Self-diffusion in sheared suspensions: Violation of the Einstein relation

Grzegorz Szamel,* Jerzy Bławzdziewicz,† and Jan A. Leegwater‡

Instituut voor Theoretische Fysica, Rijksuniversiteit te Utrecht, P.O. Box 80.006, 3508 TA Utrecht, The Netherlands

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Starting from the Smoluchowski equation we derive exact microscopic expressions for the self-diffusion and the self-mobility coefficients of a sheared suspension of interacting colloidal particles in a semidiluted regime. We find that the usual Einstein relation between the self-mobility and the self-diffusion matrices is no longer valid for this nonequilibrium situation. The self-mobility and self-diffusion matrices are explicitly calculated in a low-shear-rate regime for a charge-stabilized colloidal suspension.

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Recently, there have been a number of very interesting experimental and theoretical investigations of the properties of suspensions of interacting colloidal particles in presence of a shear flow [1,2]. The structural relaxation time \( \tau_R \) of a suspension, the time a colloidal particle needs in order to diffuse over its radius, is some 9 orders of magnitude larger than a corresponding time for an atomic fluid (Ref. [2], Sec. I). Therefore in experiments with colloidal suspensions one can easily achieve shear rates \( \gamma \) comparable to, or greater than, the intrinsic relaxation rate \( \tau_R^{-1} \) [3]. As a consequence, a profound dependence of both the microscopic structure and the macroscopic properties of suspensions upon the shear rate can be observed.

In recent experiments Qiu et al. [4] have studied self-diffusion processes in charge-stabilized colloids. They have found a pronounced shear rate dependence of the diffusion coefficients. This dependence is different from the enhancement of the diffusion due to a coupling between the convective flow and the diffusion along the gradient of the velocity field, known as Taylor dispersion [5]. Qiu et al. have observed that the self-diffusion coefficients, measured in various directions with respect to the flow, increase approximately linearly with the shear rate. The effect is absent in noninteracting suspensions and increases monotonically with the interaction strength. A similar result has also been found in Brownian dynamics computer simulations by Xue and Grest [6]. However, they have found that the enhancement of the diffusion coefficients is approximately proportional to the square root of the shear rate.

In this paper we present the first theoretical analysis of transport processes of a tagged particle in a suspension of interacting Brownian particles under a steady shear flow [7]. In previous studies [8] the diffusion of independent Brownian particles under shear was analyzed. For sheared suspensions of interacting colloidal particles only the structure factor [9,10] and the shear viscosity [11–14] have been investigated. Structure [15] and transport coefficients [16,17] of sheared atomic fluids also have been analyzed. For simplicity, we consider a semidilute limit, i.e., we calculate the self-diffusion and the self-mobility coefficients to linear order in the density, so that only the two-particle evolution equation is needed. In all our considerations we ignore hydrodynamic interactions. This is a reasonable approximation for a charge-stabilized colloidal system for which usually the effective interparticle interaction potential is of a much larger diameter than the hydrodynamic core (Ref. [2], Sec. IIIA).

We derive here exact but formal expressions for the shear rate dependent self-diffusion and self-mobility coefficients. These expressions are valid for arbitrary shear rates and are given in terms of solutions of a diffusion-convection equation for a pair of interacting Brownian particles. We find that for suspensions under shear Einstein’s relation between the self-mobility matrix and the self-diffusion matrix is violated. This is not in conflict with statistical mechanics, as here we study a nonequilibrium steady state.

Consider a suspension of identical colloidal particles interacting via a pairwise-additive potential \( V(r) \). The suspension undergoes a steady shear flow with the velocity field \( v(r) \) of the form

\[
v(r) = \gamma \vec{F} \cdot \vec{r},
\]

where the tensor \( \vec{F} \) has the components \( \Gamma_{ij} = 1 \) and \( \Gamma_{ij} = 0 \) for \( (ij) \neq (xy) \). We assume that one of the particles, mechanically identical to others, is tagged. We describe the linear transport processes of the tagged particle induced by thermodynamic forces (self-diffusion) and an external force \( F_{\text{ext}} \) (tracer-particle sedimentation). We consider a semidilute suspension and evaluate transport coefficients to linear order in the density of untagged particles \( n \). We neglect the hydrodynamic interactions completely.

The time evolution of the density \( n_t(r; t) \) of the tagged particle is described by the following set of equations, equivalent to the Smoluchowski equation for a sheared suspension [14]: First, we have the continuity equation for \( n_t \):

\[
\frac{\partial n_t(r; t)}{\partial t} = -\vec{v}_t \cdot \left[ v(r_t)n_t(r; t) + j(r_t; t) \right],
\]

where \( \vec{v}_t = \vec{v}/\partial \vec{r}_1 \) and \( j(r_t; t) \) is the tagged-particle current density, measured in the reference frame in which the fluid is locally at rest. The current density \( j(r_t; t) \) is given
by the formula
\[
j(r_1; t) = -D_0 \nabla_1 n_2(r_1; t) + \mu_0 n_2(r_1; t) F^{ext}(r_1) + \mu \int dr_2 F(r_1, r_2) n_2(r_1, r_2; t),
\]  
(3)
where \( D_0 \) and \( \mu_0 \) are the diffusion and the mobility coefficients, respectively, for the infinitely diluted suspension. It follows from the generalized Faxen theorem [18] that \( \mu_0 \) is not modified by the steady shear flow of the form (1). We assume that the same is true for \( D_0 \) and that both coefficients are related through Einstein’s formula \( D_0 = k_B T \mu_0 \). In Eq. (3), \( n_2(r_1, r_2; t) \) denotes the two-particle density of the tagged particle at \( r_1 \) and an untagged particle at \( r_2 \), and \( F(r_1) = -\nabla_1 V(r_1) \) is the interparticle force.

In a semidilute regime the equation for the two-particle density \( n_2 \) is closed,
\[
\frac{\partial n_2(r_1, r_2; t)}{\partial t} = \hat{\Omega}_c n_2(r_1, r_2; t) - \mu_0 \nabla_1 \cdot F^{ext}(r_1) n_2(r_1, r_2; t),
\]  
(4)
where \( \hat{\Omega}_c \) denotes the diffusion-convection operator for two interacting particles
\[
\hat{\Omega}_c = \hat{\Omega} + \gamma \hat{C},
\]  
(5)
with \( \hat{\Omega} \) denoting the two-particle Smoluchowski operator,
\[
\hat{\Omega} = -\sum_{j=1}^{N} \nabla_j \cdot \left[ -D_0 \nabla_j - \mu_0 \nabla_j V(r_{12}) \right],
\]  
(6)
and \( \hat{C} \) describing the contribution due to the convective
\[
\left[ \frac{\partial}{\partial t} - \hat{\Omega}_c \right] \delta n_2(r_1, r_2; t) = -\left[ \mu_0 n_2 \gamma g_2(r_1, r_2) \right] \cdot n_2(r_1; t) F^{ext}(r_1) - \left[ 2\mu_0 n_2 \gamma g_2(r_1, r_2) - \mu_0 F(r_1) n_2 \right] \cdot \left[ -k_B T \nabla_1 n_2(r_1; t) \right],
\]  
(10)
where \( \beta = 1/k_B T \). Note that since we are looking for the linear transport coefficients we have neglected the external force term in the evolution operator acting on \( \delta n_2 \). We have only kept the terms of lowest order in density \( n \).

The two terms at the RHS of Eq. (10) result from the fact that the first term in the decomposition (8) of \( n_2 \) is not preserved by the time evolution, and hence additional correlations are created that are described by \( \delta n_2 \). In the end, the sources of these correlations are the thermodynamic force \( -k_B T \nabla_1 n_2 \) and the external force \( n_2 F^{ext} \).

In absence of the shear flow we have \( g_2 = \exp(-\beta V) \) and then both forces produce equivalent contributions. This is no longer true for the nonequilibrium situation that is studied here and this causes the violation of the Einstein relation.

Equation (10) for \( \delta n_2 \) can be formally solved in terms of \( -k_B T \nabla_1 n_2 \) and \( F^{ext} \). After inserting the result into Eq. (3) and taking the long-time, long-wavelength limit we get the required constitutive relation
\[
j = -\nabla_1 n_2 + \bar{\mu} n_2 F^{ext}.
\]  
(11)
[For symmetry reasons there is no contribution due to the first term at the RHS of the decomposition (8).] The current \( j \) is defined with respect to the reference frame in which the fluid is locally at rest [see Eq. (2)]. Hence the effective self-mobility matrix \( \tilde{\mu} \) and the matrix of the effective self-diffusion coefficients \( \tilde{D} \) in Eq. (11) describe the transport of the tagged particle relative to the convective flow. This is in contrast to effective diffusivities calculated in Ref. [8]. For a clear discussion of this point in a case of self-diffusion in atomic fluids under shear see Ref. [16].

The effective self-mobility matrix \( \tilde{\mu} \) and the matrix of the effective self-diffusion coefficients \( \tilde{D} \) are given by the following expressions:
\[
\tilde{\mu} = \mu_0 \left[ I + n \mu_0 \int dr F(r) \hat{\Omega}_c^{-1} \gamma g_2^{\infty}(r) \right] 
\]  
(12)
and
\[
\tilde{D} = D_0 \left[ I + n \mu_0 \int dr F(r) \hat{\Omega}_c^{-1} \left[ 2\gamma g_2^{\infty}(r) - \beta F(r) g_2^{\infty}(r) \right] \right].
\]  
(13)
In Eqs. (12) and (13) $\mathbf{I}$ is the identity matrix, $\mathbf{V} = \nabla / \partial r$, and for a given function $s(r)$, $f(r) = \nabla^{-1} s(r)$ is the solution of the diffusion-convection equation for the relative coordinate

$$[-V \cdot V f + 2[D_0 V^2 - \mu_0 V \cdot F(r)]] f(r) = s(r),$$

with the boundary condition that $f(r)$ vanishes at infinity.

One can see from the expressions (12) and (13) that in a nonequilibrium steady state we have, in general, that $\mathbf{D} \neq k_B T \mu$. Therefore the Einstein relation between the self-mobility matrix $\mu$ and the self-diffusion matrix $\mathbf{D}$ is not valid. It can be shown that the term modifying the Einstein relation incorporates the effect of the steady-state-like drift velocity of the tagged particle due to the presence of other particles. Such drift introduces an additional change of the tagged-particle density and creates dynamical correlations only for nonuniform $n_i$. Therefore it contributes to the self-diffusion process but does not effect the average motion of the tagged particle under the influence of an applied force. We remark that the shear rate dependent correction to Einstein’s relation is, essentially, an integral from a steady-state time correlation function. Therefore it cannot be assigned to equal time properties such as a change of the osmotic pressure in the steady state due to the shear.

The expressions (12) and (13) constitute the most important result of the present paper. The explicit evaluation of the transport coefficients requires solving the two-particle diffusion-convection equation. Finding the steady-state pair distribution $g_3^s$ that appears in the expressions for the transport coefficients also involves the solving of such an equation, with a different source term. For arbitrary shear rates this is a very difficult problem that, to our knowledge, has not been resolved [19]. However, up to the linear order in $\gamma$ solutions of the diffusion-convection equation can be obtained. We describe results of such calculations below, for a screened Coulomb and hard-sphere potentials. We note that the theoretical results in the linear regime cannot be directly compared with available experimental data. Scattering experiments indicate that the shear rate dependent contribution to $g_3^s$ is linear in $\gamma$ up to $\gamma \sigma^2 / D_0 \sim 10^{-1}$ ( $\sigma$ is the characteristic range of the interaction). The measurements of the self-diffusion constant and the computer simulations were made for much higher shear rates.

To obtain the expansion of the matrices $\mu$ and $\mathbf{D}$ up to the linear terms in $\gamma$ we insert into expressions (12) and (13) the perturbative expansion of $\mathbf{D}^{-1}$:

$$\mathbf{D}^{-1} = \mathbf{D}^{-1}_0 - \mathbf{D}^{-1}_0 \mathbf{g}_3^s \mathbf{D}^{-1}_0 + o(\gamma).$$

We also use the expansions of the pair distribution $g_3^s$:

$$g_3^s = g_3^s + (\gamma g_3^s + o(\gamma)),$$

where $g_3^s$ is the equilibrium pair distribution. The expansion (16) can be obtained from a perturbative solution of the stationary-state equation (9) (see, e.g., Ref. [3], p. 49).

By inserting the above expansions into Eqs. (12) and (13) one can find the corresponding expansions for the matrices $\mu$ and $\mathbf{D}$ with their matrix elements given in terms of solutions of a two-particle diffusion equation with different source terms. By taking into account Eqs. (15) and (16) and symmetry properties of the shear flow of the form (1) one can show that the matrices $\mu$ and $\mathbf{D}$ have the form

$$\mu = \left( \mu_0 + \mu^{(0)} \right) + (\gamma \sigma^2 / D_0) (\mu^{(1)} \mathbf{I} + \mu^{(0)} \mathbf{I}^2) + o(\gamma),$$

$$\mathbf{D} = (D_0 + D^{(0)}) \mathbf{I} + (\gamma \sigma^2 / D_0) (D^{(1)} \mathbf{I} + D_0 \mathbf{I}^2) + o(\gamma),$$

where $D^{(0)} = k_B T \mu^{(0)}$ is the first density correction to the diffusion coefficient in equilibrium, and $\mathbf{I}_r$ and $\mathbf{I}_a$ are the symmetric part and the antisymmetric part of the matrix $\mathbf{I}$, respectively. On the linear level only the off-diagonal elements of the matrices $\mu$ and $\mathbf{D}$ are modified by the shear, and for the antisymmetric parts we have that $D_a^{(1)} = k_B T \mu_a^{(1)}$.

Before presenting explicit results we would like to point out that the perturbation of the diffusion equation by the shear flow is singular at large distances, and the dependence of transport coefficients on $\gamma$ is nonanalytic. This nonanalyticity is of higher-than-linear order, and our calculation is correct [20]. Yet, a naive perturbative solution based on the expansion (15) produces divergent results when continued beyond the linear level as was pointed out by Ronis for the shear rate dependent viscosity [12].

Using Eqs. (12) and (13) and the expansions (15) and (16) we have explicitly evaluated the linear-in-shear corrections to the friction and the self-diffusion coefficients. We have considered two model systems: a system of Brownian particles interacting via a screened Coulomb potential and a hard-sphere model system. For

![FIG. 1. First density corrections to the transport coefficients in a suspension under shear for the screened Coulomb potential $V(r)/k_T = -(\alpha / r) \exp (-(\alpha / r - 1))$ as a function of the inverse hardness index $1/\alpha$. Solid line: the first density correction to the equilibrium self-diffusion coefficient (normalized by the hard-sphere result) $D^{(0)}/2\alpha D_0$. Dashed line: the first shear rate correction to the symmetric part of the self-mobility coefficient (normalized by the zero shear rate value) $\mu^{(1)}/\mu^{(0)}$. Dotted line: the normalized first shear rate correction to the symmetric part of the self-diffusion coefficient, $D^{(1)}/D^{(0)}$. The difference between the dashed and the dotted lines manifests the breakdown of the Einstein relation. Dash-dotted line: the normalized first shear rate correction to the antisymmetric part of the self-diffusion and self-mobility coefficients $D_a^{(1)}/D^{(0)} = \mu_a^{(1)}/\mu^{(0)}$.](image)
the screened Coulomb potential

\[ \frac{V(r)}{k_B T} = \frac{\sigma}{r} e^{-a(r/\sigma - 1)}, \]

we have calculated the transport coefficients numerically. To this end one has to invert the diffusion operator \( \hat{\mathcal{D}} \) [see Eq. (15)]. This we have done by the discretization of the radial part of the diffusion operator which then becomes a tridiagonal matrix that can efficiently be inverted. Unfortunately this method works only if the angular dependence can be separated, hence only the low shear rate limit can be treated without a huge numerical effort. The results are presented in Fig. 1, plotted against the dimensionless parameter \( a \) measuring the hardness of the potential. We note that for \( a^{-1} > 0 \) the Einstein relation is violated. If \( a^{-1} \) tends to 0 the potential (19) approaches that of hard spheres with diameter \( \sigma \). In this limit the transport coefficients can be calculated analytically. The final results are

\[ \frac{D^{(1)}}{D^{(0)}} = \frac{\mu^{(1)}}{\mu^{(0)}}, \]

where \( \phi = \pi \sigma^3 / 6 \) is the particle volume fraction; \( D^{(1)} / D^{(0)} = \mu^{(1)} / \mu^{(0)} = \frac{\sigma}{6} \); and

\[ \frac{D^{(1)}}{D^{(0)}} = \frac{\mu^{(1)}}{\mu^{(0)}} = - \frac{1}{4}. \]

To summarize, we presented a theory for the diffusion and sedimentation processes of a tagged particle in a semi-diluted colloidal suspension undergoing steady shear flow. We gave formal expressions for the shear rate dependent transport coefficients in terms of solutions of a two-particle diffusion-convection equation. We found that the equilibrium Einstein relation between the self-diffusion and self-mobility coefficients is in general not valid for a sheared suspension. To linear order in the shear rate, we explicitly evaluated the transport coefficients for Brownian particles interacting through a screened Coulomb potential or hard-sphere potential. The theory can be extended to higher densities using the approach derived recently by two of the present authors [21] or the approach of Cichocki [22].

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*On leave of absence from the Institute of Theoretical Physics, Warsaw University, Warsaw, Poland.
1Present address: Institute of Fundamental Technological Research, Polish Academy of Sciences, Świętokiezyska 21, Warsaw, Poland.
2Present address: Department of Chemistry, University of Rochester, Rochester, NY 14627.
[2] For a recent review, see P. N. Pusey, in Liquids, Freezing and the Glass Transition, edited by D. Levesque, J.-P. Hansen, and J. Zinn-Justin (Elsevier, Amsterdam, 1990), Sec. VI C.
[7] For a different problem of so-called shear induced diffusion in suspensions of large particles for which the Brownian motion can be neglected, see D. Leighton and A. Acrivos, J. Fluid Mech. 181, 415 (1987), and references cited therein.
[19] Usually while solving the two-particle diffusion-convection equation one neglects the interaction term in the two-particle Smoluchowski operator (6); see, e.g., Refs. [10,11]. A similar approximation is implicit in a fluctuation-diffusion equation approach of Ronis [9,12].
[20] Indeed, even at the linear level one encounters the technical problem that one of the equations considered does not have a required solution that vanishes at infinity, but it tends to a constant instead. By considering a finite system (for which the problem does not exist) and taking the infinite-volume limit one can show that the result obtained from this finite solution is correct.