The contribution of Brownian motion to the stress in a colloidal suspension

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The deviatoric stresses of colloidal suspensions are routinely calculated using the expression introduced by Batchelor [J. Fluid Mech. 83, 97–117 (1977)]. We show by example that the central feature in its derivation, the thermodynamic force driving particles down the density gradient, is inconsistent with the motion of the colloids. A new expression for the stress is proposed.

I. INTRODUCTION

Adding rigid colloids or flexible polymers to simple fluids is well-known to affect the flow behaviour of the fluid, raising the viscosity and giving rise to visco-elastic phenomena like shear thinning. Einstein famously derived that the viscosity of a dilute suspension of spherical colloids increases linearly with the colloidal volume fraction. Batchelor presented a general expression for the deviatoric stress of non-dilute colloidal suspensions of spherical colloids, which has become widely accepted as the standard expression. It is therefore disconcerting to note that the forces entering Batchelor’s stress calculation differ from those entering the equations of motion of the colloids. The problems are tracked down to the use of a non-existent ‘thermodynamic force’ and the omission of a subtle correction for the configuration-dependence of the hydrodynamic matrix. A modified stress expression is proposed.

II. BACKGROUND

In a famous Gedankenexperiment, Einstein considered the equilibrium probability distribution function $P(x)$ of a dilute suspension of identical colloidal particles in an external potential $\Phi(x)$. In equilibrium, the particle flux due to the external potential is balanced by the flux due to Fickian diffusion against the concentration gradient. The macroscopic flux $J(x)$ then vanishes at every point $x$, following

$$ J = -PM\nabla \Phi - D\nabla P = 0, \quad (1) $$

where $M$ denotes the mobility matrix and $D$ the diffusion matrix. By inserting Boltzmann’s equilibrium distribution,

$$ P(x) = P_0 e^{-\beta \Phi(x)}, \quad (2) $$

where $\beta = 1/(k_B T)$ with Boltzmann constant $k_B$ and absolute temperature $T$, Einstein showed that equilibrium implies $M = \beta D$. Using Stokes’ expression for the mobility of a spherical particle of radius $a$ in a fluid of viscosity $\eta$, Einstein obtained the diffusion coefficient

$$ D = \frac{k_B T}{6\pi\eta a}. \quad (3) $$

While the Stokes-Einstein expression was derived for colloids subject to an external force, it is equally valid for unforced colloids.

In a sequel paper, Einstein likened the action of the diffusive term to a force acting on every particle, while the central equation he solved was still a flux balance. Batchelor described this interpretation as follows: ‘the particle flux due to Brownian migration is the same here as if a certain steady force acted on the particles (this force being equal and opposite to the external force $F^{\Phi} = -\nabla \Phi$ that, in the equilibrium situation, produces a convective flux which balances the diffusive flux).’ The flux balance in Eq. (1) is rewritten as

$$ -P \left( M\nabla \Phi + \frac{1}{P} D\nabla P \right) = PM (F^{\Phi} + F^{T}) = 0, \quad (4) $$

which is ‘the same as if a steady force

$$ F^{T}(x) = -k_B T \nabla \ln P(x) \quad (5) $$

acted on the particle[s]. It is of course not to be supposed that the interaction of a particle with the molecules of the surrounding medium is literally equivalent to the exertion of a steady force on the particle. When the probability density of the particle position is non-uniform, the mean Brownian velocity of a particle, conditional upon it being near a point $x$, is non-zero simply as a consequence of the fact that the particle is more likely to have come from a direction in which the probability density increases than from one in which it decreases; and it is this bias in the statistics of particle velocities at $x$ (which is quite consistent with zero mean of the Brownian velocity of a given particle in the absence of an applied force) that is equivalent, so far as its effect on the diffusive flux is concerned, to the action of the steady force (3.5) on the particle’.

The thermodynamic force experienced by the particles near $x$, see Eq. (5), results in a thermodynamic force on...
colloid \( i \) given by

\[
\mathbf{F}^T_i = -k_B T \frac{\partial}{\partial x_i} \ln P(x_1, \ldots, x_N),
\]

where \( P(x_1, \ldots, x_N) \) is the joint probability distribution function of all \( N \) particles. These thermodynamic forces reproduce the statistical bias in the random walks of the particles which results from the non-uniformity of the joint-probability distribution function. Batchelor uses the thermodynamic force as an actual force on the particles in the derivation of his widely used expression for the stress in a suspension of Brownian colloids.

**III. THE THERMODYNAMIC FORCE REVISITED**

In the reinterpretation of the flux balance as a force balance, it follows from Eq. (4) that the particles in an equilibrium suspension experience a vanishing nett force. But the colloids are obviously not stationary, as they are continuously subjected to rapidly fluctuating interactions with the surrounding solvent molecules in perpetual thermal motion. These fluctuating Brownian forces are not contained in the thermodynamic force, which is devoid of information on the dynamical properties of the solvent, like the viscosity, or those of the solvent molecules. Consequently, the individual colloids must also be experiencing fluctuating Brownian forces \( \mathbf{F}^B_i \), with vanishing average \( \langle \mathbf{F}^B_i \rangle = 0 \) so as not to alter the force balance of Eq. (4). As explained in the above citation of Batchelor, these Brownian forces are the origin of the diffusive flux in Eq. (3) and the thermodynamic force in Eq. (4). Randomly fluctuating Brownian forces are central to any study on the dynamics of colloids in fluids. The thermodynamic force, however, is not: the dynamics of colloidal particles is routinely solved without reference to the thermodynamic force. One obvious problem is that the probability distribution \( P \), and hence \( \mathbf{F}^T_i \), is not at hand in particle-based simulations, which require explicit expressions in the particle positions – the work-around by Batchelor is given in Eq. (20). But that is not the only cause of concern.

Consider a dilute suspension of identical spherical colloids, each with the same positive excess mass \( m \) relative to the volume of fluid they displace, in a gravity field acting along the negative \( z \) direction. Using the flux \( J \) defined by the l.h.s. of Eq. (3), the evolution of the one-dimensional overall probability distribution \( P(z, t) \) follows from the conservation expression known as the Fokker-Planck-Smoluchowski equation,

\[
\frac{\partial P}{\partial t} = -\frac{\partial J}{\partial z} = \frac{mg}{\gamma} \frac{\partial P}{\partial z} + D \frac{\partial^2 P}{\partial z^2},
\]

where in the second step the effective mass \( m \), the friction coefficient \( \gamma \), the acceleration by gravity \( g \) and the diffusion coefficient \( D \) are assumed constant. In dilute systems, this equation applies to both the macroscopic concentration profile and the probability distribution function of an individual particle. The equilibrium solution, in the presence of a wall restricting the motion to \( z \geq 0 \), recovers the Boltzmann distribution,

\[
P_{eq}(z) = P_{eq}(0) e^{-\beta mg z},
\]

as is readily confirmed by using Einstein’s relation \( D = k_B T / \gamma \). Focus now on the subset of those particles that are at a specific height \( z_0 \), with \( z_0 \gg 0 \), at time 0. Their probability distribution function at a later time \( t \) is obtained as the Green’s function to the Smoluchowski equation

\[
P(z, t | z_0) = \frac{1}{\sqrt{4 \pi D t}} \exp \left[ \frac{(z - (z_0 + \nu_{\beta} t))^2}{4 D t^2} \right],
\]

with drift velocity \( \nu_{\beta} = -mg / \gamma \). This solution expresses that the colloids in an equilibrium distribution are not hovering around a constant height but have a propensity to gradually sink to the bottom of the container, where the Boltzmann probability distribution reaches its maximum. Because this subset of colloids is part of a larger system at equilibrium, it follows that a flux balance of the overall density at the macroscopic level, as in Eq. (1), does not translate into a balance of potential and thermodynamic forces at the microscopic level, as implied in the re-interpretation of the flux balance as a force balance in Eq. (4). Colloids are not subject to an effective force that drives them down the concentration gradient; rather, a concentration gradient turns the random Brownian motion of particles into a macroscopic flux down the concentration gradient. The inevitable conclusion is that colloids do not experience the thermodynamic force envisaged by Einstein and Batchelor, and expressions derived using the thermodynamic force are to be considered with care. In particular, a new expression for the stress in a Brownian suspension will be derived in the next section.

For completeness, the colloids initially at \( z_0 \) will evidently not sink forever. Interactions with the wall at \( z = 0 \) will eventually cause deviations from Eq. (20), and for long times the conditional probability converges to the equilibrium distribution, \( P(z, \infty | z_0) = P_{eq}(z) \). This limiting behaviour is only obtained on a very long time scale, with the particles bouncing off the wall numerous times. For a macroscopic system in equilibrium, comprising many particles interacting with the wall at any moment, both the flux balance of Eq. (4) and a force balance between gravity and wall forces are obeyed nearly instantaneously. For an individual particle in this system, however, its force balance between gravity and wall forces is reached only on a very long time scale; on the far shorter Smoluchowski time scale of motion over a fraction of its size, the persistent pull by gravity results in a downward mean motion with super-imposed Brownian fluctuations.
IV. THE STRESS

For an isolated non-Brownian particle in a flow field \( \mathbf{u}(r) = \mathbf{E} r \) with constant strain rate \( \mathbf{E} \), i.e. the traceless symmetric \((3 \times 3)\) velocity gradient matrix, the hydrodynamic drag force \( \mathbf{F}^H \) and stress \( \mathbf{S}^H \) experienced by the colloid are expressed in Stokesian flow conditions as:

\[
\begin{pmatrix}
\mathbf{F}^H \\
\mathbf{S}^H
\end{pmatrix} = - \begin{pmatrix}
\mathbf{R}_{Fu} & \mathbf{R}_{FE} \\
\mathbf{R}_{Su} & \mathbf{R}_{SE}
\end{pmatrix} \begin{pmatrix}
\mathbf{v} - \mathbf{u}(x) \\
-\mathbf{E}
\end{pmatrix}.
\] (10)

Here \( \mathbf{R} \) is the grand resistance matrix, whose elements are evaluated by solving the flow and pressure fields surrounding the moving particle; we refer the interested reader to the literature for the details and several freely available numerical solvers.\textsuperscript{2-12} The stress (unit Nm) is obtained as the symmetric first moments of the deviatoric stress field \( \mathbf{\sigma}(r) \) integrated over the surface of the particles; the division by volume is omitted to remove a system size dependence. The velocity of the particle experiencing a potential force \( \mathbf{F}^\Phi \) and the concomitant stress \( \mathbf{S} \) exerted by the particle on the fluid are obtained from force and stress balances,

\[
\mathbf{F}^\Phi + \mathbf{F}^H = 0,
\] (11a)

\[
\mathbf{S} + \mathbf{S}^H = 0,
\] (11b)

resulting in

\[
\begin{pmatrix}
\mathbf{v} - \mathbf{u} \\
\mathbf{S}
\end{pmatrix} = \begin{pmatrix}
\mathbf{M}_{uF} & \mathbf{M}_{uE} \\
\mathbf{M}_{SF} & \mathbf{M}_{SE}
\end{pmatrix} \begin{pmatrix}
\mathbf{F}^\Phi \\
-\mathbf{E}
\end{pmatrix},
\] (12)

where \( \mathbf{M} \) is the grand mobility matrix. The two grand matrices are related by

\[
\mathbf{M} = \begin{pmatrix}
\mathbf{R}_{Fu}^{-1} & -\mathbf{R}_{Fu}^{-1} \mathbf{R}_{FE} \\
\mathbf{R}_{Su} \mathbf{R}_{Fu}^{-1} & \mathbf{R}_{SE} - \mathbf{R}_{Su} \mathbf{R}_{Fu}^{-1} \mathbf{R}_{FE}
\end{pmatrix}.
\] (13)

Rotational motions of the colloids and fluid are omitted here for clarity of presentation, as in previous studies on the stress expression.\textsuperscript{3,7}

For an isolated Brownian particle in a quiescent fluid, the probability distribution \( P(x, t) \) is obtained from the Smoluchowski equation

\[
\frac{\partial P}{\partial t} = -\nabla \cdot \left[ \left( -\mathbf{M}_{uF} \nabla \Phi + \nabla \cdot \mathbf{D} \right) P \right] + \nabla \cdot (\mathbf{D} P),
\] (14)

where, unlike in Eq. (7), it is assumed that the mobility matrix, the diffusion matrix \( \mathbf{D} = k_B T \mathbf{M}_{uF} \), and the potential are functions of the colloidal position. From this standard form of the Smoluchowski equation,\textsuperscript{5,31} it follows that the particle experiences, in addition to the potential force \( \mathbf{F}^\Phi = -\nabla \Phi \), an effective mobility-related force

\[
\mathbf{F}^M = k_B T \mathbf{M}_{uF}^{-1} \nabla \cdot \mathbf{M}_{uF}.
\] (15)

This term arises because a first order equation of motion is constructed to describe the dynamics resulting from a second order equation of motion including a Brownian term with a position-dependent strength. The equation of motion in the It\( \widehat{o} \) interpretation then reads as

\[
\mathbf{\dot{x}} = \mathbf{M}_{uF} \left( \mathbf{F}^\Phi + \mathbf{F}^M + \mathbf{F}^B \right),
\] (16)

where the Brownian force, with \( \langle \mathbf{F}^B \rangle = 0 \), obeys the fluctuation-dissipation theorem,

\[
\langle \mathbf{F}^B(t) \otimes \mathbf{F}^B(t') \rangle = 2k_B T \mathbf{R}_{Fu} \delta(t - t'),
\] (17)

and where the matrices \( \mathbf{M}_{uF} \) and \( \mathbf{R}_{Fu} \) are evaluated using the positions \( \mathbf{x} \) before their incremental change due to the velocity \( \mathbf{\dot{x}} \). The displacements of the particles over a simulation time step \( \Delta t \) are approximated by the forward Euler scheme

\[
\mathbf{x}(t + \Delta t) - \mathbf{x}(t) = (\mathbf{M}_{uF} \mathbf{F}^\Phi + k_B T \mathbf{\nabla} \cdot \mathbf{M}_{uF}) \Delta t + \sqrt{2k_B T \mathbf{M}_{uF}^{1/2} \mathbf{\theta}(t) \mathbf{\theta}(t)^t},
\] (18)

where the vector \( \mathbf{\theta}(t) \) contains three random numbers of zero mean, unit variance and devoid of correlations; again, the forces and matrices entering the equation are evaluated at time \( t \), before the position update. Ermakov and McCammon\textsuperscript{10} derived this equation starting from the second order Langevin equation of motion of a colloid.

For a Brownian particle in a flow, the combination of Eqs. (12) and (16) naturally yields

\[
\begin{pmatrix}
\mathbf{v} - \mathbf{u} \\
\mathbf{S}
\end{pmatrix} = \begin{pmatrix}
\mathbf{M}_{uF} & \mathbf{M}_{uE} \\
\mathbf{M}_{SF} & \mathbf{M}_{SE}
\end{pmatrix} \begin{pmatrix}
\mathbf{F}^\Phi + \mathbf{F}^M + \mathbf{F}^B \\
-\mathbf{E}
\end{pmatrix},
\] (19)

where the Brownian-related forces are treated on an equal footing with the potential forces both in the velocity and stress calculations. In addition to the two usual stress terms related to the potential force and the strain, there are two Brownian-relates stress contributions, namely a fluctuating term

\[
\mathbf{S}^B = \mathbf{M}_{SF} \mathbf{F}^B = \mathbf{R}_{Su} \mathbf{M}_{uF} \mathbf{F}^B
\] (20)

and a systematic term

\[
\mathbf{S}^M = \mathbf{M}_{SF} \mathbf{F}^M = k_B T \mathbf{R}_{Su} \nabla \cdot \mathbf{M}_{uF}.
\] (21)

In the last step of both above equations, repeated use was made of Eq. (13) to show their equivalence to the stress expressions obtained by combining Eqs. (10) and (16).

The above derivation is readily extended to a collection of \( N \) particles. Upon re-interpreting \( \mathbf{x}, \mathbf{F}^B \) etc. as vectors comprising all particle positions, all Brownian forces, etc., the above equations remain unaltered. One then ob-
tains for the \(i\)th particle,
\[
\begin{pmatrix}
\mathbf{v}_i - \mathbf{u}(\mathbf{x}_i) \\
\mathbf{S}_i
\end{pmatrix}
= \sum_{j=1}^{N} \begin{pmatrix}
M^{ji}_{FF} & M^{ji}_{SE} \\
M^{ij}_{SF} & M^{ij}_{SE}
\end{pmatrix} \begin{pmatrix}
\mathbf{F}^\Phi + \mathbf{F}^M + \mathbf{F}^B \\
-\mathbf{E}
\end{pmatrix},
\] (22)

with fluctuation-dissipation theorem
\[
\langle \mathbf{F}^B_i(t) \otimes \mathbf{F}^B_j(t') \rangle = 2k_B T R_{ij} \delta(t - t'),
\] (23)

and so on, where it should be noted that the many-particle matrices \(M\) and \(R\) are related by Eq. (13), whereas the two-particle matrices \(M^{ij}\) and \(R^{ij}\) are not. In this extension, the hydrodynamic matrices account for hydrodynamic interactions between the particles, \(i.e.\) a force acting on particle \(j\) contributes to the velocity and stress of particle \(i\), and vice versa. With the potential limited to inter-particle interactions, \(i.e.\) in the absence of external interactions, the overall deviatoric stress exerted on the fluid at a strain rate \(\mathbf{E}\) is obtained as
\[
\mathbf{s}^\Sigma = 2\eta_0 \mathbf{E} - \frac{1}{V} \sum_i \mathbf{S}_i - \frac{1}{V} \hat{\mathbf{P}} \sum_{i<j} \mathbf{x}_{ij} \otimes \mathbf{F}_{ij},
\] (24)

where the first term on the r.h.s. is the stress in the suspending fluid with viscosity \(\eta_0\), the second term accounts for hydrodynamic interactions between the particles and the fluid, including fluid-mediated interactions between the particles, and the third term is a regular virial expression arising from direct inter-particle interactions, where the projection
\[
\hat{\mathbf{P}} \mathbf{X} = (\mathbf{X} + \mathbf{X}^T)/2 - \text{det}(\mathbf{X}) \mathbf{1}
\] (25)

returns the symmetric traceless part of a matrix \(\mathbf{X}\). This total stress \(\mathbf{s}^\Sigma\) is normalized by the volume, recovering the regular unit of \(N/m^2\).

V. CONCLUSIONS

The ‘thermodynamic force,’ introduced by Batchelor as ‘an alternative and much simpler method for the statistical mechanics part of the investigation which is a generalization of the argument used by Einstein and which gives the asymptotic or long-time statistical properties of the displacement of particles in terms of the thermal energy of the medium’ was disproven by a simple example. Theories building on this concept, like the common stress expressions for colloidal suspensions are to be considered with care. A new stress expression was derived, see Eqs. (22) and (24), in which the effective forces entering the stress calculation match those entering the equation of motion.

Batchelor’s stress expression is similar in structure to Eqs. (22) and (24), but misses out on the Brownian terms \(\mathbf{S}^B_i\) and replaces \(\mathbf{S}_i\) with a thermodynamic stress \(\mathbf{S}^T_i\) deriving from the thermodynamic force. As mentioned earlier, one would like to evaluate the stress in a given configuration without knowing the probability distribution, in which case the thermodynamic force is not accessible. Hence, the thermodynamic stress was argued to reduce to
\[
\mathbf{S}^T_i = k_B T \mathbf{v}_i \cdot \mathbf{C}_i = k_B T \mathbf{v}_i \cdot \sum_i \mathbf{M}^{ij}_{SE},
\] (26)

up to second order in the concentration and up to any order.7 Bossis and Brady derived a stress expression from the discretized equation of motion, Eq. (18), by constructing a matching first order equation of motion deviant from Eq. (16); the stress then follows by integration of \(\mathbf{R}_S(x(t))\mathbf{x}(t)\) over the time step, recovering Batchelor’s expression. This approach is hampered, however, by Eq. (16) being the exact expression in the Itô interpretation while Eq. (18) is an approximation to its integration over a time step. We note that, despite the superficial similarities as \(k_B T\) times the derivative of blocks of the mobility matrix, the stresses \(\mathbf{S}^T\) and \(\mathbf{S}^M\) are of a markedly different origin. The former is derived from the non-zero average Brownian force \(\mathbf{F}^T\) of the particles arriving at \(x\), and – to paraphrase Batchelor – is therefore a consequence of the usual zero-mean Brownian forces \(\mathbf{F}^B\) at the particles’ places of departure. The latter, \(i.e.\) \(\mathbf{S}^M\), results from the subtly non-zero average Brownian force \(\mathbf{F}^M\) of the particles leaving from \(x\); this effective force arises when using a first order equation of motion to describe Brownian forces with a position-dependent strength affects the displacements during the time step and hence contributes to the stress.

In its current form, Eq. (22) applies to suspensions under shear, in which case the fluctuating Brownian stress contributions average to zero, \(\langle \mathbf{S}^B \rangle = 0\). For viscosity calculations at zero shear, using the Green-Kubo formalism, a fluctuating Brownian stresslet must be added, as discussed elsewhere.

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