# Scaling of the time-dependent self-diffusion coefficient and the propagation of hydrodynamic interactions

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We discuss the role of the dynamic Oseen tensor in setting the time scales involved in the scaling of the time-dependent self-diffusion coefficient measured by diffusing wave spectroscopy. We elucidate the paradoxical short time behavior for which scaling is observed and clarify the possible discrepancies between theory and experiments.

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Time-dependent hydrodynamic interactions play a crucial role in the dynamics of colloidal particles at the time scales of the decay of the velocity of the particles. This has been most evidenced by diffusion wave spectroscopy (DWS) which allows one to explore amazingly short time and space scales. Since its advent [1] this technique has triggered a number of experimental [2], theoretical [3,4], and computer simulation studies [5,6] of the self-diffusion of colloidal suspensions at different concentrations at the short time scales where the velocity of the colloidal particles has still not relaxed and the particles do not follow a classical Brownian motion.

A scaling property of the time-dependent self-diffusion coefficient $D(t)$ at different concentrations has been found experimentally [2], and confirmed by a computer simulation [5]. This scaling suggests that the colloidal particles move as if they were alone but in an effective medium with the suspension viscosity. However, the raw $D(t)$ curves for different volume fractions separate from each other at times much shorter than the time required for the vorticity to travel the typical distance between particles. The scaling is satisfied at very short times also. This has been a puzzling question [2,5] because it is argued that there is not enough time for the hydrodynamic interactions to have been established at these short time scales.

The purpose of this paper is to study in detail the propagation of time-dependent hydrodynamic interactions by looking at the form of the dynamic Oseen tensor in real space [7]. We emphasize that hydrodynamic interactions in incompressible fluids are established instantaneously and that the dominant effects come from very short times. Although there is a time scale associated with the diffusive propagation of vorticity, we show that it plays a secondary role. Therefore, there is no paradox about the fact that particles influence each other at very short times, thus modifiying their diffusion properties.

The time-dependent self-diffusion coefficient $D(t)$ is defined as

$$D(t) \equiv \frac{1}{6}\frac{d}{dt}\langle \Delta \mathbf{R}^2(t)\rangle = \int_0^t C(t')dt', \tag{1}$$

where $\langle \Delta \mathbf{R}^2(t)\rangle$ is the mean-square displacement and $C(t) \equiv \frac{1}{3}\langle \mathbf{u}\cdot\mathbf{u}(t)\rangle$ is the velocity autocorrelation function. $D(t)$ has been measured for suspensions of hard spheres (monodisperse polystyrene latex spheres of radius $a = 1.53$ $\mu$m and $a = 3.09$ $\mu$m in water) [2]. At the smallest volume fraction ($\phi = 0.021$), $D(t)$ is accurately described by the hydrodynamic theory of Brownian motion [8,9] instead of the classical exponential Langevin result $D(t) = D_0(1-\exp\{-t/\tau_B\})$, where $\tau_B = m/(6\pi\eta a)$, $D_0 = k_BT/(6\pi\eta a)$. This is the Stokes-Einstein relation for the diffusion coefficient of a single particle, $\eta$ being the shear viscosity of the solvent and $a$ the radius of the spherical particles in suspension. The hydrodynamic theory of Brownian motion for a single particle predicts [10]

$$D(t) = D_0\left\{1 + \frac{3}{(5-8\Sigma)^{1/2}}\left[\frac{1}{\alpha_+}\exp\{\alpha_+^2\tau\}\mathrm{erfc}(\alpha_+\tau^{1/2}) - \frac{1}{\alpha_-}\exp\{\alpha_-^2\tau\}\mathrm{erfc}(\alpha_-\tau^{1/2})\right]\right\}, \tag{2}$$

where $\tau = t/\tau_\nu$ is a scaled time and $\tau_\nu = a^2\rho/\eta$ is a typical time required for the vorticity to diffuse a distance equal to a particle radius. Also, $\mathrm{erfc}(x)$ is the complex compliment of the error function, $\alpha_\pm = 3[3 \pm (5-8\Sigma)^{1/2}]/(2+4\Sigma)$ and $\Sigma = \rho_B/\rho$, where $\rho_B$ and $\rho$ are the densities of the colloidal particle and the solvent, respectively.

At higher volume fractions there are substantial deviations from the single particle result Eq. (2) [2]. Nevertheless, a striking scaling property is observed by which $D(t)$ at a finite volume fraction can be fitted by the $\phi = 0$ result (2) by substituting $\tau_\nu$ and $D_0$ by volume fraction dependent quantities $\tau(\phi)$ and $D(\phi)$. In this way, the scaling relationship is $D(t) = D_s(\phi)d(t/\tau(\phi))$ where $d(x)$ can be found from (2) and satisfies $\lim_{x\to\infty} d(x) = 1$. Several scaling scenarios have been considered [2]. A particularly interesting one is obtained when the theoretically predicted [11] short-time self-diffusion coefficient $D_s(\phi) = D_0[1 - 1.83\phi]$ is used. Then, the time scale is given quite accurately by $\tau(\phi) = a^2\rho/\eta^\infty(\phi)$, where $\eta^\infty(\phi)$ is the suspension high-frequency shear viscosity

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as calculated by Beenakker [12].

This scaling strongly suggests that the dynamics of a given particle in a concentrated suspension is the same as if the particle would move alone in an effective medium with viscosity equal to the suspension viscosity. However, this appealing picture is apparently paradoxical in two related aspects. First, the deviation of the time-dependent self-diffusion coefficient in a concentrated suspension from the dilute result occurs at times much shorter than $\tau_\nu$, the time required for the vorticity to diffuse the average interparticle distance (which in the experiments is of the order of two to six particle radius depending on the volume fraction). Second, the observed scaling extends to times much shorter than $\tau_\nu$.

The dynamic Oseen tensor is the Green's function of the linearized Navier-Stokes equations and contains all the information about the time scales involved in the hydrodynamic interactions. The incompressibility and Navier-Stokes equations are

$$\begin{aligned}\nabla \cdot \mathbf{v}(\mathbf{r},t) &= 0 \\ \rho \partial_t \mathbf{v}(\mathbf{r},t) &= -\nabla p(\mathbf{r},t) + \eta \nabla^2 \mathbf{v}(\mathbf{r},t) + \mathbf{F}(\mathbf{r},t),\end{aligned} \tag{3}$$

where $\mathbf{v}(\mathbf{r},t)$ is the velocity field, $p(\mathbf{r},t)$ is the pressure field, and $\mathbf{F}(\mathbf{r},t)$ is a force density field that includes external forces like gravity and induced forces due to boundary conditions. The solution of (3) is

$$\mathbf{v}(\mathbf{r},t) = \mathbf{v}_0(\mathbf{r},t) + \int_0^t dt' \int d^3r' \mathbf{P}(\mathbf{r}-\mathbf{r}', t-t') \frac{\mathbf{F}(\mathbf{r}',t')}{\rho}, \tag{4}$$

where the dynamical Oseen tensor is defined by

$$\mathbf{P}(\mathbf{r}-\mathbf{r}', t-t') \equiv \int \frac{d^3\mathbf{k}}{(2\pi)^3} \exp\{-\nu(t-t')k^2 + i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')\} \left[\mathbf{1} - \frac{\mathbf{kk}}{k^2}\right] \tag{5}$$

and $\mathbf{v}_0(\mathbf{r},t)$ is the unperturbed velocity field. The explicit form of the dynamical Oseen tensor in (5) is

$$\mathbf{P}(r,t) = p(r,t)\mathbf{1} - q(r,t)\frac{\mathbf{rr}}{r^2}, \tag{6}$$

where

$$\begin{aligned} p(r,t) &= \left(1 + \frac{2\nu t}{r^2}\right) f(r,t) - \frac{g(r,t)}{r^2}, \\ q(r,t) &= \left(1 + \frac{6\nu t}{r^2}\right) f(r,t) - \frac{3g(r,t)}{r^2}, \\ f(r,t) &= \int \frac{d^3\mathbf{k}}{(2\pi)^3} \exp\{-\nu t k^2 + i\mathbf{k}\cdot\mathbf{r}\} \\ &= \frac{1}{(4\pi\nu t)^{3/2}} \exp\left\{-\frac{r^2}{4\nu t}\right\}, \\ g(r,t) &= \int \frac{d^3k}{(2\pi)^3} \frac{1}{k^2} \exp\{-\nu t k^2 + i\mathbf{k}\cdot\mathbf{r}\} \\ &= \frac{1}{4\pi r} \Phi\left(\frac{r}{(4\nu t)^{1/2}}\right), \end{aligned} \tag{7}$$

and $\Phi(x)$ is the error function.

It is illustrative to consider two particular temporal dependences of the external force. If an external stationary local force of the form $\mathbf{F} = \mathbf{F}_0\delta(\mathbf{r})$ is applied at the origin, then the velocity field is also stationary and given by

$$\mathbf{v}(\mathbf{r}) = \frac{1}{\rho}\int_0^\infty \mathbf{P}(\mathbf{r},t)dt\mathbf{F}_0 = \mathbf{T}(\mathbf{r})\mathbf{F}_0. \tag{8}$$

The static Oseen tensor $\mathbf{T}(\mathbf{r})$, which is the time integral of the dynamical Oseen tensor, has the well-known explicit form

$$\begin{aligned}\mathbf{T}(\mathbf{r}) &\equiv \frac{1}{\rho}\int \frac{d^3\mathbf{k}}{(2\pi)^3} \exp\{i\mathbf{k}\cdot\mathbf{r}\} \frac{1}{\nu k^2}\left[\mathbf{1} - \frac{\mathbf{kk}}{k^2}\right] \\ &= \frac{1}{8\pi\eta r}\left[\mathbf{1} + \frac{\mathbf{rr}}{r^2}\right].\end{aligned} \tag{9}$$

On the other hand, an impulsive local force of the form $\mathbf{F} = \mathbf{F}\delta(\mathbf{r})\delta(t)$ applied on a fluid originally at rest produces a velocity field per unit force of the form $\mathbf{v}(\mathbf{r},t) = \mathbf{P}(\mathbf{r},t)\mathbf{F}_0/\rho$. This shows that the dynamic Oseen tensor describes the effects of a disturbance local in space and time. If the impulsive force is in the direction of the $z$ axis, $\mathbf{F} = F\delta(\mathbf{r})\delta(t)e_\mathbf{z}$ then the velocity field per unit force under an impulsive force is

$$\frac{\mathbf{v}(\mathbf{r},t)}{F/\rho} = p(r,t)e_\mathbf{z} - q(r,t)(\cos\theta)\frac{\mathbf{r}}{r}, \tag{10}$$

where $\theta$ is the angle between the position vector $\mathbf{r}$ and the $z$ axis.

In the case of a colloidal suspension, we can interpret the force $\mathbf{F}(r,t)$ in Eq. (3) as the induced force necessary to produce the same effects on the flow field as those produced by the boundary conditions on the colloidal particles [7,9]. This force $\mathbf{F}(r,t)$ is quite localized in space and time because, due to Brownian motion, it provides essentially instantaneous kicks to the solvent. Therefore, Eq. (10) is a good approximation to the velocity field around a colloidal particle once a Brownian fluctuation has occurred.

The most relevant feature of the velocity field in Eq. (10) is that it becomes *instantaneously* (at $t = 0^+$) different from zero in all points. The functions $f, g, p, q$ have the following nonzero values at the initial time $f(r,0^+) = \delta^3(\mathbf{r})$, $g(r,0^+) = 1/4\pi r$, $p(r,0^+) = \delta^3(\mathbf{r}) - 1/4\pi r^3$, and $q(r,0^+) = \delta^3(\mathbf{r}) - 3/4\pi r^3$. This infinite velocity of propagation is obviously an artifact of the assumed incompressibility of the fluid. In a more elaborate compressible theory one expects that there is a delay of order $r/c$, where $c$ is the (finite) speed of sound, from the moment that an initial kick at the origin is produced until the velocity field at a point $r$ reaches its maximum value of the order $1/(4\pi r^3)$. However, the scaling observed in the DWS experiments is not due to compressibility effects. A simple comparison of the sound traversal time defined as $\tau_c = R/c$ where $R$ is a typical interparticle distance ($\sim 1$ $\mu$m) and $c$ is the speed of sound in water ($\sim 1500$ m/s) shows that $\tau_c \sim 10^{-9}$ s which is much smaller than the smallest time scales probed in the experiments ($\sim 10^{-7}$ s). Therefore, an incompressible theory should be perfectly adequate to describe the hydro-

dynamic interactions between particles in these experiments.

At later times the velocity field induced in all space relaxes in the form of a vortex ring. This is clearly seen in Fig. 1 [the velocity field in Eq. (10) has axial symmetry]. Let us remark that this vortex ring generation is the fundamental mode of reaction of a fluid under an external force, that is, the vortex ring is a representation of the Green's function of the problem. As time proceeds, the vortex ring expands. In order to have a better quantitative idea we plot (in Fig. 2) the $z$ component of the velocity field $v_{\|}(r,t)$ at different distances ahead of the origin in the axis of the direction of the perturbing force, as a function of time. In this axis, the direction of the velocity field is parallel to the perturbing force, by symmetry requirements. We observe that the maximum velocity occurs at the initial time. In Fig. 3 we plot the velocity field $v_{\perp}(r,t)$ at different distances in the plane containing the origin and normal to the direction of the perturbing force, as a function of time. Also, the velocity in this plane is necessarily parallel to the force, by symmetry arguments. At very short times the velocity at any point different from the origin is negative, i.e., opposite to the direction of the force. This is because an instantaneous vortex ring has been formed. As time proceeds, the circumference of points where the velocity field is zero moves apart from the origin. Because of

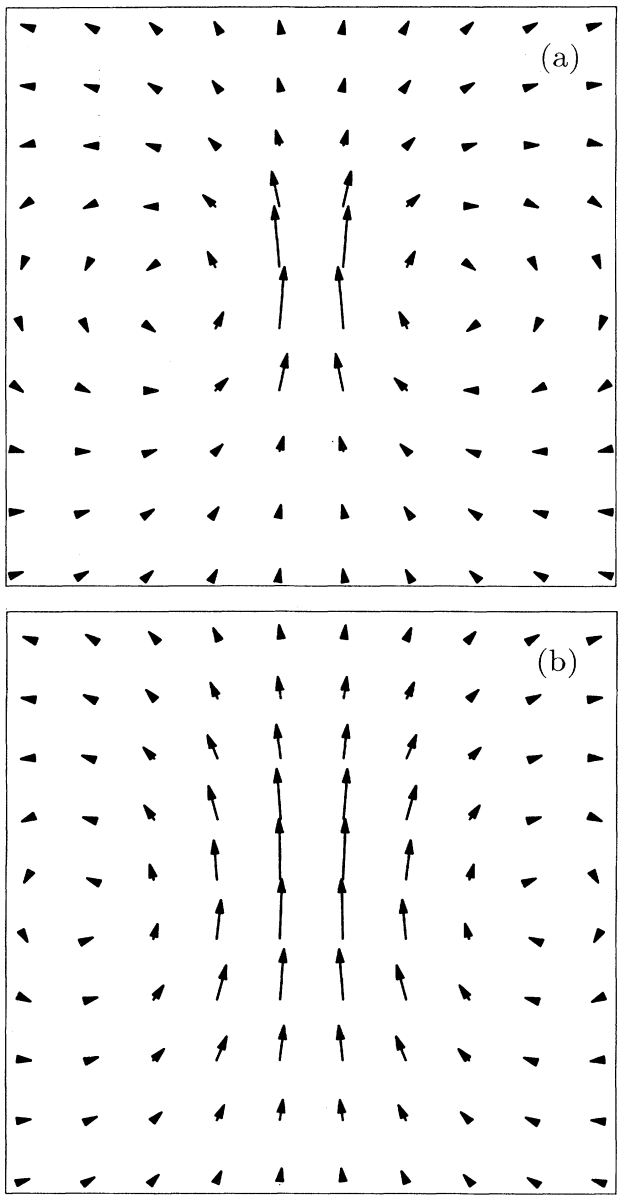


FIG. 1. Section in the plane $zx$ of the vortex ring at two different times (a) $t = 0.006$ and (b) $t = 0.03$, respectively. In each snapshot the magnitude of the velocity field is scaled to the maximum value of the velocity (which occur near the origin). It is clear that once the initial vortex is stablished (in short sonic time scales not captured by an incompressible theory) there is a relaxation of the velocity field by diffussion of the vorticity.

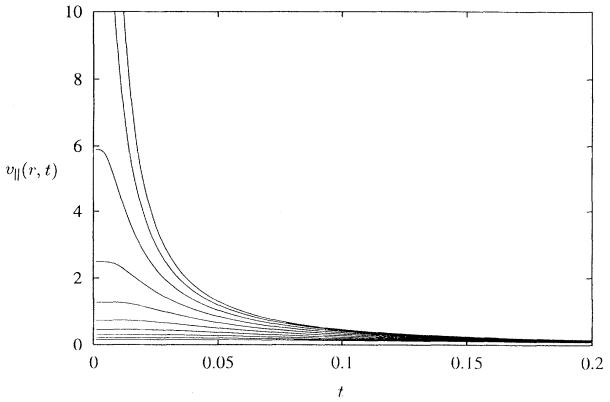


FIG. 2. The velocity field $v_{\|}(r,t)$ (per unit perturbing force) on the points ahead in the axis containing the perturbing force. In descending order $r = 0.1, \ldots, 0.9, 1$ and the units are such that $\nu = 1$.

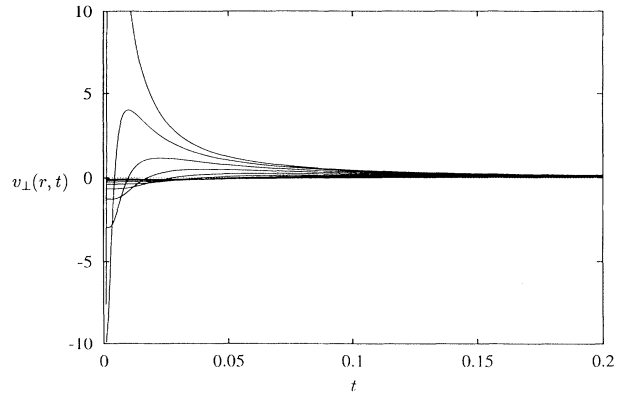


FIG. 3. The velocity field $v_{\perp}(r,t)$ (per unit perturbing force) on the points of the plane containing the origin and perpendicular to the direction of the perturbing force. In descending order, $r = 0.1, \ldots, 0.9, 1$. We choose units such that $\nu = 1$. The maximum of $p(r,t)$ occurs for $t_{max} = r^2/4\nu$ and at this time the value is $f(r, t_{max}) \propto r^{-3}$. At long times the decay is proportional to $t^{-3/2}$.

$v_\perp(r,t) = p(r,t) = \Psi(r^2/\nu t)/r^3$, the radius of the vortex ring occurs at a constant value of $r^2/\nu t$, growing diffusively. At long times, the velocity field in the normal plane at a given point will have a positive velocity because the vortex ring will have already drifted beyond that point. Eventually the velocity field will decay as a power law $t^{-3/2}$. This decay is the ultimate cause for the long-time tails in the velocity autocorrelation function of a particle [13].

In conclusion, there is no paradox about the scaling of the time-dependent self-diffusion coefficient at short times because the hydrodynamic interactions are established instantaneously and then decay by the diffusion of the vorticity. In addition, the most important effects occur at $t = 0$ when the overall magnitude of the velocity field is larger.

The above discussion does not offer any explanation about the cause of the scaling. We are aware of only two theoretical approaches to the study of the time-dependent self-diffusion coefficient at short times. Milner and Liu [4] use a method of reflections and assume pair additivity of hydrodynamic interactions in order to compute the mobility and, through the fluctuation-dissipation theorem, the time-dependent self-diffusion coefficient. They find a form of scaling at long times. However, because a low-frequency expansion is made, their approximation is limited to long times. Then, from their approach it is not possible to assess whether pair additivity is sufficient to give scaling at short times.

On the other hand, Clercx and Schram [3] make use of a general numerical scheme for calculating the mobility matrix. For the case of two spheres and assuming pair additivity of the hydrodynamic interactions, they calculate the time-dependent self-diffusion coefficients for different values of the density ratio $\Sigma$ and different volume fractions $\phi$. Pair additivity should be a good approximation for low enough $\phi$. Unfortunately, the scaling properties of the curves have not been analyzed. At the highest volume fractions considered ($\phi \simeq 0.3$), and for Brownian particle densities larger than the solvent density, there is a maximum in $D(t)$ which is not present at lower $\phi$ (see Fig. 3 in Ref. [3]). This precludes scaling at these values of the volume fractions. The question is whether pair additivity is valid in these cases. The comparison with three-body calculations is essential in order to assess the range of $\phi$ for which the two-body results are correct. It is suggested in Ref. [3] that for all the concentrations considered ($\phi < 0.3$) the assumption of pair additivity is justified from the fact that the asymptotic values of $D(t)$ are given correctly by the well-known result $D(\phi) = D_0[1 - 1.83\phi]$ (which is obtained under the assumption of pair additivity). However, one should be cautious about extrapolating the validity of pair approximation at long times to short times. It may well happen that during the time-dependent regime, many-body interactions are more important than in the asymptotic long-time regime. This would reduce the range of volume fractions for which the pair approximation is valid. Another possible approach to the same problem is through the numerical scheme put forward by Ladd for the computation of many-body interactions [14], by considering short times.

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