Faxén's theorem for nonsteady motion of a sphere through a compressible linear viscoelastic fluid in arbitrary flow

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(Received 5 August 2012; published 5 March 2013)

A generalization of the Faxén's theorem to the nonsteady motion of a sphere through a compressible linear viscoelastic fluid in arbitrary flow is presented. From this result, expressions for the velocity autocorrelation function (VAF) and the time-dependent diffusion coefficient of the particle can be obtained. We analyze the behavior of the VAF and the time-dependent diffusion coefficient for different physical regimes of the suspending fluid. The relevance of the theorem to microrheology is discussed.

DOI: 10.1103/PhysRevE.87.032301 PACS number(s): 46.35.+z, 66.20.Cy

I. INTRODUCTION

The velocity autocorrelation function (VAF) of a Brownian particle in a highly viscous fluid probes time scales for which compressibility effects are important. To have an estimate of these effects, consider the different time scales that appear when a small spherical particle of radius a is immersed in a fluid. There is a sonic time scale $t_c = a/c$, which is the time a sound wave of speed c takes to travel a distance equal to the particle's radius. A second characteristic time scale is a viscous one, $t_\nu = a^2/\nu$, which is the time that a shear wave takes to diffuse over the same particle's radius, where ν is the kinematic viscosity of the fluid. For a particle of radius $a = 1\ \mu$m suspended in water, typically $t_c \sim 10^{-9}$ s and $t_\nu \sim 10^{-6}$ s, and these two time scales are well separated, meaning that on the time scales in which the velocity decays (around t_ν) the fluid behaves in all respects as incompressible ($c \to \infty$). For the same particle suspended in glycerol, however, these time scales are comparable: $t_c \sim 10^{-9}$ s and $t_\nu \sim 10^{-9}$ s. That is, for highly viscous fluids, the vorticity diffuses very rapidly (on time scales comparable to the sound traversal time) and compressibility becomes important. Note that the ratio of these time scales gives the dimensionless number ac/ν which is also the ratio between the length scale of the particle a and a fluid length scale $\lambda_{\nu c} = \nu/c$. We expect compressible effects to become important as the size of the particle is reduced. For water, this length scale is very small $\lambda_{\nu c} = 6.6 \times 10^{-10}$ m, but for glycerol it takes the value $\lambda_{\nu c} = 6.2 \times 10^{-7}$ m. This implies that for glycerol, compressibility is important already for micron-sized particles, while for water it becomes important for nanoscopic particles.

In addition, all fluids behave viscoelastically at sufficiently short time scales because molecular relaxation is not instantaneous. For example, glycerol behaves viscoelastically with a Maxwell relaxation time $\tau = 0.6 \times 10^{-9}$ s [1], which is comparable to the previous two times discussed above. Therefore, we expect that in order to describe the velocity autocorrelation function of a micron-sized particle in glycerol, one needs to take into account both viscoelasticity and compressibility. Viscoelasticity becomes important also for nanoscopic particles in water or any simple liquid, a fact that was already appreciated in the pioneering work of Zwanzig and Bixon [2] [see [3] for the correction of a small error in their work]. For micron-sized particles in water, elastic relaxation is so fast compared to the time scale of the velocity decay that the fluid can be safely assumed to be Newtonian. On the other hand, in the case of a Brownian particle suspended in a wormlike micellar system, for example, a fluid known to behave as a viscoelastic Maxwell fluid with a single relaxation mode [4], typical time scales are $t_c = 10^{-9}$ s, $t_\nu = 10^{-9}$ s, $\tau = 10^{-2}$ s [5]. In this case, we have that sound and viscous times are comparable and well separated from the viscoelastic relaxation time. This situation can occur in several polymeric fluids (generally characterized by large elastic relaxation times) for sufficiently small probe particles. For low viscosity wormlike micellar systems, we may readily reach regimes in which we have the three time scales well separated, i.e., $t_c \ll t_\nu \ll \tau$. It is therefore apparent that, depending on the type of solvent and the size of the suspended particle, a large variety of cases might exist in which the different processes can interplay. The analysis of particle diffusion on such small time scales is not a purely academic problem, but thanks to recent improvements in the experimental capabilities, sub-Å spatial precision at nanosecond time frames in the detection of a particle trajectory is becoming accessible [6,7].

The understanding of the behavior of the velocity autocorrelation function of a colloidal particle in a fluid has a long history and is still a fascinating lively topic [6–11]. The usual approach is to consider the time- (or frequency-) dependent force acting on a sphere due to the surrounding fluid. This force is proportional to the velocity of the particle with a frequency-dependent friction coefficient. From the knowledge of the friction coefficient, one can directly infer the behavior of the velocity autocorrelation function. The force on a sphere in an *incompressible Newtonian* fluid can be computed by solving the linearized equations of hydrodynamics around the sphere and integrating the stress tensor [12]. An equivalent elegant alternative is to use the method of induced forces introduced by Mazur and Bedeaux [13]. Bedeaux and Mazur also have solved the problem of computing the memory friction of a Brownian particle suspended in a *compressible Newtonian* fluid [14]. This is done in the form of a generalization of Faxén's theorem that allows one to relate the force on the sphere with the unperturbed arbitrary flow of the fluid. The effects of harmonic trapping on the VAF of a particle in a compressible fluid have been addressed

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in Ref. [15]. On the other hand, Grimm *et al.* [16] have considered the VAF of an *incompressible viscoelastic* fluid of the Maxwell type. To the authors' knowledge, there are no results for the force on a sphere immersed in a *compressible non-Newtonian* fluid, nor of the corresponding VAF. The formulation of Faxén's theorem for a compressible linear viscoelastic fluid represents an extension of Stokes' theorem in the sense that it provides not only the force on a quiescent fluid (and hence the memory friction which is relevant for passive microrheology experiments), but also the force on *arbitrary flows* of the solvent surrounding the particle which can be important under specifically designed active microrheology experiments.

The behavior of the VAF and its corresponding time integral that gives the time-dependent diffusion coefficient in a viscoelastic fluid represents a crucial issue in *passive microrheology* experiments [17]. In these experiments, the video tracking of the position of a diffusing Brownian particle is used in order to infer the viscoelastic properties of the media. Many new techniques have appeared for the study of such fluids involving embedded colloidal particles, such as one-particle [18–21], two-particle [22–24], and many-particle microrheology [25,26] as well as optical tweezers [27,28]. The extraction of the viscoelastic properties from the diffusion of the particles is done through a generalized Stokes-Einstein relation (GSER), which is a heuristic approximate expression relating the particle mean square displacement with the complex modulus of the suspending fluid. The limits of validity of the GSER have been thoroughly discussed in Ref. [17]. In particular, inertia of both probe particle and medium are neglected in the GSER so that the standard microrheology is inaccurate at high frequency where inertia is important. For incompressible fluids, it has been recently shown [29] that the contributions to inertia in one-particle passive microrheological analysis can be properly taken into account. In other words, it is not necessary to use the approximate GSER and one can use (1) the direct connection of the velocity autocorrelation function with the friction memory in the (exact) generalized Langevin equation of the Brownian particle, and (2) the direct connection of the friction memory with the force exerted by a viscoelastic incompressible fluid on a sphere. In this way, it is possible to obtain the viscoelastic modulus as a function of the mean square displacement, without further approximations beyond the assumed incompressibility and linear viscoelastic behavior, permitting us to extend the range of frequencies available to quantitative microrheology [29]. As the range of frequencies available experimentally is increased, it seems relevant to address what the effects of compressibility are in the VAF of particles suspended in viscoelastic fluids.

The outline of the paper is the following: In Sec. II, Faxén's theorem is generalized to the case of a compressible viscoelastic fluid with inertia, and an explicit form of the friction memory is evaluated. In Sec. III, the velocity autocorrelation function (VAF) based on the viscoelastic friction memory is calculated for a particular linear viscoelastic model, the Oldroyd-B model, and its behavior under different fluid regimes investigated. We end up with some comments on the use of the results of this paper for passive microrheology.

II. FAXÉN'S THEOREM

We consider a macroscopic sphere of radius a immersed in a linear viscoelastic compressible fluid. The effects of heat conductivity are neglected and the fluid is isothermal. The linearized conservation equations for the mass and momentum densities of a viscoelastic fluid are given by

$$\begin{aligned} \frac{\partial}{\partial t}\delta\rho(\mathbf{r},t) &= -\rho^{\mathrm{eq}}\nabla\cdot\delta\boldsymbol{v}(\mathbf{r},t), \quad |\mathbf{r}|>a \\ \rho^{\mathrm{eq}}\frac{\partial}{\partial t}\delta\boldsymbol{v}(\mathbf{r},t) &= -\nabla\cdot\boldsymbol{P}(\mathbf{r},t)+\boldsymbol{F}_{\mathrm{ext}}(\mathbf{r},t), \quad |\mathbf{r}|>a \end{aligned} \tag{1}$$

with usual stick boundary conditions on the surface. Here, $\delta\rho,\delta\mathbf{v}$ are the perturbations with respect to equilibrium of the hydrodynamic fields, $\boldsymbol{F}_{\mathrm{ext}}(\mathbf{r},t)$ is an external body force acting on the fluid, and $\boldsymbol{P}(\mathbf{r},t)$ is the pressure tensor which is linear with respect to the velocity gradient. The pressure tensor for a compressible linear viscoelastic fluid is assumed to be of the form

$$\begin{aligned} \boldsymbol{P}(\mathbf{r},t) = p\mathbf{1} &- \int_{-\infty}^{t} S(t-t')\nabla\cdot\delta\boldsymbol{v}(\mathbf{r},t')dt'\mathbf{1} \\ &- \int_{-\infty}^{t} G(t-t')\{\nabla\delta\boldsymbol{v}(\mathbf{r},t')+[\nabla\delta\boldsymbol{v}(\mathbf{r},t')]^{T}\}dt', \end{aligned} \tag{2}$$

where p is the hydrostatic pressure which is given as a function of the density of the fluid in terms of the equation of state

$$\nabla p(\mathbf{r},t) = c_0^2\nabla\rho(\mathbf{r},t), \tag{3}$$

where $c_0=\sqrt{dp/d\rho}$ is the total speed of sound of the fluid, obtained from a total pressure p made by a solvent pressure contribution p_s and a usual osmotic polymeric correction p_0, generally small in dilute polymer solutions. The memory functions $G(t-t')$ and $S(t-t')$ define the compressible viscoelastic response. For a Newtonian fluid, these memory functions are extremely short ranged in time and can be modeled as proportional to Dirac delta functions

$$G(t-t')=\eta\delta(t-t'), \quad S(t-t')=\left(\eta_v-\tfrac{2}{3}\eta\right)\delta(t-t'), \tag{4}$$

where η and η_v are the shear and bulk viscosities, respectively. Therefore, the memory functions generalize shear and bulk viscosities in the viscoelastic realm. For a dilute polymer solution, aside from the Newtonian contribution, there exists a polymer contribution which is proportional to the polymer concentration [see for example, the Oldroyd-B model in Eq. (26)]. Obviously, for very dilute solutions, the non-Newtonian effects will be proportionally small. Note that the constitutive model (2) for compressible linear viscoelasticity that we adopt in this work is the most general *isotropic* relationship between the stress tensor and the shear rate tensor.

In order to solve the hydrodynamic equations (1) in the presence of the sphere and evaluate the forces acting on it, we follow here the pioneering work of Mazur and Bedeaux based on the method of induced forces [13]. In this formulation, the fluid equations are extended to all points of space, including the space occupied by the sphere. The presence of the sphere, which is conventionally taken into account through boundary conditions on the surface of the sphere, is now accounted for

by a set of induced force densities $\boldsymbol{F}_{\rm ind}(\mathbf{r},t)$ whose target is to reproduce the same effect that the boundary conditions would have on the fluid motion. In this way, for all $\mathbf{r}$ we have

$$\rho^{\rm eq}\frac{\partial}{\partial t}\delta\boldsymbol{v}(\mathbf{r},t) = -\nabla\cdot\boldsymbol{P} + \boldsymbol{F}_{\rm ind}(\mathbf{r},t) + \boldsymbol{F}_{\rm ext}(\mathbf{r},t). \quad (5)$$

The induced force density $\boldsymbol{F}_{\rm ind}$ is nonzero only inside, and on the surface of the sphere, this is $\boldsymbol{F}_{\rm ind}(\mathbf{r},t) = 0$, $r > a$. The continuity equation remains the same, but now it is valid for all $\mathbf{r}$. In the case of stick boundary conditions, $\boldsymbol{F}_{\rm ind}$ is chosen in such a way that

$$\begin{aligned}\delta\boldsymbol{v}(\mathbf{r},t) &= \boldsymbol{u}(t) + \boldsymbol{\Omega}(t)\times\mathbf{r}, \quad |\mathbf{r}| \leqslant a\\ \delta\rho(\mathbf{r},t) &= 0, \quad |\mathbf{r}| < a\end{aligned} \quad (6)$$

where $\boldsymbol{u}(t)$ and $\boldsymbol{\Omega}(t)$ are, respectively, the linear and angular velocities of the sphere. By this choice, we ensure that the resulting fluid motion is the same as that evaluated from Eq. (1) with stick boundary conditions. The induced force for $r < a$ takes the form

$$\boldsymbol{F}_{\rm ind}(\boldsymbol{r},t) = \rho\frac{\partial}{\partial t}[\boldsymbol{u}(t) + \boldsymbol{\Omega}(t)\times\boldsymbol{r}] \quad (7)$$

Indeed, with Eq. (7), the fields (6) are the solution of Eq. (5) with Eq. (2), the latter containing memory effects. The induced force contains, in addition, a singular surface contribution proportional to $\delta(r-a)$ as detailed in Ref. [13]. The explicit form of this singular contribution can be found in particular simple flows as shown in Ref. [13] where the singular induced force is seen to depend on the flow. When memory is present, we expect that the way this surface singular induced force depends on the flow will contain also memory effects. However, in the method of Mazur and Bedeaux, this is not important because the explicit knowledge of form of the induced force is not used, only integrals over the sphere of the induced forces are required. These integrals are readily obtained in terms of flow properties, as detailed in Ref. [13].

By defining the Fourier transform of a field $a(\mathbf{r},t)$ with the convention

$$a(\mathbf{r},\omega) \equiv \int_{-\infty}^{\infty} e^{i\omega t}a(\mathbf{r},t)dt, \quad (8)$$

we may transform the equations of motion for the fluid to Fourier space, obtaining

$$\begin{aligned}&[-i\omega\rho^{\rm eq} - G^+(\omega)\Delta]\delta\boldsymbol{v}(\mathbf{r},\omega)\\ &\quad = -\gamma(\omega)\nabla\delta\rho(\mathbf{r},\omega) + \boldsymbol{F}_{\rm ind}(\mathbf{r},\omega) + \boldsymbol{F}_{\rm ext}(\mathbf{r},\omega),\\ &[-\omega^2 - c^2(\omega)\Delta]\delta\rho(\mathbf{r},\omega)\\ &\quad = -\nabla\cdot[\boldsymbol{F}_{\rm ind}(\mathbf{r},\omega) + \boldsymbol{F}_{\rm ext}(\mathbf{r},\omega)],\end{aligned} \quad (9)$$

where the following definitions have been introduced:

$$\begin{aligned}\gamma(\omega) &\equiv c_0^2 - \frac{i\omega}{\rho^{\rm eq}}[G^+(\omega) + S^+(\omega)],\\ c^2(\omega) &\equiv c_0^2 - \frac{i\omega}{\rho^{\rm eq}}[2G^+(\omega) + S^+(\omega)],\end{aligned} \quad (10)$$

$$G^+(\omega) \equiv \int_0^{\infty} e^{i\omega t}G(t)dt, \quad S^+(\omega) \equiv \int_0^{\infty} e^{i\omega t}S(t)dt. \quad (11)$$

These Equations (9)–(11) are formally identical to those obtained by Bedeaux and Mazur [see Eqs. (2.12) and (2.13) of Ref. [14]]. The only difference is in the definition of $\gamma(\omega), c(\omega)$ given in Eq. (10), which in Ref. [14] has the following form, valid for a Newtonian fluid only:

$$\gamma(\omega) \equiv c_0^2 - \frac{i\omega}{\rho^{\rm eq}}\left(\frac{\eta}{3} + \eta_v\right), \quad c^2(\omega) \equiv c_0^2 - \frac{i\omega}{\rho^{\rm eq}}\left(\frac{4\eta}{3} + \eta_v\right). \quad (12)$$

In this way, Eq. (11) is obtained from Eq. (12) by replacing η by $\eta(\omega)$ and η_v by $\eta_v(\omega)$, where

$$\eta(\omega) = G^+(\omega), \quad \eta_v(\omega) = S^+(\omega) + \tfrac{2}{3}G^+(\omega). \quad (13)$$

The calculation required to compute the total force $\mathbf{K}(\omega)$ remains unchanged from that of Bedeaux and Mazur under the transformation $\eta \to \eta(\omega)$ and $\eta_v \to \eta_v(\omega)$. Therefore, we can simply read off the final expression for the total force on the particle from the expression given in Eq. (3.14) of Ref. [13]; this is

$$\begin{aligned}\boldsymbol{K}(\omega) = &-12\pi G^+(\omega)a(\alpha a)^2\left[\left(\frac{i\omega a}{c}\right)^2 A(\omega) + 2(\alpha a)^2 B(\omega)\right]^{-1}\\ &\times\left\{\left[\left(1 + \alpha a + \frac{1}{9}(\alpha a)^2\right)B(\omega) - \frac{1}{9}\left(\frac{i\omega a}{c}\right)^2 A(\omega)\right]\right.\\ &\times\boldsymbol{u}(\omega) - B(\omega)\left[(1+\alpha a)\delta\overline{\boldsymbol{v}}_o^s(\omega) + \frac{1}{3}(\alpha a)^2\delta\overline{\boldsymbol{v}}_0^v\right]\\ &\left.+\frac{1}{9}\frac{i\omega}{\rho^{\rm eq}}\left[\left(\frac{i\omega a}{c}\right)^2 A(\omega) - (\alpha a)^2 B(\omega)\right]\overline{\mathbf{r}\delta\rho_0}^v\right\}\end{aligned} \quad (14)$$

(note a wrong sign in the original equation). We have introduced the following definitions:

$$\begin{aligned}&A(\omega) \equiv 1 + \alpha a + \frac{1}{3}\alpha^2 a^2, \quad B(\omega) \equiv 1 + i\omega a/c + \frac{1}{3}(i\omega a/c)^2,\\ &\alpha(\omega) \equiv \left(-\frac{i\omega\rho^{\rm eq}}{G^+(\omega)}\right)^{1/2}, \quad {\rm Re}(\alpha) > 0\\ &\delta\overline{\boldsymbol{v}}_0^s(\omega) \equiv \frac{1}{4\pi a^2}\int\delta\boldsymbol{v}_0(a\boldsymbol{n},\omega)dS,\\ &\delta\overline{\boldsymbol{v}}_0^v(\omega) \equiv \frac{3}{4\pi a^3}\int_{r<a}\delta\boldsymbol{v}_0(\mathbf{r},\omega)d\mathbf{r},\\ &\overline{\mathbf{r}\delta\rho_0}^v(\omega) \equiv \frac{3}{4\pi a^3}\int_{r<a}\mathbf{r}\delta\rho_0(\mathbf{r},\omega)d\mathbf{r}.\end{aligned} \quad (15)\ (16)$$

Here, $\delta\rho_0$ and $\delta\boldsymbol{v}_0$ are the solutions of Eq. (1) in the absence of induced forces, that is, the flow fields unperturbed by the presence of the spherical particle. The integration of $\delta\overline{\boldsymbol{v}}_0^s$ is made over the surface of the spherical particle, while for $\delta\overline{\boldsymbol{v}}_0^v$ it is made over its volume.

Equation (14) represents a generalization of Faxén's theorem to a compressible linear viscoelastic fluid and it provides the force $\boldsymbol{K}(\omega)$ acting on a particle moving with velocity $\boldsymbol{u}(\omega)$ through an arbitrary inhomogeneous, unsteady velocity field $\delta\boldsymbol{v}_0(\omega,\mathbf{r})$. When the unperturbed fluid is homogeneous and at rest, this is $\delta\boldsymbol{v}_0 = 0$ and $\delta\rho_0 = 0$, the force on the particle

reduces to

$$\boldsymbol{K}(\omega) = -\zeta^{+}(\omega)\boldsymbol{u}(\omega), \tag{17}$$

where the frequency-dependent friction coefficient is given by

$$\zeta^{+}(\omega) = 6\pi G^{+}(\omega)a\phi(\omega) \tag{18}$$

and

$$\phi(\omega) = (\alpha a)^2 \frac{\left[1+\alpha a+\frac{1}{9}(\alpha a)^2\right]B(\omega) - \frac{1}{9}\left(\frac{i\omega a}{c}\right)^2 A(\omega)}{\frac{1}{2}\left(\frac{i\omega a}{c}\right)^2 A(\omega) + (\alpha a)^2 B(\omega)}. \tag{19}$$

Equation (18) is the Stokes formula for a compressible linear viscoelastic fluid. The Newtonian case given by Bedeaux and Mazur [13] is recovered after substituting the Newtonian memory functions

$$G^{+}(\omega) = \eta, \quad S^{+}(\omega) = \eta_v - \tfrac{2}{3}\eta, \tag{20}$$

which are the Fourier transforms of Eq. (4).

The incompressible limit is obtained formally by taking $c_0 \to \infty$ in Eq. (18). This leads to the memory friction for an incompressible linear viscoelastic fluid

$$\zeta^{+}(\omega) = 6\pi G^{+}(\omega)a\left(1+\alpha a+\tfrac{1}{9}(\alpha a)^2\right). \tag{21}$$

This result has been presented recently in Ref. [29]. In the Newtonian limit for which (20) applies, one recovers from Eq. (21) the result given by Mazur and Bedeaux in Ref. [14] for an incompressible Newtonian fluid.

III. VELOCITY AUTOCORRELATION FUNCTION

In this section we compute, with the help of Faxén's theorem, the velocity autocorrelation function of a spherical Brownian particle moving in a compressible linear viscoelastic fluid, particularized to the case of the Oldroyd-B model, and we analyze its behavior for different physical fluid regimes.

The equation of motion for a single particle of mass m and velocity $\mathbf{u}(t)$ suspended in an equilibrium solvent can be obtained from the microscopic dynamics with a projector operator technique [30]. In this technique, a few relevant variables are selected as those that allow us to describe the dynamics of the system. By splitting the dynamics into relevant and irrelevant parts with the help of a projection operator and solving formally for the latter in terms of the former results in a closed, formally exact equation of motion for the selected variables. The formally exact result when the relevant variable is the velocity of a colloidal particle is

$$m\dot{\mathbf{u}}(t) = -\int_{-\infty}^{t} \zeta(t-t')\mathbf{u}(t')dt' + \tilde{\mathbf{F}}(t), \tag{22}$$

where $\zeta(t)$ is a friction memory function and $\tilde{\mathbf{F}}(t)$ is a microscopically defined "random" force that satisfies the fluctuation-dissipation theorem

$$\langle \tilde{\mathbf{F}}(t)\tilde{\mathbf{F}}(t')\rangle = k_B T\zeta(|t-t'|)\mathbf{1}, \tag{23}$$

where $\mathbf{1}$ is the unit tensor. If we average Eq. (22) over initial conditions and transform in frequency domain, we obtain an equation that is identical to Eq. (17). We may, therefore, *model* the microscopic friction memory $\zeta^{+}(\omega)$ in terms of the memory obtained from the continuum theory. This fact allows us to transfer the information gathered with the macroscopic continuum equations (1) to the realm of microrheology where thermal fluctuations responsible for the diffusion of probe particles are monitored.

We introduce the normalized autocorrelation function $c(t)$ as

$$c(t) = \frac{m}{3k_B T}\langle \mathbf{u}(t)\cdot\mathbf{u}\rangle \tag{24}$$

that satisfies $c(0) = 1$. In the Appendix it is shown that the normalized autocorrelation function $c(t)$ can be obtained from $\zeta^{+}(\omega)$ as

$$c(t) = \frac{2}{\pi}m\int_0^\infty d\omega\, \cos(\omega t) \times \frac{\mathrm{Re}[\zeta^{+}(\omega)]}{\{\mathrm{Re}[\zeta^{+}(\omega)]\}^2 + \{\mathrm{Im}[\zeta^{+}(\omega)] - m\omega\}^2}. \tag{25}$$

In what follows, we use the linear viscoelastic compressible result in Eq. (18) for the memory friction $\zeta^{+}(\omega)$. Details are given in the Appendix. We need to further specify the functional form of the moduli $G^{+}(\omega), S^{+}(\omega)$ and we choose the Oldroyd-B model for explicit results. In this model, the moduli are given by

$$G^{+}(\omega) = \eta + \frac{\eta_p}{1-i\omega\tau}, \qquad S^{+}(\omega) = \eta_v - \frac{2}{3}\eta - \frac{2\eta_p}{1-i\omega\tau}, \tag{26}$$

where τ is the relaxation time of the fluid and $\eta_p = n_p k_B T\tau$ its polymeric viscosity, determined by the concentration of polymers n_p, the Boltzmann constant k_B, and the temperature T.

We study the effect of the speed of sound, viscosity, and elastic relaxation time on the velocity autocorrelation function by solving numerically the integral in Eq. (25). The full set of parameters in the system is given by $m, a, k_B T, \rho_b, \rho_f, \eta, \eta_v, \eta_p, c, \tau$, where ρ_b and ρ_f are, respectively, the particle and fluid densities. We choose units such that $k_B T = 1, a = 1, \rho_f = 1$ and construct the following dimensionless numbers: the buoyancy parameter $b = \rho_b/\rho_f$, the ratio of bulk and shear viscosities $\alpha = \eta_v/\eta$, the ratio of solvent and polymer viscosities $\beta = \eta/(\eta+\eta_p)$, and the following quantities obtained from the thermal velocity $v_T = \sqrt{k_B T/m}$: a dimensionless sound speed $c^* = c/v_T$, a dimensionless viscosity $\eta^* = \eta/(a v_T \rho)$, and a dimensionless elastic time $\tau^* = v_T\tau/a$.

We reduce the high dimensionality of the parameter space by choosing a neutrally buoyant particle $b = 1$, taking $\alpha = 0$ (no bulk viscosity), and choosing $\beta = 0.5$. A number of characteristic time scales are important in the system that are given in terms of the previous parameters as thermal time $t_T = a/v_T$, sonic time $t_c = a/c$, viscous time $t_v = a^2\rho/\eta$, and relaxation time τ.

We have studied the particle VAF $c(t)$ and the time-dependent diffusion coefficient $D(t) = \int_0^t c(t)\,dt$ under different choices of the model fluid parameters and the results are reported in Figs. 1–3. As time increases, the function $D(t)$ reaches a plateau that corresponds to the value of the diffusion coefficient of the Brownian particle, given in terms of the usual Green-Kubo formula $D = \int_0^\infty c(t)\,dt$.

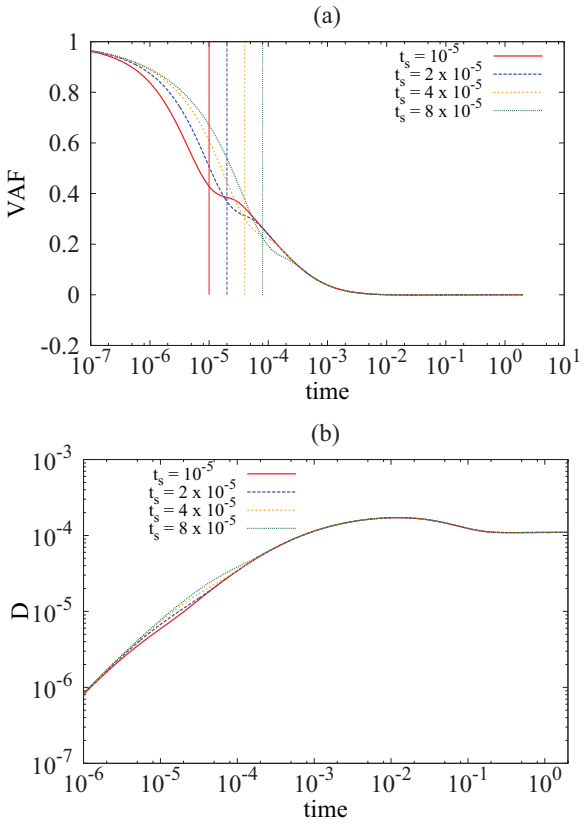

FIG. 1. (Color online) VAF(t) and $D(t)$ for c^* from 5.26×10^4 to 4.166×10^5, while $\eta^* = 4.166 \times 10^3$, $\tau^* = 2.4 \times 10^{-2}$. The sonic times for the four sets of parameters have been indicated with vertical lines, showing the correlation with the sonic bumps.

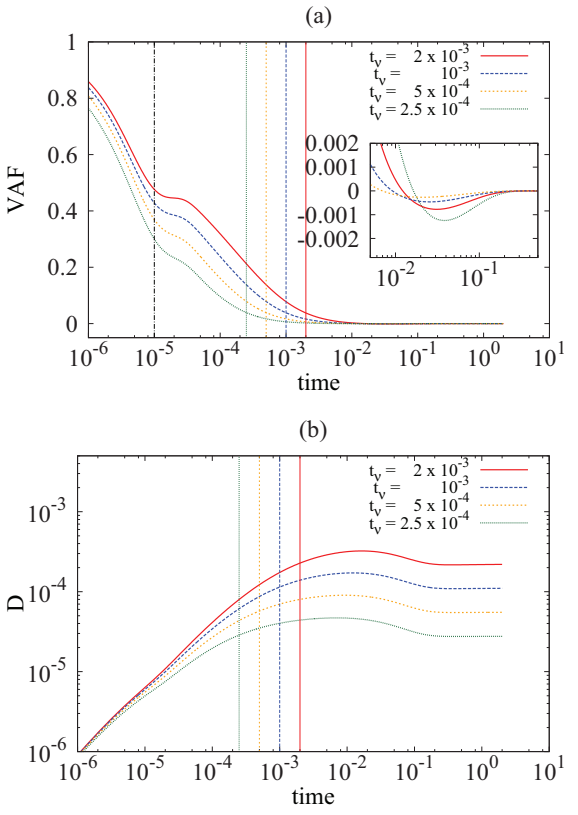

FIG. 2. (Color online) VAF(t) and $D(t)$ for η^* from 2.0833×10^3 to 1.6×10^4 while $c^* = 4.166 \times 10^5$, $\tau^* = 2.4 \times 10^{-2}$. The viscous and sonic times have been drawn with vertical lines.

In Fig. 1, we have fixed the dimensionless viscosity η^* and the dimensionless elastic time τ^* to $\eta^* = 4.166 \times 10^3$ and $\tau^* = 2.4 \times 10^{-2}$, and the effect of changing c^*, namely compressibility, is studied in the range $c^* \in [5.26 \times 10^4 - 4.1666 \times 10^5]$. In terms of typical fluid times, the viscous and elastic times are fixed, respectively, to $t_\nu = 0.001$ and $\tau = 0.1$, while the sonic time is in the range $t_s \in [10^{-5} - 8 \times 10^{-5}]$. The resulting VAF and $D(t)$ plotted in Fig. 1 show that the only difference for the different set of parameters is in the location of a sonic bump (corresponding to the self-interaction of the particle velocity with the pressure wave generated by its movement) which correlates very well with the value of the sonic time t_s, represented by the vertical lines in the figure. It is worth noting that the diffusion coefficient of the Brownian particle is unaffected by the compressibility of the fluid.

In a second setup, the dimensionless sound speed c^* and the dimensionless elastic time τ^* are fixed, respectively, to $c^* = 4.166 \times 10^5$ and $\tau^* = 2.4 \times 10^{-2}$, and the effect of the dimensionless viscosity η^* is studied by changing it in the range $\eta^* \in [2.0833 \times 10^3 - 1.6 \times 10^4]$. The resulting curves are plotted in Fig. 2. Note the identical location of the sonic bumps in all cases, corresponding to t_s. The different t_ν characterize the times when the particle velocity becomes approximately uncorrelated (VAF smaller than 5% of its initial value). Note that an *anticorrelation* appears in the VAF on time scale of the order of the elastic relaxation time (inset Fig. 2), which tends to be enhanced for smaller values of η^*, namely, for increasing viscous time scales, approaching τ. This rebound effect, which is maximal when the relaxation time τ and the viscous time t_ν are similar, has also been observed recently in Ref. [16]. When a clear scale separation exists ($t_\nu \ll \tau$), the phenomena are strongly attenuated. This anticorrelation is reflected in the behavior of $D(t)$ as a local maximum located around τ.

Finally, in Fig. 3 we show the VAF and $D(t)$ functions for different values of the dimensionless elastic time $\tau^* \in [2.4 \times 10^{-3} - 2.4 \times 10^{-1}]$, keeping the dimensionless viscosity η^* and the dimensionless sound speed c^* fixed, respectively, to $\eta^* = 4.166 \times 10^3$ and $c^* = 4.166 \times 10^5$. The VAFs are very similar except for the anticorrelation effect discussed above. As expected, the time scale characterizing anticorrelation is moved to larger time for increasing τ and, accordingly, is strongly attenuated as result of the increased scale separation with the fixed viscous time. It is interesting to note that the effect of a so small change in the VAF produces a significant change in the behavior of the time-dependent diffusion coefficient $D(t)$, where the elastic bumps can be clearly detected. This observation could be used to characterize unambiguously the longest elastic relaxation time of complex liquids from measurements of the particle diffusion.

IV. DISCUSSION

By using the method of induced forces, we have obtained the force that a compressible linear viscoelastic fluid in

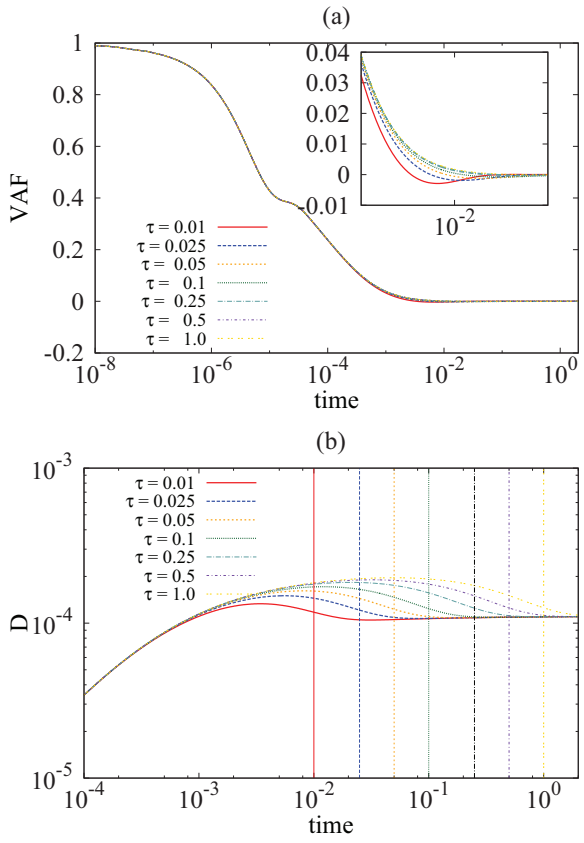

FIG. 3. (Color online) VAF(t) and $D(t)$ for τ^* numbers from 2.4×10^{-3} to 2.4×10^{-1} while $\eta^* = 4.166 \times 10^3$ and $c^* = 4.166 \times 10^5$. The elastic times for the different set of parameters have been drawn as vertical lines.

arbitrary flow exerts on a suspended sphere. This result, valid for any linear compressible viscoelastic model, can be obtained from the compressible Newtonian results of Bedeaux and Mazur [14] by changing the shear and bulk viscosities η, η_v of the Newtonian case by the corresponding viscosities $\eta(\omega), \eta_v(\omega)$ of the viscoelastic model. This is consistent with the result given in Ref. [29] for an incompressible fluid. Also, general expressions for the calculation of the velocity autocorrelation function of a spherical particle embedded in a general compressible viscoelastic fluid have been derived. For the particular case of an Oldroyd-B model, we have analyzed the VAF and the time-dependent diffusion coefficient under different physical regimes of the suspending fluid.

In this paper, we have considered a given viscoelastic fluid (modeled as a compressible Oldroyd-B fluid) and have computed the velocity autocorrelation function by using Faxén's theorem. The inverse problem, that is, given the velocity autocorrelation function to infer the properties $G^+(\omega), S^+(\omega)$ of the viscoelastic fluid, is the main aim of passive microrheology. The friction memory $\zeta^+(\omega)$ is directly linked to the velocity autocorrelation function and the root mean displacement of a particle. Therefore, it is directly measurable from observations of the position of a Brownian particle. Because the friction memory $\zeta^+(\omega)$ is given in a linear viscoelastic fluid in terms of the viscoelastic memory functions $G^+(\omega)$ and $S^+(\omega)$, we wonder to what extent it is possible to infer the latter from the former. In the incompressible case, this is rather simple because (21) is a quadratic form that can be solved for $G^+(\omega)$, in terms of $\zeta^+(\omega)$. This route has been pursued successfully in Ref. [29] where the viscoelastic modulus is obtained from the measurable friction memory. In the compressible case, however, apart from the problem of finding the roots of a rational function, there is a more fundamental problem. Indeed, we have *two* memory functions $G^+(\omega), S^+(\omega)$ that need to be extracted out of *one* single memory friction $\zeta^+(\omega)$. Obviously, there is an infinite number of combinations of $G^+(\omega), S^+(\omega)$ that give the same friction memory $\zeta^+(\omega)$, therefore more information is required in order to measure both material functions. One possible approach is to consider *two* Brownian particles and extend the results of Mazur [31] to the case of compressible linear viscoelastic fluid for the case of two identical spheres (*two-point microrheology*). Because of its linearity, the problem should be relatively simple to solve: instead of a frequency-dependent friction coefficient, we would obtain a friction matrix that expresses not only the friction with the solvent, but also the hydrodynamic interactions between the two spheres. The friction matrix is expressed in terms of $G^+(\omega), S^+(\omega)$. From that result it should be possible to predict the correlation matrix of the velocities of both particles. In this way, by measuring both the autocorrelation and the cross-correlation function of the velocities of the particles, one could obtain sufficient information to extract both functions $G^+(\omega), S^+(\omega)$.

An alternative route makes use of one of the distinguishing features of Faxén's theorem, which is that it gives the force on the sphere on a viscoelastic fluid moving in an *arbitrary* flow. This force may be used to compute the velocity autocorrelation of a particle in, for example, the presence of a stationary sound wave. In this way, by measuring the VAF in such an experimental setup, an alternative procedure to measure the material functions $G^+(\omega), S^+(\omega)$ could be implemented. The numerical model to study microrheology presented in Ref. [32] would be useful to test these possibilities. We plan to present these results in future publications.

ACKNOWLEDGMENTS

We thank J. Schieber for very useful discussions. Support of the Spanish Government under Project No. FIS2007-65869-C03-03 is appreciated. A.V.-Q. thanks the projects MODELICO-CM-52009/ESP-1691 from Comunidad de Madrid and "Programa propio de la Investigación de la Universidad Nacional de Educación a Distancia, 2010" for financial support. M.E. financial support provided by the Deutsche Forschungsgemeinschaft (DFG) via the Grant No. EL503/1-2 is also gratefully acknowledged. Support from BIFI is also appreciated.

APPENDIX: CALCULATION OF THE VAF FROM THE MEMORY FUNCTION

We wish to solve Eq. (22) and we transform to Fourier space by using the following definitions:

$$f(\omega) = \int_{-\infty}^{\infty} dt \exp\{i\omega t\} f(t). \tag{A1}$$

The Fourier transform of Eq. (22) is

$$-i\omega m\mathbf{u}(\omega) = -\zeta^{+}(\omega)\mathbf{u}(\omega) + \tilde{\mathbf{F}}(\omega), \tag{A2}$$

where

$$\zeta^{+}(\omega) = \int_0^\infty dt\, \exp\{i\omega t\}\zeta(t). \tag{A3}$$

Because the friction memory is real, the following symmetry relation is satisfied:

$$\zeta^{+}(-\omega) = \overline{\zeta^{+}(\omega)}, \tag{A4}$$

where the overbar denotes complex conjugate. The solution of Eq. (A2) is

$$\mathbf{u}(\omega) = \frac{\tilde{\mathbf{F}}(\omega)}{\zeta^{+}(\omega) - i\omega m}. \tag{A5}$$

By Fourier transforming (23), we find that

$$\langle\tilde{\mathbf{F}}(\omega)\tilde{\mathbf{F}}(\omega')\rangle = k_B T 2\pi\delta(\omega+\omega')[\zeta^{+}(\omega) + \zeta^{+}(-\omega)]\mathbf{1}. \tag{A6}$$

The force correlation (A6) is a real function. By using this result (A6), one can compute the correlation of the velocity with the result

$$\langle\mathbf{u}(\omega)\mathbf{u}(\omega')\rangle = \frac{\langle\tilde{\mathbf{F}}(\omega)\tilde{\mathbf{F}}(\omega')\rangle}{[\zeta^{+}(\omega) - i\omega m][\zeta^{+}(\omega') - i\omega' m]} = k_B T 2\pi\delta(\omega+\omega')2\mathrm{Re}\left[\frac{1}{\zeta^{+}(\omega) - i\omega m}\right]\mathbf{1}.$$

By returning to real time

$$\langle\mathbf{u}(t)\mathbf{u}(t')\rangle = \frac{k_B T}{\pi}\int_{-\infty}^{\infty} d\omega\, \exp\{-i\omega(t-t')\} \times \mathrm{Re}\left[\frac{1}{\zeta^{+}(\omega) - i\omega m}\right]\mathbf{1}. \tag{A7}$$

By using the symmetry property (A4), we have that the normalized velocity correlation function (24) is real and can be written as

$$c(t) = \frac{2}{\pi}\int_0^\infty d\omega\cos(\omega t) \times \mathrm{Re}\left[\frac{1}{m^{-1}\zeta^{+}(\omega) - i\omega}\right]. \tag{A8}$$

By separating real and imaginary parts within brackets, the final form given in Eq. (25) is obtained.

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