F(t = 0)$ leads to the following relation for the fluctuating force ACF:

$$\langle \tilde{\delta F}(s) \delta F \rangle = \left( \frac{1}{s} + \frac{\tilde{M}}{s} \right)^{-1} \cdot \langle \tilde{\delta F}^+(s = 0) \delta F^+(0) \rangle \equiv U^{-1}(s) \langle \tilde{\delta F}^+(s = 0) \delta F^+(0) \rangle \quad (9)$$

where the tilda denotes a Laplace transform and $s$ is the variable conjugate to time.

The inverse of the correlation matrix of the Brownian particle momenta may be calculated in the microcanonical ensemble (appropriate for MD simulations) for a system of 2 Brownian particles of mass $M$ and $N$ bath particles of mass $m$, using the results of ref. [2]:

$$\langle PP \rangle^{-1} = \frac{1}{Mk_BT} \begin{pmatrix} \frac{1-\lambda}{\lambda} & \frac{\lambda}{1-2\lambda} \\ \frac{1-2\lambda}{\lambda} & \frac{1-2\lambda}{1-2\lambda} \end{pmatrix} \quad (10)$$

where $\lambda = \frac{M}{2M+Nm}$. If eq. (10) is substituted into eq. (9) and the thermodynamic limit is taken before the Brownian limit $M \to \infty$, the matrix $\tilde{M}$ is found to vanish, and comparison
of relation (9) taken for \( s = 0 \), with the GK relation (2) yields the following expression for the friction tensor matrix:

\[
\zeta = \frac{1}{k_B T} \int_0^\infty \langle \delta \mathcal{F}^+(0)\delta \mathcal{F}^+(\tau) \rangle \, d\tau
\]  

(11)

In other words, provided the limits are taken in the order specified above, the friction tensor is given equivalently in terms of the “bare” or “random” force ACF. For a finite system, the two estimates, say \( \zeta_N \) and \( \zeta^N \) corresponding respectively to eqs. (2) and (11) differ. However, the spurious behaviour of the bare force ACF, embodied in the result (3) which is a direct consequence of the conservation of the total momentum of a finite system, is not expected to carry over to the random (or projected) force ACF, which are associated with the fast fluid variables. Consequently no singularity is expected when the order of limits \( (N \to \infty, M \to \infty) \) is inverted, and hence the finite and infinite system results for \( \zeta^N \) should only differ by terms of order \( 1/N \), i.e.:

\[
\zeta^N = \zeta_{N=\infty} = \zeta^N + O\left(\frac{1}{N}\right)
\]

(12)

Discarding henceforth the superscript \( N \) for the tensor \( \zeta^+ \) to simplify notations, we first note that symmetry considerations imply that the tensors \( \zeta^+_{ab} \) are diagonal and

\[
\zeta^+_{11} = \zeta^+ = \zeta^+_{s\perp} (\hat{x}\hat{x} + \hat{y}\hat{y}) + \zeta^+_{s\parallel} \hat{z}\hat{z}
\]

(13.a)

\[
\zeta^+_{12} = \zeta^+_{21} = \zeta^+_{m\perp} (\hat{x}\hat{x} + \hat{y}\hat{y}) + \zeta^+_{m\parallel} \hat{z}\hat{z}
\]

(13.b)

where the indices \( s \) and \( m \) refer to “self” and “mutual”, and the \( Oz \) axis has been chosen along \( \mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2 \).

Taking the Brownian limit \( M \to \infty \) for a system with finite \( N \), it is easily found from eqs (6), (8) and (10) that the matrix \( \mathcal{U}^{-1}(s = 0) \) appearing in eq (9) goes, when \( s \to 0 \), to the finite value

\[
\{\mathcal{U}^{-1}(s = 0)\}_{ab} = \frac{1}{2} \left[ 1 + (2\delta_{ab} - 1) \right]
\]

(14)
This non-vanishing result can be directly traced back to the conservation of total (fluid + Brownian) momentum. Consequently we derive from eq. (9) the following relation between the friction tensor matrices $\zeta_N$ and $\zeta^+$, valid for any finite $N$:

$$\zeta_N^{ab} = \frac{1}{k_B T} \langle \delta F_a(s=0) \delta F_b \rangle = \frac{1}{2} \left( \zeta^+_{11} - \zeta^+_{21} \right) \cdot (2\delta_{ab} - 1) \quad (15)$$

In other words, keeping in mind eq. (12):

$$\zeta_N^{11} = -\zeta_N^{12} = \frac{\left( \zeta^+_{11} - \zeta^+_{21} \right)}{2} + O\left( \frac{1}{N} \right) \quad (16)$$

We thus have established a first relation between the true friction tensor and the tensor $\zeta^N$, which may be calculated from the total force ACF of a finite system. From the small-$s$ expansion of $U^{-1}(s)$ in eq. (9) one finds that the time integral of the force ACF $\langle \delta F(t) \delta F(0) \rangle$ relaxes exponentially towards its infinite time value. The relaxation times associated with the components of the fluctuating force perpendicular and parallel to the vector $\mathbf{R}$ are found in terms of the transverse and longitudinal components of the tensors (13), namely

$$\tau^{-1}_{1/\parallel} = \frac{2(\zeta^+_{s,\perp/\parallel} + \zeta^+_{m,\perp/\parallel})}{Nm k_BT} \quad (17)$$

These relaxation times are seen to be proportional to the system size. However, one can easily check that the difference between the time-integral of the self and mutual force ACF’s relaxes towards the difference of the corresponding friction matrices, $\zeta^+_{11} - \zeta^+_{12}$, on a much faster time scale, of the order of the correlation time of the random force. This fast relaxation is due to a compensation between the slow decays of the separate functions, and allows accurate estimates of the difference $\zeta^+_{11} - \zeta^+_{12}$ from MD simulation, as illustrated in Fig 1.

At this stage, a second relation is needed to determine the self and mutual friction coefficients separately from MD simulations of a finite system. In a spirit similar to the case of a single Brownian particle [2,3], we now consider the relaxation of the total momentum of
spheres in the presence of two infinitely massive (i.e. fixed) Brownian spheres. Summing
the two Langevin equations (4) for \( P_1 \) and \( P_2 \) in the Markovian limit, noting that \( \bar{F}_1 = -\bar{F}_2 \), and averaging over a time interval intermediate between the short time scale of the
fluctuating random force and the long time scale associated with the Brownian particles,
we find for the evolution of the total momentum \( P = P_1 + P_2 \):

\[
\dot{P}(t) = -2 \left\{ \zeta_{s11} + \zeta_{s12} \right\} \frac{P(t)}{mN}
\]

Due to the conservation of total momentum, (18) also holds for the momentum of the
fluid \( P(t) = Nm\nu(t) \), where \( \nu(t) \) denotes the center-of-mass velocity relative to the fixed
Brownian particles. We conclude that the components of the fluid momentum relax ex-
ponentially, on time scales identical to those of the integrated ACF’s, given in eq. (17).
In practice, a MD calculation of the logarithm of the normalized fluid ACF :
\[ \log F_\alpha(t) \equiv \log \left[ \frac{\langle P_\alpha(t) \cdot P_\alpha(0) \rangle_N}{Nmk_BT} \right] \]
should be a straight line with slope \( 2(\zeta_{s,\alpha}^{+} + \zeta_{m,\alpha}^{+})/(Nm\kappa B T) \), where
\( \alpha \in \{||, \perp\} \) is either a longitudinal or transverse component. An example of such a plot is
shown in Fig. 2. The slopes thus provide the second relation between the longitudinal and
transverse elements of the self and mutual friction tensors, which together with eq. (16),
entirely determine the latter.

The various coefficients depend on the distance \( R \) between the Brownian particles, and
MD simulations must be carried out for different spacings of the fixed Brownian spheres.
To illustrate the procedure, we quote the values of \( \zeta_{s,\alpha} \) and \( \zeta_{m,\alpha} \) (\( \alpha \in \{||, \perp\} \)) obtained
for a size ratio of the Brownian and fluid spheres \( \Sigma/\sigma = 2 \), and a distance \( R/\Sigma = 1 \).
The packing fraction of the fluid is \( \eta = 0.246 \). The following values are extracted from
plots as shown in Figs. 1 and 2 : \( \zeta_{s,||}^{*} = \zeta_{s,||}/m\nu m_M = 12.1, \ zeta_{s,\perp}^{*} = \zeta_{s,\perp}/m\nu m_M = 6.7, \)
\( \zeta_{m,||}^{*} = \zeta_{m,||}/m\nu m_M = -0.3, \ zeta_{m,\perp}^{*} = \zeta_{m,\perp}/m\nu m_M = -0.3, \) where \( \nu m_M \) is the collision
frequency between the bath and one Brownian particle. Contrary to the prediction of
hydrodynamics, the value remains finite when the two Brownian particles are at contact.
In general our numerical results indicate strong deviations on these scales from the $R$-dependence of the friction coefficient from hydrodynamics. More complete report, for various size ratios $\Sigma/\sigma$ and distances $R$ will be published elsewhere, and confronted with the predictions of macroscopic hydrodynamics.

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Figure 1: Time-dependence of the reduced self (upper curve) and mutual (lower curve) friction coefficient, with appropriate sign ($\epsilon_{ab} = +1$ if $a = b$ and $-1$ if $a \neq b$). $\zeta_{ab}^*(t) = \zeta_{ab}(t)/m\nu_{mM}$ is defined as the time-integral of the corresponding force ACF, up to time $t$ (see eq. (2)), with $\nu_{mM}$ the fluid-Brownian particle collision frequency. 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 time inside the fluid.

Figure 2: Logarithmic plot of the normalized ACF, $F_\alpha(t)$, of the total fluid momentum versus reduced time $\nu_{mM}t$. The solid (resp. dashed) line corresponds to the component of the momentum ACF perpendicular (resp. parallel) to $R = R_1 - R_2$. 