Brownian particles in shear flow and harmonic potentials: A study of long-time tails

Brownian particles in shear flow and harmonic potentials: A study of long-time tails

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In this paper we present the results of a study of the mean-square displacement of a Brownian particle in a harmonic potential and of a Brownian particle in shear flow. We have focused on the long-time behavior of the mean-square displacement. In contrast with earlier results, presented by others who studied the Stokes limit of these problems, we have studied this problem using the time-dependent linearized incompressible Navier-Stokes equations to describe the fluid motion. Then we see that the mean-square displacement is strongly influenced by backflow effects in the fluid, resulting, among other things, in long-time tails of correlation functions. We have compared our results with those calculated in the Stokes limit; important differences exist between them. The main differences are the long-time tails in correlation functions and, related with them, the larger time scales that should be considered to obtain diffusive behavior in the case of a Brownian particle in a harmonic potential or to obtain the cubic regime in the mean-square displacement of a Brownian particle in shear flow. Furthermore, we have studied the velocity autocorrelation function of a Brownian particle in a harmonic potential. In the overdamped case we have shown a $\tau^{-7/2}$ long-time tail instead of the exponential tail that can be obtained in the Stokes limit. Also the sign of both tails differ.

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I. INTRODUCTION

The theory of Brownian motion has been and still is a field of intensive research. There are many examples of present-day research. We can think of the effect of Brownian motion on the behavior of the low-shear-rate effective viscosity of suspensions which has been studied theoretically by, e.g., Batchelor [1]. Some other aspects of present-day research have already been mentioned by the authors in preceding articles such as the study of the translational and rotational self-diffusion coefficient (see introduction and references in [2,3]). Also much experimental research has been performed such as measurements of the time-dependent diffusion coefficient of Brownian particles by Weitz *et al.* [4]. In the field of computational physics a subdiscipline has been developed called Brownian dynamics [5]. This is a molecular-dynamics-like method to determine the trajectories of Brownian particles. With this method a system of Brownian particles can be simulated. In this article we present some results of a study of correlation functions of Brownian particles immersed in an unbounded fluid. First we shall consider the position and velocity correlation functions of a Brownian particle in a harmonic potential. Then we shall consider position correlation functions of a Brownian particle in an externally imposed shear flow. The mean-square displacement of these particles, under the circumstances described above, can be studied, and in connection with it the diffusion of the Brownian particles if a diffusional regime exists. For the moment we assume that hydrodynamic interactions are absent. Before we come to these points we give a short historical review.

In 1827 Robert Brown, a Scottish botanist, observed under the microscope the random motion of pollen grains. This was the starting point of the study of Brownian motion. In the beginning of this century some important steps in the development of the theory of Brownian motion were set by Einstein [6] and Langevin [7]. Einstein presented a relation between the diffusion coefficient D_0 of a spherical Brownian particle and the Stokes friction coefficient ζ, nowadays known as the Stokes-Einstein relation,

$$D_0=\frac{k_B T}{\zeta} , \tag{1.1}$$

where $\zeta=6\pi\eta_0 a$, with η_0 the shear viscosity of the fluid and a the radius of the Brownian particle. Moreover, k_B is the Boltzmann constant and T is the absolute temperature. This relation has been derived by using thermodynamic arguments. Besides the above-mentioned result, Einstein defined the following relation between the diffusion coefficient D_0 and the velocity autocorrelation function $\phi(t)$, although he did not use this relation to obtain Eq. (1.1),

$$D_0=\lim_{t\to\infty}\frac{\langle \Delta x^2(t)\rangle}{2t}=\int_0^\infty \phi(t)dt , \tag{1.2}$$

where $\langle \Delta x^2(t)\rangle$ is the mean-square displacement. It is obvious that the long-time behavior should be such that $t\phi(t)\to 0$ if $t\to\infty$. In the same period Langevin used another method to study diffusion of Brownian particles. He introduced an equation of motion for free Brownian particles:

$$m\dot{\mathbf{U}}(t)=-\zeta\mathbf{U}(t)+\mathbf{R}(t) , \tag{1.3}$$

with m the mass of the particle, $\mathbf{U}(t)$ its velocity. $\mathbf{R}(t)$ is

a random force exerted by the fluid molecules in collisions with the Brownian particle. The random force is assumed to be Gaussian, $\langle \mathbf{R}(t) \rangle = 0$ where $\langle\ \rangle$ denotes an ensemble average. Furthermore,

$$\langle R_i(t) R_j(t') \rangle = 2\zeta k_B T \delta_{ij} \delta(t-t') , \tag{1.4}$$

which means that successive collisions of fluid molecules are uncorrelated. With the Langevin equation an explicit expression for the velocity autocorrelation function can be derived which, in this case, is an exponentially decaying function of time [8],

$$\phi(t) = \frac{k_B T}{m} \exp\left[-\frac{\zeta}{m} t \right] . \tag{1.5}$$

In the years following these important developments several other authors have presented results of studies of the behavior of Brownian particles. We think of the work of Uhlenbeck and Ornstein who studied among other things the behavior of Brownian particles in a harmonic potential [9]. Much work on the general theory of Brownian motion has been reviewed by Chandrasekhar [10] and Wang and Uhlenbeck [11].

In the 1960s several publications concerning computer simulations to study the behavior of fluid molecules were published. Both Rahman [12,13] and Alder and Wainwright [14–16] found in computer experiments, where they simulated the motion of a tagged particle in a hard-sphere fluid, that the velocity autocorrelation function of that tagged particle has a long-time tail, instead of showing an exponential decay, viz.,

$$\phi(t) \approx C \tau_B^{-3/2}, \quad \tau_B \gg 1 , \tag{1.6}$$

with $\tau_B = (6\pi\eta_0 a/m)t$ and C a constant. Equation (1.6) is valid in the case of a three-dimensional hard-sphere fluid. In general they obtained a long-time-tail behavior $t^{-d/2}$, with d the dimensionality of the system. In one- and two-dimensional systems this long-time tail leads to divergencies in Green-Kubo integrals like Eq. (1.2). Alder and Wainwright were able to explain the long-time tail in Eq. (1.6) for three-dimensional hard-sphere fluids by considering the cooperative effect from the surrounding fluid molecules, which could be described by macroscopic hydrodynamics [15,16]. This explanation was also given by Zwanzig and Bixon [17]. Widom studied the behavior of a spherical Brownian particle in a viscous fluid by using the generalized Langevin equation, a Langevin equation with a memory kernel, viz.,

$$m\dot{\mathbf{U}}(t) = -\int_{-\infty}^{t} \zeta(t-\tau)\mathbf{U}(\tau)d\tau + \mathbf{R}(t) . \tag{1.7}$$

Apart from the different form of the Langevin equation it is important to note that the collisions of the fluid molecules with the Brownian particle are correlated, and consequently the random force autocorrelation function is not proportional to the Dirac δ function anymore, although the random force remains Gaussian. Widom was able to solve this problem analytically and showed the existence of the long-time tail in the velocity autocorrelation function of the Brownian particle [18]. The following result for the velocity autocorrelation function can be obtained:

$$\phi(t) = \frac{k_B T}{M(b-a)} [b \exp(b^2 t)\operatorname{erfc}(b\sqrt{t}\,) - a \exp(a^2 t)\operatorname{erfc}(a\sqrt{t}\,)] , \tag{1.8}$$

with

$$a = [z + (z^2 - 4\zeta M)^{1/2}]/2M ,$$
$$b = [z - (z^2 - 4\zeta M)^{1/2}]/2M .$$

In this equation we have introduced the shorthand notation $z = 6\pi a^2 \sqrt{\rho \eta_0}$, with a the radius of the Brownian particle, ρ the fluid density, and η_0 the shear viscosity of the fluid. Furthermore we have introduced the effective mass $M = m + \frac{1}{2} m_0$, with m the mass of the Brownian particle and $m_0 = \frac{4}{3}\pi a^3 \rho$, the mass of the fluid displaced by the Brownian particle. We emphasize that in the limit $t \to 0$ we have

$$\lim_{t \to 0} \phi(t) = \frac{k_B T}{M} . \tag{1.9}$$

This result is in contradiction with the equipartition theorem because the particle mass m instead of the effective mass M would be expected in Eq. (1.9). This paradox has been solved by Zwanzig and Bixon [19] (see in this context also Ref. [20]). They have shown a rapid initial decrease from $k_B T/m$ to $k_B T/M$ at very short time scales by including compressibility effects in the study of the velocity autocorrelation function. It is easy to determine the long-time behavior of the velocity autocorrelation function, using the asymptotic expansion of the product of the exponential function and complementary error function (see also Sec. II). We obtain for $\phi(t)$

$$\phi(t) \simeq k_B T \frac{z}{2\zeta^2 \sqrt{\pi}} \frac{1}{t\sqrt{t}} + O\left[\frac{1}{t^2 \sqrt{t}} \right] , \quad |a^2| t \gg 1, \ |b^2| t \gg 1 , \tag{1.10}$$

which shows the famous long-time tail.

In an analogous way one can obtain an expression for the mean-square displacement:

$$\langle \Delta x^2(t) \rangle \equiv \Psi(t) = 2D_0 \left[t - \frac{2z}{\zeta\sqrt{\pi}} \sqrt{t} + \frac{(z^2 - \zeta M)}{\zeta^2} + \frac{\zeta}{M(b-a)} [b^{-3} \exp(b^2 t)\operatorname{erfc}(b\sqrt{t}\,) - a^{-3} \exp(a^2 t)\operatorname{erfc}(a\sqrt{t}\,)] \right] . \tag{1.11}$$

This expression has already been presented by Paul and Pusey [21]. Weitz *et al.* have presented measurements which support this expression [4]. In the limit of large t we obtain the familiar result $\Psi(t)=2D_0t$.

Since that time several other authors have also studied this kind of problem [22–24] as well as the rotational counterpart of this function [25–27]. Ailawadi and Berne showed the following long-time behavior of the angular velocity autocorrelation function [25]:

$$\phi_r(t)\approx C(\tau_B^r)^{-5/2} \quad \tau_B^r \gg 1 , \tag{1.12}$$

with, in the case of spherical particles, $\tau_B^r=\frac{10}{3}\tau_B$. Finally we want to remark that these long-time tails in correlation functions of microscopic properties have appeared in many theories and are accepted among statistical physicists (see for a review, e.g., Pomeau and Résibois [28]).

In Secs. II and III we present the results of a study of the velocity autocorrelation function and the mean-square displacement of a Brownian particle in a harmonic potential and in an externally imposed shear flow, respectively. We shall concentrate on the backflow effects, which appear explicitly in the generalized Langevin equations, necessary to solve the problems mentioned above. We end with a short conclusion.

II. A BROWNIAN PARTICLE IN A HARMONIC POTENTIAL

We present the results of a study of a Brownian particle in a harmonic potential immersed in an unbounded fluid. The fluid is at rest at infinity. This model can be used to describe a Brownian particle in the equilibrium position of a potential, where small displacements can be assumed to be harmonic. We can think of small charged colloidal particles in a crystal structure. The problem of a Brownian particle confined to a restricted volume can also be roughly described by using a harmonic potential. In this study we have assumed that the particle is of such a small size that the Reynolds number of the fluid motion induced by the Brownian particle is small. So we can neglect the nonlinear term in the Navier-Stokes equations. The fluid motion is then described by the linearized incompressible time-dependent Navier-Stokes equations. Furthermore, we introduce a harmonic force in the x direction: $F(t)=-Kx(t)$. Apart from this force we consider a random force $\mathbf{R}(t)$. As is the case with the study of the free Brownian particle we can describe the problem under consideration as a one-dimensional problem because there is no coupling with positions and velocities of the y and z directions. For that reason we shall omit the vector notation. The Brownian particle has velocity $U(t)$ if $t>0$, and is assumed to be at rest if $t\le 0$. The velocity of this particle is determined by its velocity at earlier times via backflow effects in the fluid; the equation of motion is now, assuming that the particle is at the equilibrium position $x_0=0$ if $t=0$ and at rest for $t\le 0$, described by the following generalized linear Langevin equation, which is called the Stokes-Boussinesq equation (with a harmonic force). It can be derived by solving the time-dependent Navier-Stokes equations describing the system under consideration [29,30]:

$$m\dot{U}(t)=-6\pi\eta_0 aU(t)-\tfrac{1}{2}m_0\dot{U}(t) -6a^2\sqrt{\pi\rho\eta_0}\int_0^t\frac{1}{\sqrt{t-\tau}}\dot{U}(\tau)d\tau-Kx(t)+R(t) . \tag{2.1}$$

The first term of Eq. (2.1) is the ordinary Stokes's friction, the second is connected with the virtual mass of a sphere in an incompressible fluid, and the third is a memory term associated with the hydrodynamic retardation effects and related to the penetration depth of viscous unsteady flow around a sphere. The motion of the Brownian particle in the y and z directions can be determined by solving an analogous equation without the harmonic term. The results for this case are summarized in Sec. I. The equation of motion of the particle in the x direction can be solved by either using the theory of Fourier transforms or the theory of Laplace transforms. We use the latter method for convenience because it is the appropriate one if studying Brownian particles in shear flow (see Sec. III). The Laplace transform of a function $f(t)$ has the following form [31]:

$$\tilde{f}(s)=\int_0^\infty e^{-st}f(t)dt, \quad \mathrm{Re}(s)>0 . \tag{2.2}$$

Via the Laplace transform of Eq. (2.1) we obtain

$$\tilde{U}(s)=\tilde{A}(s)\tilde{R}(s), \quad \tilde{A}(s)=\frac{s}{(Ms^2+zs\sqrt{s}+\zeta s+K)} , \tag{2.3}$$

with z, ζ, and M already introduced in Sec. I [below Eqs. (1.1) and (1.8)]. The Laplace transform of the velocity autocorrelation function is now

$$\langle\tilde{U}(s)\tilde{U}(s')\rangle=\tilde{A}(s)\tilde{A}(s')\langle\tilde{R}(s)\tilde{R}(s')\rangle . \tag{2.4}$$

Taking $x(0)=0$ and using the fact that the position $x(t)$ is the time integral of the velocity of the Brownian particle, we find for the position autocorrelation function

$$\langle\tilde{x}(s)\tilde{x}(s')\rangle=\tilde{B}(s)\tilde{B}(s')\langle\tilde{R}(s)\tilde{R}(s')\rangle , \quad \tilde{B}(s)=\tilde{A}(s)/s . \tag{2.5}$$

This function is used to determine the mean-square displacement of the Brownian particle. It is obvious that it is necessary to know a relation between the Laplace transform of the random force autocorrelation function and the functions $\tilde{A}(s)$ and $\tilde{B}(s)$ to evaluate the Laplace inverse of both expressions above [Eqs. (2.4) and (2.5)]. We start with the Fourier transform of the random force autocorrelation function derived by Bedeaux and Mazur. They used a generalized Faxén theorem and obtained [32]

$$\langle R(\omega)R^*(\omega')\rangle=4\pi k_BT\delta(\omega-\omega')(\zeta+\tfrac{1}{2}z\sqrt{2|\omega|}) \equiv 2\pi\hat{\theta}(|\omega|)\delta(\omega-\omega') . \tag{2.6}$$

From the properties of the equation above we can conclude that the random force autocorrelation function has the following form:

$$\langle R(t_1)R(t_2)\rangle=\theta(|t_2-t_1|) . \tag{2.7}$$

The Laplace transform of Eq. (2.7) is (see Ref. [33], p. 195)

$$\langle \tilde{R}(s)\tilde{R}(s')\rangle = \frac{\tilde{\theta}(s)+\tilde{\theta}(s')}{s+s'} . \tag{2.8}$$

A simple relation can be derived between $\tilde{\theta}(s)$ and $\tilde{A}(s)$ [Eq. (2.3)] [33],

$$\tilde{A}(s)\tilde{\theta}(s) = k_B T[1 - Ms\tilde{A}(s) - K\tilde{B}(s)] , \tag{2.9}$$

and the Laplace transform of the velocity autocorrelation function is now

$$\langle \tilde{U}(s)\tilde{U}(s')\rangle = k_B T\left[\frac{\tilde{A}(s)+\tilde{A}(s')}{s+s'} - M\tilde{A}(s)\tilde{A}(s') - K\tilde{B}(s)\tilde{B}(s')\right] . \tag{2.10}$$

The inverse Laplace transformation, with the use of tables of Laplace transforms [34], results in the following expression:

$$\langle U(t_1)U(t_2)\rangle = k_B T[A(|t_2-t_1|) - MA(t_1)A(t_2) - KB(t_1)B(t_2)] , \tag{2.11}$$

with the functions $A(t)$ and $B(t)$,

$$A(t) = \frac{1}{M}\left[\frac{a^3\exp(a^2t)\operatorname{erfc}(a\sqrt{t})}{(a-b)(a-c)(a-d)} + \frac{b^3\exp(b^2t)\operatorname{erfc}(b\sqrt{t})}{(b-a)(b-c)(b-d)} + \frac{c^3\exp(c^2t)\operatorname{erfc}(c\sqrt{t})}{(c-a)(c-b)(c-d)} + \frac{d^3\exp(d^2t)\operatorname{erfc}(d\sqrt{t})}{(d-a)(d-b)(d-c)}\right] , \tag{2.12}$$

$$B(t) = \int_0^t A(\tau)d\tau = \frac{1}{M}\left[\frac{a\exp(a^2t)\operatorname{erfc}(a\sqrt{t})}{(a-b)(a-c)(a-d)} + \frac{b\exp(b^2t)\operatorname{erfc}(b\sqrt{t})}{(b-a)(b-c)(b-d)} + \frac{c\exp(c^2t)\operatorname{erfc}(c\sqrt{t})}{(c-a)(c-b)(c-d)} + \frac{d\exp(d^2t)\operatorname{erfc}(d\sqrt{t})}{(d-a)(d-b)(d-c)}\right] . \tag{2.13}$$

The function $\operatorname{erfc}(z)$ is the complementary error function as defined in [35]. The (complex) coefficients a, b, c, and d can be obtained by writing the denominator in the expression of $\tilde{A}(s)$ [or $\tilde{B}(s)$] in the following form:

$$Ms^2 + zs\sqrt{s} + \zeta s + K = M(\sqrt{s}+a)(\sqrt{s}+b)(\sqrt{s}+c)(\sqrt{s}+d) . \tag{2.14}$$

We assume for the moment that the coefficients a, b, c, and d all differ from each other. If two or more coefficients are equal there are two ways to proceed. We can come to an expression for the velocity autocorrelation function, in that special case, by taking the appropriate limits in Eqs. (2.12) and (2.13). We may also rederive Eqs. (2.12) and (2.13) by studying the Laplace inverse of the function $\tilde{A}(s) = sM^{-1}[(\sqrt{s}+a)^2(\sqrt{s}+c)(\sqrt{s}+d)]^{-1}$, where we have assumed that $a=b$. Other combinations of equal coefficients may be studied in the same way.

We are interested in the stationary part of Eq. (2.11), which can be obtained by studying the limit $t_1\to\infty$, $t_2\to\infty$, but $t_2-t_1\equiv\tau\geq 0$ remains finite. We can conclude from Eqs. (2.12) and (2.13) that both $A(t)\to 0$ and $B(t)\to 0$ if $t\to\infty$ by considering its asymptotic expansion via

$$\exp(a^2t)\operatorname{erfc}(a\sqrt{t}) \simeq \frac{1}{a\sqrt{\pi}\sqrt{t}} - \frac{1}{2\sqrt{\pi}a^3t\sqrt{t}} + \frac{3}{4\sqrt{\pi}a^5t^2\sqrt{t}} - \frac{15}{8\sqrt{\pi}a^7t^3\sqrt{t}} + O\left[\frac{1}{t^4\sqrt{t}}\right] , \quad |a^2|t\gg 1 . \tag{2.15}$$

It should be noted that the coefficient a in Eq. (2.15) can be complex. Finally we obtain

$$\langle U(t_1)U(t_1+\tau)\rangle^{\infty} \equiv \phi(\tau) = k_B T A(\tau) , \tag{2.16}$$

where $\langle\ \rangle^{\infty}$ denotes the long-time limit described above. We are now interested in the long-time behavior of this expression. Replacement of the complementary error functions in our expression of $A(\tau)$ by the asymptotic expansion (2.15) gives

$$\phi(\tau) \simeq k_B T\frac{15z}{8K^2\sqrt{\pi}}\frac{1}{\tau^3\sqrt{\tau}} + O\left[\frac{1}{\tau^4\sqrt{\tau}}\right] , \quad |a^2|\tau\gg 1 \text{ etc} . \tag{2.17}$$

In the derivation of this asymptotic expansion we have used the following relations between the coefficients a to d, which we shall not demonstrate here:

$$\frac{a^n}{(a-b)(a-c)(a-d)} + \frac{b^n}{(b-a)(b-c)(b-d)} + \frac{c^n}{(c-a)(c-b)(c-d)} + \frac{d^n}{(d-a)(d-b)(d-c)} = 0 , \quad n\in\{-2,0,2\} \tag{2.18}$$

and

$$\frac{a^{-4}}{(a-b)(a-c)(a-d)}+\frac{b^{-4}}{(b-a)(b-c)(b-d)}+\frac{c^{-4}}{(c-a)(c-b)(c-d)}+\frac{d^{-4}}{(d-a)(d-b)(d-c)}=-\frac{zM}{K^2}\ . \tag{2.19}$$

Instead of an exponentially decaying velocity autocorrelation function we have obtained again a long-time tail, although this tail has a lower power in $1/\sqrt{\tau}$ in comparison to the free particle case, viz., $\tau^{-7/2}$ vs $\tau^{-3/2}$ [see Eq. (1.10)], respectively. On top of that this long-time tail has a positive sign. In the Stokes limit the velocity autocorrelation function has the following form:

$$\phi(\tau)=\frac{k_BT}{m}\left[\frac{\beta\exp(-\beta\tau)-\alpha\exp(-\alpha\tau)}{\beta-\alpha}\right], \tag{2.20}$$

with

$$\alpha=\frac{\zeta}{m}-\left[\left(\frac{\zeta}{m}\right)^2-4\frac{K}{m}\right]^{1/2},$$

$$\beta=\frac{\zeta}{m}+\left[\left(\frac{\zeta}{m}\right)^2-4\frac{K}{m}\right]^{1/2}.$$

We see that, in the overdamped case ($\zeta\gg\sqrt{Km}$), this equation has a negative exponentially decaying tail. In the strongly overdamped case two separate time scales can be distinguished. On the smaller the particle does not feel the harmonic force and the behavior of the velocity autocorrelation function is comparable to the free-particle case, including the existence of the $\tau^{-3/2}$ long-time tail. Then, at intermediate times, it can be shown by numerical means that Eq. (2.16) also has a negative part before the positive $\tau^{-7/2}$ tail becomes dominant.

A Brownian particle in a colloidal crystal can be described by the overdamped case discussed above. We use some data of Derksen (Ref. [36], pp. 40,44). Consider a colloidal crystal in water built up of polystyrene spheres, with radii $a\approx5\times10^{-8}$ m, with charge $Q\approx10^{-16}C$, with a lattice parameter $R\approx9\times10^{-7}$ m, and suppose the particle is displaced by an amount $\Delta\ll R$; then the potential energy changes by

$$\psi(R+\Delta)+\psi(R-\Delta)-2\psi(R)\cong\Delta^2\frac{d^2\psi(R)}{dR^2}=\tfrac{1}{2}K\Delta^2\ , \tag{2.21}$$

where we have assumed nearest-neighbor interactions only. $\psi(R)$ is the screened Coulomb potential,

$$\psi(R)=\frac{Q^2\exp(-\kappa R)}{4\pi\epsilon R}\ , \tag{2.22}$$

where the screening arises from the counterions in the ambient fluid. It follows that

$$K=2\frac{d^2\psi(R)}{dR^2}=\frac{Q^2\exp(-\kappa R)}{\pi\epsilon R^3}(1+\kappa R+\tfrac{1}{2}\kappa^2R^2)\ . \tag{2.23}$$

In the experiment of Derksen: $\kappa R\approx3$. Furthermore $\epsilon=\epsilon_0\epsilon_r\approx7\times10^{-10}$ ($\epsilon_r\approx80$) the dielectric constant of water. The shear viscosity of water is $\eta_0\approx10^{-3}$ Pa s. In this case $\zeta\approx10^{-9}$ N s m^{-1} and $\sqrt{Km}\approx10^{-12}$ N s m^{-1}. Later we shall show that there exists a maximum value for Δ, and with the data presented above $\Delta_{\max}\ll R$.

The position autocorrelation function can be determined in the same way. The final expression is

$$\langle\tilde{x}(s)\tilde{x}(x')\rangle=k_BT\left[\frac{\tilde{C}(s')}{s}+\frac{\tilde{C}(s)}{s'}-\frac{\tilde{C}(s)+\tilde{C}(s')}{s+s'}-M\tilde{B}(s)\tilde{B}(s')-K\tilde{C}(s)\tilde{C}(s')\right], \tag{2.24}$$

where $\tilde{C}(s)=\tilde{B}(s)/s$. The asymptotic part of the mean-square displacement is

$$\langle[x(t_1+\tau)-x(t_1)]^2\rangle^{\infty}\equiv\Psi(\tau)=2k_BTC(\tau)\ , \tag{2.25}$$

with

$$C(\tau)=\frac{1}{K}+\frac{1}{M}\left[\frac{\exp(a^2\tau)\operatorname{erfc}(a\sqrt{\tau})}{a(a-b)(a-c)(a-d)}+\frac{\exp(b^2\tau)\operatorname{erfc}(b\sqrt{\tau})}{b(b-a)(b-c)(b-d)}+\frac{\exp(c^2\tau)\operatorname{erfc}(c\sqrt{\tau})}{c(c-a)(c-b)(c-d)}+\frac{\exp(d^2\tau)\operatorname{erfc}(d\sqrt{\tau})}{d(d-a)(d-b)(d-c)}\right]. \tag{2.26}$$

Using the asymptotic expansion of Eq. (2.26) we obtain

$$\lim_{\tau\to\infty}\psi(\tau)=2D_0\frac{\zeta}{K}\ , \tag{2.27}$$

which is the same result as that obtained in the Stokes limit [9,11]. At this point we can make a remark about the validity of Eqs. (2.21) and (2.23). With the data of Derksen [36] we obtain at room temperature $\Delta_{\max}\approx\sqrt{2D_0\zeta/K}\cong5\times10^{-8}\ll R$. From Eq. (2.27) we may conclude that a diffusion coefficient cannot be defined, although in case of $\zeta\gg\sqrt{Km}$ a diffusional regime exists. As mentioned before we can distinguish two time scales. On the smaller the mean-square displacement of the Brownian particle behaves like the one of the free Brownian particle and diffusionlike behavior can be expected. The characteristic time of this scale in the experiment of Derksen is $m/\zeta\cong6\times10^{-10}$ s. At the larger time scale the effects of the harmonic potential become dominant and the mean-square displacement tends to a constant value. In the overdamped case, using data of Derksen [36], the characteristic time of this behavior is $\zeta/K\cong3\times10^{-4}$ s. These time scales have been discussed

already in the context of the velocity autocorrelation function. In the Stokes limit diffusive behavior can be shown over several decades of the Brownian time $\tau_B=(6\pi\eta_0 a/m)t$ if $\zeta/\sqrt{Km}\geq 100$. This diffusive behavior is shown by the expression $\psi(\tau)\approx 2D_0\tau$ for large τ, but τ small enough so that the correlation functions are not influenced by the harmonic potential. However, if we include backflow effects the system does not reach the diffusional regime unless $\zeta/\sqrt{Km}\geq 10^6$. In the colloidal crystal described above a diffusional regime cannot be expected because $\zeta/\sqrt{Km}\approx 10^3$, in contrast with the conclusions drawn if the quasistatic (Stokes) approach is used.

A third time scale is that of hydrodynamic interactions (which are neglected throughout this paper). A characteristic time scale may be defined as the time of propagation of the flow field to a neighboring particle and back. This time is, in the experiment of Derksen, of the order $(2R)^2/\nu\cong 3\times 10^{-6}$ s (ν is the kinematic viscosity). It is in between the characteristic times mentioned earlier. Therefore the domain of diffusionlike behavior can hardly be influenced by hydrodynamic interactions; at most it can be expected that a slight modification of the long-time behavior of the velocity autocorrelation function will occur, but this will not change the general conclusions drawn above concerning the velocity correlation function and the mean-square displacement in this specific case where we apply a one-particle result to a system with a finite, but small, concentration of Brownian particles. Furthermore, the influence of hydrodynamic interactions in the regime of dominant harmonic potential can be described approximately by quasistatic theory. In the experiment of Derksen the volume fraction is of the order $\varphi\cong 10^{-3}$. Hydrodynamic interactions are therefore not expected to be very important, although it should be emphasized that in highly ordered systems, such as colloidal crystals, hydrodynamic interactions are more important than in random suspensions.

III. A BROWNIAN PARTICLE IN SHEAR FLOW

We consider a Brownian particle in a shear flow. Suppose this shear flow, denoted by $\mathbf{U}_0$, is in the x direction with a velocity gradient in the z direction,

$$\mathbf{U}_0=(\lambda z,0,0)\ , \tag{3.1}$$

with λ the velocity gradient. We assume that λ is very small. The total fluid velocity field, composed of the shear flow and the fluid motion induced by the small Brownian particle, will then satisfy the linear Navier-Stokes equations. We do not consider rotational motion. San Miguel and Sancho solved this problem in the Stokes limit [37]. They showed the following long-time behavior of the position auto- and cross-correlation functions, respectively:

$$\langle x^2(t)\rangle\simeq\tfrac{2}{3}D_0\lambda^2t^3,\quad \langle y^2(t)\rangle=\langle z^2(t)\rangle=2D_0t\ , \tag{3.2}$$

$$\langle x(t)z(t)\rangle\simeq D_0\lambda t^2\ . \tag{3.3}$$

We see that the mean-square displacement is proportional to t^3, assuming that at $t=0$ the particle is in the origin. Consequently there is no diffusional behavior in the x direction any longer. As can be expected isotropy has disappeared. This behavior can be understood as follows: the rms displacement Δz is proportional to $\sqrt{t}$, which results in rms displacement in the x direction proportional to $\lambda t\Delta z\simeq\lambda t\sqrt{t}$. The mean-square displacement in the x direction is then proportional to λ^2t^3. Derksen has presented some results of experiments to measure this behavior [36]. Bedeaux, Rubi, and Pérez-Madrid have studied a similar problem including the nonlinear term in the Navier-Stokes equations [38–40]. First they determined the friction tensor belonging to a spherical particle in a fluid with elongational flow. This friction tensor is modified by terms related to the rate of elongation. Consequently this modified friction tensor leads, via the fluctuation-dissipation theorem, to a modified version of the random force autocorrelation function. They have calculated the velocity correlation function and the mean-square displacement of a Brownian particle in elongational flow [39], but in the diffusional regime only. They have not presented results for the convective regime. This section aims at the determination of these functions in the convective regime for simple shear flow, but under such conditions that we can linearize the Navier-Stokes equations. This is possible because we linearize these equations in the perturbation of the fluid velocity, caused by the moving particle, and furthermore we see that $(\mathbf{U}_0\cdot\nabla)\mathbf{U}_0=\mathbf{0}$ [Eq. (3.1)]. Consequently the friction tensor remains unchanged [38].

We now present the results of a study of this problem, where we have used a Stokes-Boussinesq-like equation of motion. Using the generalized Faxén theorem, derived by Bedeaux and Mazur [32], we can derive the following equation of motion of a Brownian particle in shear flow:

$$\begin{aligned}M\dot{U}_x(t)=&-6\pi\eta_0aU_x(t)-6a^2\sqrt{\pi\rho\eta_0}\int_0^t\frac{1}{\sqrt{t-\tau}}\dot{U}_x(\tau)d\tau\\&+\lambda\left[6\pi\eta_0az(t)\right.\\&\quad+6a^2\sqrt{\pi\rho\eta_0}\int_0^t\frac{1}{\sqrt{t-\tau}}U_z(\tau)d\tau\\&\quad\left.+\tfrac{3}{2}m_0U_z(t)\right]+R_x(t)\ ,\end{aligned} \tag{3.4}$$

$$\begin{aligned}M\dot{U}_z(t)=&-6\pi\eta_0aU_z(t)\\&-6a^2\sqrt{\pi\rho\eta_0}\int_0^t\frac{1}{\sqrt{t-\tau}}\dot{U}_z(\tau)d\tau+R_z(t)\ .\end{aligned} \tag{3.5}$$

In the y direction the problem can be described by using the results of the free Brownian particle. We assume that $\mathbf{U}(t)=\mathbf{0}$ if $t\leq 0$. We present the results for the mean-square displacement only. To obtain that quantity we solve this set of equations by studying the Laplace transforms of both equations, which are

$$\tilde{x}(s)=\tilde{B}(s)\tilde{D}(s)\tilde{z}(s)+\tilde{B}(s)\tilde{R}_x(s)\ , \tag{3.6}$$

$$\tilde{z}(s)=\tilde{B}(s)\tilde{R}_z(s)\ , \tag{3.7}$$

where

$$\tilde{B}(s)=\frac{1}{s(Ms+z\sqrt{s}+\zeta)}, \quad \tilde{D}(s)=\lambda(\zeta+z\sqrt{s}+\tfrac{3}{2}m_0 s) . \tag{3.8}$$

Substitution of Eq. (3.7) for $\tilde{z}(s)$ in Eq. (3.6) gives

$$\tilde{x}(s)=\tilde{B}^2(s)\tilde{D}(s)\tilde{R}_z(s)+\tilde{B}(s)\tilde{R}_x(s) . \tag{3.9}$$

The position autocorrelation function $\langle\tilde{x}(s)\tilde{x}(s')\rangle$ now becomes

$$\langle\tilde{x}(s)\tilde{x}(s')\rangle=\langle\tilde{x}(s)\tilde{x}(s')\rangle_\lambda + \tilde{B}(s)\tilde{B}(s')\langle\tilde{R}_x(s)\tilde{R}_x(s')\rangle , \tag{3.10}$$

where the last part of this equation is again a contribution already known from the study of the free Brownian particle. The term $\langle\tilde{x}(s)\tilde{x}(s')\rangle_\lambda$ is the pure shear contribution and has the form

$$\langle\tilde{x}(s)\tilde{x}(s')\rangle_\lambda=\tilde{B}_\lambda(s)\tilde{B}_\lambda(s')\langle\tilde{R}_z(s)\tilde{R}_z(s')\rangle , \tag{3.11}$$

with $\tilde{B}_\lambda(s)=\tilde{B}^2(s)\tilde{D}(s)$. Only this term will be studied. In the derivation of Eq. (3.10) we have used the property of the random forces that cross correlations are zero [32]. Furthermore, the following position cross-correlation function can be determined:

$$\langle\tilde{x}(s)\tilde{z}(s')\rangle=\langle\tilde{x}(s)\tilde{z}(s')\rangle_\lambda =\tilde{B}_\lambda(s)\tilde{B}(s')\langle\tilde{R}_z(s)\tilde{R}_z(s')\rangle . \tag{3.12}$$

We know [see Sec. II, Eq. (2.8)] that

$$\langle\tilde{R}_z(s)\tilde{R}_z(s')\rangle=\frac{\tilde{\theta}(s)+\tilde{\theta}(s')}{s+s'} . \tag{3.13}$$

Furthermore, we can derive

$$\tilde{B}_\lambda(s)\tilde{\theta}(s)=k_BT[\tilde{C}_\lambda(s)-Ms\tilde{B}_\lambda(s)] , \quad \tilde{C}_\lambda(s)=\tilde{B}(s)\tilde{D}(s)/s . \tag{3.14}$$

With both results we come to the following relation describing the shear flow depending part of the Laplace transform of the position autocorrelation function:

$$\langle\tilde{x}(s)\tilde{x}(s')\rangle_\lambda=k_BT\left[\frac{\tilde{B}_\lambda(s)\tilde{C}_\lambda(s')+\tilde{B}_\lambda(s')\tilde{C}_\lambda(s)}{s+s'} -M\tilde{B}_\lambda(s)\tilde{B}_\lambda(s')\right] . \tag{3.15}$$

To derive the inverse Laplace transform we refer again to the review article of Fox (Ref. [33], p. 195). In line with the derivation shown there to calculate a double Laplace transform we obtain

$$\int_0^\infty dt_1\int_0^\infty dt_2\exp(-st_1)\exp(-s't_2)\int_0^{t_2}d\tau_2\int_0^{t_1}d\tau_1 f(t_1-\tau_1)g(t_2-\tau_2)\delta(|\tau_2-\tau_1|) =\int_0^\infty dt_2\int_0^\infty dt_1\exp(-st_1)\exp(-s't_2)\int_0^{t_1}f(t)g(t+\tau)dt=\frac{\tilde{f}(s)\tilde{g}(s')}{s+s'} , \tag{3.16}$$

where we assume that $\tau=t_2-t_1\geq 0$. The function $\delta(t)$ is the Dirac δ function. The inverse Laplace transform of Eq. (3.15) is now

$$\langle x(t_1)x(t_2)\rangle_\lambda=k_BT\left[\int_0^{t_1}B_\lambda(t)C_\lambda(t+\tau)dt + \int_0^{t_1}B_\lambda(t+\tau)C_\lambda(t)dt -MB_\lambda(t_1)B_\lambda(t_2)\right] . \tag{3.17}$$

In an analogous way the Laplace transform of the position cross-correlation function becomes

$$\langle\tilde{x}(s)\tilde{z}(s')\rangle_\lambda=k_BT\left[\frac{[\tilde{B}_\lambda(s)/s']+\tilde{C}_\lambda(s)\tilde{B}(s')}{s+s'} -M\tilde{B}_\lambda(s)\tilde{B}(s')\right] . \tag{3.18}$$

Finally Laplace inversion gives

$$\langle x(t_1)z(t_2)\rangle_\lambda=k_BT\left[\int_0^{t_1}B_\lambda(t)dt+\int_0^{t_1}B(t+\tau)C_\lambda(t)dt -MB_\lambda(t_1)B(t_2)\right] . \tag{3.19}$$

We have now derived some formal expressions for the position auto- and cross-correlation functions, but must evaluate the functions $B(t)$, $B_\lambda(t)$, and $C_\lambda(t)$. We confine ourselves to an outline of these derivations only. They can be obtained with the help of tables of Laplace transforms [34]. We know [Eq. (3.8)]

$$\tilde{B}(s)=\frac{1}{s(Ms+z\sqrt{s}+\zeta)} . \tag{3.20}$$

The inverse Laplace transform of $\tilde{B}(s)$ is

$$B(t)=\frac{1}{\zeta}\left[1+\frac{1}{(b-a)}[a\exp(b^2t)\operatorname{erfc}(b\sqrt{t}) -b\exp(a^2t)\operatorname{erfc}(a\sqrt{t})]\right] , \tag{3.21}$$

with a and b defined below Eq. (1.8). For the moment we

assume that $a \neq b$. The function $\tilde{B}_\lambda(s)$ is defined as

$$\tilde{B}_\lambda(s)=\tilde{B}^2(s)\tilde{D}(s)=\lambda\{[\tilde{B}(s)/s]+(m_0-m)s\tilde{B}^2(s)\} . \tag{3.22}$$

Laplace inversion of the first part of Eq. (3.22) gives, via $\tilde{B}(s)/s=\tilde{C}(s)$, the function $C(t)$,

$$C(t)=\frac{1}{\zeta}\left[t-\frac{2z}{\zeta\sqrt{\pi}}\sqrt{t}+\frac{(z^2-\zeta M)}{\zeta^2}+\frac{\zeta}{M(b-a)}[b^{-3}\exp(b^2t)\operatorname{erfc}(b\sqrt{t})-a^{-3}\exp(a^2t)\operatorname{erfc}(a\sqrt{t})]\right] . \tag{3.23}$$

The Laplace inverse of the second part of Eq. (3.22) can be obtained using the convolution theorem. The final result is

$$B_\lambda(t)=\lambda\left[C(t)+(m_0-m)\int_0^t\frac{dB(\tau)}{d\tau}B(t-\tau)d\tau\right] . \tag{3.24}$$

The function $\tilde{C}_\lambda(s)$ is defined as

$$\tilde{C}_\lambda(s)=\tilde{B}(s)\tilde{D}(s)/s=\frac{\lambda}{s^2}+\lambda(m_0-m)\tilde{B}(s) , \tag{3.25}$$

and the inverse Laplace transform is

$$C_\lambda(t)=\lambda[t+(m_0-m)B(t)] . \tag{3.26}$$

The position correlation functions can now be determined and the final results evaluated both analytically and numerically, but we restrict ourselves to the long-time behavior of these correlation functions. If $t_1=t_2=t$ we have

$$\langle x^2(t)\rangle_\lambda=k_BT\left[2\int_0^tB_\lambda(\tau)C_\lambda(\tau)d\tau-MB_\lambda^2(t)\right] \tag{3.27}$$

and

$$\langle x(t)z(t)\rangle_\lambda=k_BT\left[\int_0^tB_\lambda(\tau)d\tau+\int_0^tB(\tau)C_\lambda(\tau)d\tau-MB_\lambda(t)B(t)\right] . \tag{3.28}$$

In the long-time limit there is no need to evaluate the functions $B(t)$, $B_\lambda(t)$, and $C_\lambda(t)$ in detail. These functions can be rewritten as follows:

$$B(t)=\frac{1}{\zeta}-\frac{z}{\zeta^2\sqrt{\pi}}\frac{1}{\sqrt{t}}+B_1(t) , \tag{3.29}$$

$$B_\lambda(t)=\lambda\frac{t}{\zeta}\left[1-\frac{2z}{\zeta\sqrt{\pi}}\frac{1}{\sqrt{t}}+\frac{1}{\zeta^2}[z^2-M\zeta+(m_0-m)\zeta]\frac{1}{t}+B_2(t)\right] , \tag{3.30}$$

$$C_\lambda(t)=\lambda\frac{t}{\zeta}\left[\zeta+(m_0-m)\frac{1}{t}+C_1(t)\right] . \tag{3.31}$$

The long-time behavior is given by asymptotic expansions of $B_1(t)$, $B_2(t)$, and $C_1(t)$. The leading terms of these functions are $O(t^{-3/2})$. Substitution of these expressions for the functions $B(t)$, $B_\lambda(t)$, and $C_\lambda(t)$ in the Eqs. (3.27) and (3.28), respectively, gives the following expressions:

$$\langle x^2(t)\rangle_\lambda=\tfrac{2}{3}D_0\lambda^2t^3\left[1-\frac{12z}{5\zeta\sqrt{\pi}}\frac{1}{\sqrt{t}}+\frac{3}{2\zeta^2}[z^2-2M\zeta+2(m_0-m)\zeta]\frac{1}{t}+O\left[\frac{1}{t\sqrt{t}}\right]\right] , \tag{3.32}$$

$$\langle x(t)z(t)\rangle_\lambda=D_0\lambda t^2\left[1-\frac{2z}{\zeta\sqrt{\pi}}\frac{1}{\sqrt{t}}+\frac{1}{\zeta^2}[z^2-2M\zeta+2(m_0-m)\zeta]\frac{1}{t}+O\left[\frac{1}{t\sqrt{t}}\right]\right] . \tag{3.33}$$

These results can be compared with the expressions obtained by San Miguel and Sancho [37], which are the expressions above in the Stokes limit,

$$\langle x^2(t)\rangle_\lambda=\tfrac{2}{3}D_0\lambda^2t^3\left[1-\frac{6m}{\zeta}\frac{1}{t}+O(t^{-2})\right] , \tag{3.34}$$

$$\langle x(t)z(t)\rangle_\lambda=D_0\lambda t^2\left[1-\frac{4m}{\zeta}\frac{1}{t}+O(t^{-2})\right] . \tag{3.35}$$

These relations can also be obtained by taking the limits $m_0\to 0$ and $z\to 0$ in Eqs. (3.32) and (3.33). It is clear that no diffusional regime on these time scales exists. Furthermore, we can estimate the value of τ_B for which the expressions of $\langle x^2(t)\rangle_\lambda$ become nearly cubic in time. In the Stokes limit this will take place if $\tau_B\approx O(10^4)$, but by including backflow effects we reach this point if $\tau_B\approx O(10^7)$. Finally we want to point out that the term proportional to t^2 in Eq. (3.32) [or the term proportional to t in Eq. (3.33)] disappears if $\sigma=\frac{11}{8}$, with $\sigma=\rho_B/\rho$ the ratio between the density of the Brownian particle and the fluid density, in contrast with the results obtained by San Miguel and Sancho [Eqs. (3.34) and (3.35)].

It is also possible to study a combination of both situations described in Secs. II and III, a Brownian particle in a harmonic potential and in shear flow. In the Stokes limit some results are available, obtained by van den Broeck, Sancho, and San Miguel [41]. With the methods presented in this section it is possible to include backflow effects in such a problem. However, we refrain from such calculation because of the disproportion between the mathematical complexity and the modesty of insights gained.

IV. CONCLUSION

We have been able to extend the theory of Brownian motion, including backflow effects, to the case of a Brownian particle in a harmonic potential and of a Brownian particle in an externally imposed shear flow. A significant point is that these two problems can be studied by using the same mathematical tools as used for the free-Brownian-particle problem. These tools are also useful for the study of a Brownian particle in a combined shear flow and harmonic potential, although we have not demonstrated this explicitly. An important conclusion from this chapter is that the mean-square displacement, determined with the Stokes-Boussinesq equation of motion, differs considerably from the same function obtained in the Stokes limit, up to large values of the dimensionless time τ_B. We have seen that a Brownian particle in a harmonic potential, described in Sec. II, cannot reach the diffusive regime, while in the Stokes limit this diffusive regime is reached in otherwise comparable circumstances. We can also see that the velocity autocorrelation function of a particle in a harmonic potential shows long-time-tail behavior, although the algebraic power of this tail is lower in comparison to the free-particle case, viz., $t^{-7/2}$ vs $t^{-3/2}$. In the case of shear flow the leading asymptotic terms of the mean-square displacement functions are the same as in the Stokes limit. Other terms are quite different, however. Even more significant is the fact that the relaxation time in which the asymptotic regime is reached is much larger if backflow effects are taken into account.

In this chapter we have neglected hydrodynamic interactions. These become important only if the volume fraction of dispersed Brownian particles becomes large. In a previous article we have presented results of a study of the influence of retarded hydrodynamic interactions on transport coefficients of suspensions [42].

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