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Brownian motion and correlation functions in a viscoelastic fluid

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Abstract. A model for a solid sphere undergoing Brownian motion in a viscoelastic (Maxwell) fluid is described in terms of a non-Markovian Langevin equation. By solving this equation exactly, the particle's density-density and current-current time correlation functions are calculated. From the former, the time-dependent self-diffusion coefficient, $D(t)$, is evaluated for an ensemble of Brownian particles. Then a numerical estimation of $D(t)$ is performed for typical values of the sphere's parameters and for two viscoelastic fluids describable by Maxwell's model. A comparison of this result with the corresponding expressions for $D(t)$ for a Newtonian fluid in the Stokes and Boussinesq-Basset approximations for the drag, shows that for the Maxwell fluid the behaviour of $D(t)$ is analytic and similar to that of the Newtonian fluid in the Stokes regime. We find that elasticity has a minor influence on $D(t)$ and that persistent correlations (long time tails) in diffusion do not occur for this model. We also compare our results with other related works.

1. Introduction

The prominent role that time correlation functions have played in the description of macroscopic phenomena stems from their close connection with the transport properties of a system. Indeed, transport coefficients can be obtained from time-dependent correlations of suitable fluxes (Zwanzig 1965) and the scattering properties of a medium are derivable from the density-density correlation function (van Hove 1954).

Different time-dependent correlation functions have been analysed for a wide class of linear transport phenomena in Newtonian fluids. For instance, the Brownian motion of a particle in a fluctuating fluid has been extensively studied within the familiar Stokes approximation for the drag acting on the particle. The stochastic dynamics is described by means of the usual linear Langevin equation and the most important assumption in these calculations is that the driving forces in the fluid are characterised by a Gaussian Markovian process (Chandrasekhar 1943, Zwanzig 1964, Fox and Uhlenbeck 1970). In this case one finds that there exists an instantaneous relation between the force acting on the Brownian particle and its velocity. As a consequence a microscopic process, such as the correlation in the particle's velocity, decays exponentially and there is a wide separation between the timescales of this process and a macroscopic one like the diffusion of the particle.

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However, when the Boussinesq–Basset (Landau and Lifshitz 1960) corrections to the drag are taken into account, significant changes occur in the stochastic description: there appears a non-instantaneous relationship between the drag and the velocity of the particle, implying that the Langevin equation is no longer Markovian. This memory is represented by a slowly decreasing function ($t^{-3/2}$) and, as a result, the force and the velocity are correlated over long time intervals, affecting the behaviour of the transport properties of the system. This persistence of correlations destroys the well defined separation of timescales mentioned above (Case 1971, Hauge and Martin-Löf 1973, Dufty 1974).

Although these effects have been well studied for Newtonian fluids, much less is known for rheological fluids. The purpose of this paper is to consider some of these questions within the context of a simple model for Brownian motion in a viscoelastic fluid. This type of model has been discussed before (Berne *et al* 1966, Zwanzig and Bixon 1970, Chow and Hermans 1972, Volkov and Pokrovsky 1983, Volkov and Vinogradov 1984); however, the present approach and the quantities to be calculated are different. Actually, the analysis of the following sections is an application of the method used by Dufty in connection with a Newtonian fluid with memory. More specifically, we investigate if the memory introduced by the viscoelasticity on the diffusion coefficient is of the same type as the one found by Dufty for a Newtonian fluid with memory. To this end we first calculate the self-diffusion coefficient, $D(t)$, and then perform a numerical estimation of this quantity for latex spheres in silicone oil and in a glucose–separan solution. When these values for $D(t)$ are compared with the corresponding ones for a Newtonian fluid (water) in the Stokes and Boussinesq–Basset regimes, we find that the time behaviour of $D(t)$ is analytic. No long time tails ensue and therefore no persistent correlation appears due to the memory effects.

The paper is organised as follows. In § 2 we describe the model and set up the associated non-Markovian Langevin equation. In § 3 this equation is solved exactly for given initial conditions and the corresponding conditional probability density is obtained. Then in § 4 this result is used to calculate the density–density and current–current correlation functions. Next, we calculate the (self-)diffusion coefficient for an ensemble of Brownian particles and finally, in § 5, we summarise the main results of our work and make some further physical remarks.

2. A Gaussian model for Brownian motion

In this section we review in some detail the main features of the model introduced by Volkov and co-workers (Volkov and Pokrovsky 1983, Volkov and Vinogradov 1984) for the Brownian motion of a sphere in a Maxwell fluid. Consider an incompressible quiescent and unbounded viscoelastic fluid characterised by a single relaxation time λ_0 . At some time in the remote past, a large hard spherical particle of radius σ and mass m is put into the fluid at point $\mathbf{R}(t)$ with the velocity $\mathbf{U}(t)$, both quantities defined with respect to the laboratory reference frame. Following Volkov *et al* we assume that the size and speed of the particle are such that the Reynolds and Weissenberg numbers for the fluid are small, i.e.

$$\text{Re} = \rho\eta^{-1}\sigma U \ll 1 \quad \text{Ws} = \lambda_0 U \sigma^{-1} \ll 1. \quad (2.1)$$

Here ρ and η denote the mass density and the shear viscosity of the fluid respectively. The restriction on Re limits the applicability to creeping flow, while the more severe Ws limitation restricts the analysis to a slight degree of fluid elasticity on the flow field.

As a consequence of (2.1) the inertial and non-linear convective terms in the equations of motion and rheological equation of state may be neglected (Astarita and Marrucci 1974). Hence the dynamics of the fluid may be described by

$$\frac{\partial v_i}{\partial x_i} = 0 \quad (2.2a)$$

$$\frac{\partial p}{\partial x_i} = \frac{\partial}{\partial x_j} \tau_{ij}. \quad (2.2b)$$

v_i is the perturbed velocity field and τ_{ij} the symmetric traceless part of the stress tensor of the fluid. It will be assumed that τ_{ij} obeys Maxwell's rheological equation of state (Bird *et al* 1977), namely

$$\frac{d}{dt} \tau_{ij} = -\lambda_0^{-1} (\tau_{ij} - \dot{\tau}_{ij}). \quad (2.3)$$

$\dot{\tau}_{ij} \equiv 2\eta\gamma_{ij}$ is the Newtonian stress tensor and γ_{ij} is the rate of strain tensor. Note that due to assumption (2.1), $d/dt = \partial/\partial t$.

For simplicity we shall assume stick boundary conditions, so equations (2.2) are supplemented with the following boundary conditions:

$$\mathbf{v}(\mathbf{x}, t) = \mathbf{U}(\mathbf{x}, t) \quad \text{if } |\mathbf{x} - \mathbf{R}(t)| = \sigma \quad (2.4a)$$

$$\mathbf{v}(\mathbf{x}, t) \rightarrow \mathbf{0} \quad \text{when } |\mathbf{x} - \mathbf{R}(t)| \rightarrow \infty. \quad (2.4b)$$

Let us now turn our attention to the motion of the sphere. The drag force acting on the particle is given by

$$\mathbf{F} = \int \boldsymbol{\tau} \cdot d\mathbf{S} \quad (2.5)$$

where $d\mathbf{S}$ denotes a surface element of the sphere directed into the fluid. Actually, this force is the sum of two contributions: $\mathbf{F}^{(1)}$ produced by the deviator part of the stress tensor and $\mathbf{F}^{(2)}$ generated by the hydrodynamic pressure p . Now, using (2.2), (2.3) and (2.5) it is straightforward to derive a relaxation equation for \mathbf{F} (see the appendix in Volkov and Vinogradov 1984), namely

$$\frac{d}{dt} \mathbf{F} = -\lambda_0^{-1} (\mathbf{F} - \mathbf{F}^{(0)}). \quad (2.6)$$

Here $\mathbf{F}^{(0)}$ is the drag force arising from the Newtonian stress tensor $\dot{\boldsymbol{\tau}}$ and is given by Stokes law

$$\mathbf{F}^{(0)} = -6\pi\sigma\eta\mathbf{U} = -\zeta\mathbf{U}. \quad (2.7)$$

Thus, for times long compared with the initial time, the drag on the sphere is

$$\mathbf{F}(t) = -\zeta\lambda_0^{-1} \int_{-\infty}^t ds \exp[-\lambda_0^{-1}(t-s)] \mathbf{U}(s). \quad (2.8)$$

This result shows that, indeed, the viscoelastic properties induce a non-local effect in time on the drag acting on the sphere, even when the inertial effects of the flow are

neglected. Using this result we can then provide for a complete description of the sphere's Brownian motion through the following set of generalised Langevin equations:

$$\frac{d}{dt} R_i(t) = U_i(t) \quad (2.9a)$$

$$m \frac{d}{dt} U_i(t) = - \int_{-\infty}^t ds \gamma(t-s) U_i(s) + \phi_i(t) \quad (2.9b)$$

where we have identified

$$\gamma(t) = \zeta \lambda_0^{-1} \exp(-\lambda_0^{-1} t). \quad (2.10)$$

By analogy with the well known case of Brownian motion in an incompressible Newtonian fluid fluctuating about equilibrium (Zwanzig 1964, Fox and Uhlenbeck 1970), we assume that the fluctuating force ϕ_i is a Gaussian process. Moreover, in order to calculate equilibrium correlation functions in the next section, we shall explicitly assume that the initial particles' velocities obey a Maxwell-Boltzmann distribution. Thus it is necessary to guarantee that the model is compatible with an equilibrium distribution. In this respect Kubo *et al* (1985), as well as others (Case 1971, Hauge and Martin-Löf 1973), have shown that a stochastic process such as the one defined by equations (2.9) or (2.12) below, will have an equilibrium canonical distribution if ϕ_i (or f_i defined by (2.13)) satisfies the following form of the fluctuation-dissipation theorem

$$\langle \phi_i(t_0) \phi_j(t_0 + t) \rangle = \kappa_B T \gamma(|t|) \delta_{ij}. \quad (2.11)$$

Here κ_B is Boltzmann's constant and T is the equilibrium temperature. As shown explicitly by Kubo *et al*, the fulfilment of (2.11) requires that $\text{Re}\{\gamma[\omega]\} > 0$ (for real ω), where $\gamma[\omega]$ stands for the Fourier-Laplace transform of $\gamma(t)$. Since this condition is clearly satisfied by (2.10), we expect that (2.11) is indeed a reasonable assumption for a viscoelastic solvent.

It is convenient to rewrite (2.9b) in the form

$$m \frac{d}{dt} U_i(t) = - \int_0^t ds \gamma(t-s) U_i(s) + f_i(t) \quad (2.12)$$

where the new fluctuating force f_i is now defined as

$$f_i(t) = \phi_i(t) - \int_{-\infty}^0 ds \gamma(t-s) U_i(s). \quad (2.13)$$

Using (2.11) and following the steps indicated in appendix B of Dufty's paper, one can show that f_i has the following stochastic properties:

$$\langle U_i(0) f_j(t) \rangle = 0 \quad (2.14a)$$

$$\langle f_i(t_0) f_j(t_0 + t) \rangle = \kappa_B T \gamma(|t|) \delta_{ij}. \quad (2.14b)$$

At this point it is convenient to emphasise that, although the model defined by (2.9a), (2.12) and (2.14) represents a non-Markovian process, it is still linear and Gaussian. In the next section we use these features to solve (2.12) exactly and calculate the conditional probability density $W(\mathbf{R}, \mathbf{U}, t; \mathbf{R}_0, \mathbf{U}_0, 0)$ for this process.

3. The solution of the generalised Langevin equations

The Green function, $M(t)$, associated with (2.12) satisfies the equation

$$m \frac{d}{dt} M(t) + \int_0^t ds \gamma(t-s) M(s) = \delta(t) \quad (3.1)$$

with the initial condition $M(0) = 1$ and where $\gamma(t)$ is given by (2.10). By Laplace transformation we find that

$$M(t) = \frac{1}{2} \Delta^{-1} [a \exp(\frac{1}{2}bt) + b \exp(-\frac{1}{2}at)] \quad (3.2a)$$

or equivalently

$$M(t) = \Delta^{-1} \exp(-t/2\lambda_0) (\lambda_0^{-1} \sinh \frac{1}{2}\Delta t + \Delta \cosh \frac{1}{2}\Delta t) \quad (3.2b)$$

where we have defined

$$\Delta = \lambda_0^{-1} (1 - 4\zeta\lambda_0 m^{-1})^{1/2} \quad (3.3a)$$

and a, b turn out to be

$$a = (\Delta + \lambda_0^{-1}) > 0 \quad (3.3b)$$

$$b = (\Delta - \lambda_0^{-1}) < 0. \quad (3.3c)$$

In terms of $M(t)$ and for given initial values $\mathbf{R}_0, \mathbf{U}_0$, the formal solutions to (2.12) and (2.9a) are, respectively,

$$\mathbf{U}(t) - M(t)\mathbf{U}_0 = \mathbf{A}(t) \quad (3.4)$$

$$\mathbf{R}(t) - \mathbf{R}_0 - \mathbf{U}_0 \int_0^t ds M(s) = \mathbf{B}(t) \quad (3.5)$$

where the right-hand sides are the stochastic quantities

$$\mathbf{A}(t) = \int_0^t ds M(t-s) \mathbf{f}(s) \quad (3.6a)$$

$$\mathbf{B}(t) = \int_0^t ds \int_0^s ds' M(s-s') \mathbf{f}(s'). \quad (3.6b)$$

It will also be convenient to denote the left-hand sides of (3.4) and (3.5), respectively, as

$$\mathbf{X}(t) \equiv \mathbf{U}(t) - M(t)\mathbf{U}_0 \quad (3.7a)$$

$$\mathbf{Y}(t) \equiv \mathbf{R}(t) - \mathbf{R}_0 - \mathbf{U}_0 \int_0^t ds M(s). \quad (3.7b)$$

Now, Dufty has shown that the conditional probability density $W(\mathbf{R}, \mathbf{U}, t; \mathbf{R}_0, \mathbf{U}_0, 0)$ of the linear, Gaussian, non-Markovian process of the type considered here is given by

$$\begin{aligned} W(\mathbf{R}, \mathbf{U}, t; \mathbf{R}_0, \mathbf{U}_0, 0) &= \frac{1}{8} \pi^{-3} (FG - H^2)^{-3/2} \\ &\times \exp[-\frac{1}{2}(FG - H^2)^{-1} (GY^2 - 2HY \cdot \mathbf{X} + FX^2)] \end{aligned} \quad (3.8)$$

with

$$F = \langle \mathbf{B}^2 \rangle \quad G = \langle \mathbf{A}^2 \rangle \quad H = \langle \mathbf{A} \cdot \mathbf{B} \rangle \quad (3.9)$$

where the angular brackets denote an equilibrium average. Equation (3.8) is that solution of (2.12) which satisfies the initial condition that the Brownian particle is at \mathbf{R}_0 with velocity U_0 at $t = 0$. This result is entirely similar to the one obtained originally by Chandrasekhar (1943) for a Gaussian–Markovian process, but with different function F , G and H . For the present model these functions are calculated from (2.14), (3.2) and (3.6) with the following results:

$$\begin{aligned} G(t) &= \kappa_B T m^{-1} [1 - M^2(t)] \\ &= \kappa_B T m^{-1} \{ (2\Delta)^{-1} [a \exp(\frac{1}{2}bt) + b \exp(-\frac{1}{2}at)]^2 \} \end{aligned} \quad (3.10)$$

$$\begin{aligned} H(t) &= \kappa_B T m^{-1} [1 - M(t)] I(t) \\ &= \kappa_B T m^{-1} \Delta I(t) \{ 1 - (2\Delta)^{-1} [a \exp(\frac{1}{2}bt) + b \exp(-\frac{1}{2}at)] \} \end{aligned} \quad (3.11)$$

$$\begin{aligned} F(t) &= 2\kappa_B T m^{-1} \left(\int_0^t ds (t-s) M(s) - \frac{1}{2} I^2(t) \right) \\ &= 2\kappa_B T m^{-1} \{ \Delta^{-1} [ab^{-2}(\exp(\frac{1}{2}bt) - 1) \\ &\quad + ba^{-2}(\exp(-\frac{1}{2}at) - 1) + t(ba^{-1} - ab^{-1})] - \frac{1}{2} I^2(t) \} \end{aligned} \quad (3.12)$$

with

$$I(t) = \int_0^t ds M(s) = \Delta^{-1} \{ ab^{-1} [\exp(\frac{1}{2}bt) - 1] - ba^{-1} [\exp(-\frac{1}{2}at) - 1] \}. \quad (3.13)$$

4. The correlation functions

We now calculate the equilibrium density–density and current–current time-dependent correlation functions for this model. If for simplicity we take the initial position for the particle to be at $\mathbf{R}_0 = \mathbf{0}$, in terms of the conditional probability density $W(\mathbf{R}, \mathbf{U}, t; \mathbf{R}_0, \mathbf{U}_0, 0)$ these correlation functions are, respectively, given by

$$G(\mathbf{R}, t) = \int f(U_0) W(\mathbf{R}, \mathbf{U}, t; U_0) d^3 U_0 d^3 U \quad (4.1)$$

$$G_{ij}(\mathbf{R}, t) = \int f(U_0) W(\mathbf{R}, \mathbf{U}, t; U_0) U_{0i} U_j d^3 U_0 d^3 U. \quad (4.2)$$

Here $f(U_0)$ stands for the Maxwell–Boltzmann distribution function since the correlation functions are evaluated in equilibrium. Substitution of (3.8), (3.10), (3.11) and (3.12) into (4.1) and (4.2) yields Gaussian integrals which are simple but tedious to evaluate. After performing all the operations indicated in (4.1) and (4.2) we arrive at the following expressions for the above correlations:

$$\begin{aligned} G(\mathbf{R}, t) &= m^{3/2} (2\pi\kappa_B T)^{-3/2} [I^2 + m(\kappa_B T)^{-1} F]^{-3/2} \\ &\quad \times \exp\{ -m(2\kappa_B T)^{-1} R^2 [I^2 + m(\kappa_B T)^{-1} F]^{-1} \} \end{aligned} \quad (4.3)$$

and

$$G_{ij}(\mathbf{R}, t) = [I^2 + m(\kappa_B T)^{-1} F]^{-2} [(FM - HI)(I^2 + m(\kappa_B T)^{-1} F)\delta_{ij} + I^2 R_i R_j] G(\mathbf{R}, t) \quad (4.4)$$

where the time-dependent quantities M, I, F have been defined in the previous section.

Let us now turn our attention to the (self-)diffusion coefficient defined by

$$D(t) = \frac{1}{3} \int_0^t ds \int_{-\infty}^{\infty} d\mathbf{R} G_{ii}(\mathbf{R}, s). \tag{4.5}$$

Upon substitution of (4.4) we find that

$$D(t) = m^{-1} \kappa_B T I(t) = D_0 \{1 + \lambda_0 (4\Delta)^{-1} [b^2 \exp(-\frac{1}{2}at) - a^2 \exp(\frac{1}{2}bt)]\} \tag{4.6}$$

where we have defined the diffusion constant D_0 by

$$D_0 = \lim_{t \rightarrow \infty} D(t) = \kappa_B T \zeta^{-1}. \tag{4.7}$$

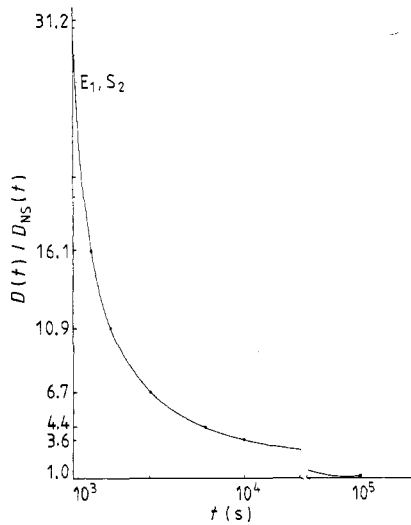


Figure 1. The ratio $D(t)/D_{NS}(t)$ as calculated from (4.6) and (4.8) for silicone oil (S_2) and a glucose-separan solution (E_1).

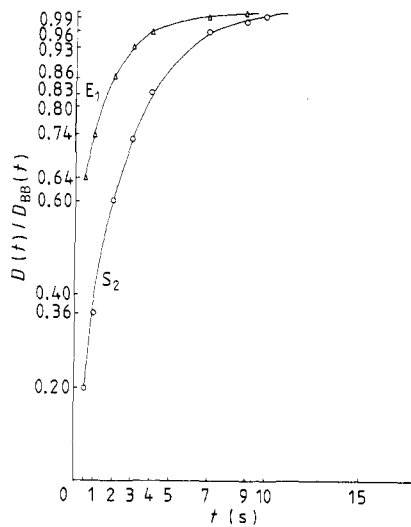


Figure 2. The ratio $D(t)/D_{BB}(t)$ for S_2 (\circ) and E_1 (Δ) as calculated from (4.6) and (4.9).

Now, at this point it is convenient to recall that, on the one hand, for a spherical Brownian particle in an incompressible fluid fluctuating about equilibrium and within the familiar Stokes law approximation, $D(t)$ is

$$D_{NS}(t) = D_0[1 - \exp(-m^{-1}\zeta t)] \quad (4.8)$$

with ζ defined by (2.7). On the other hand, when the Boussinesq–Basset corrections to Stokes law are considered, Dufty (1974) has shown that the asymptotic ($t \rightarrow \infty$) behaviour of $D(t)$ exhibits long time tails,

$$D_{BB}(t) \approx D_0[1 - \pi^{-1/2}A(\zeta t)^{-1/2}] \quad (4.9)$$

where

$$A = (6\sigma^3\rho)^{1/2} \quad (4.10)$$

ρ is the mass density of the fluid.

From (4.6)–(4.9) it is apparent that after the relaxation of the stress tensor of the Maxwell fluid has taken place, the non-Newtonian diffusion coefficient $D(t)$ reaches the same asymptotic value, D_0 , as the Newtonian coefficients $D_{NS}(t)$ and $D_{BB}(t)$. Although this could have been anticipated, it is clear that the approach towards D_0 is different in the three cases. To exhibit these differences in more detail we evaluate numerically the ratios $D(t)/D_{NS}(t)$ and $D(t)/D_{BB}(t)$ for two viscoelastic fluids, namely silicone oil (S_2) and a solution of 0.02% separan MG500+2% water in glucose MCY43N (E_1). Chhabra *et al* (1980) have studied the rheological properties of these fluids and according to their shear stress and normal stress data, S_2 would be classified as a weakly elastic fluid, whereas E_1 is exceedingly elastic. From their data we take for S_2 a (Maxwell's) relaxation time $\lambda_0 = 1.03 \times 10^{-3}$ s at 22 °C, a (zero frequency) viscosity of $\eta_0 = 137.1$ P and a density of $\rho = 0.971$ g cm $^{-3}$. For E_1 we take $\lambda_0 = 0.18$ s at 19 °C, $\eta_0 = 173$ P and $\rho = 1.414$ g cm $^{-3}$.

As for the viscosity and density of the Newtonian fluid we take typical values for water at 20 °C, namely, $\eta = 1.0019 \times 10^{-2}$ P and $\rho = 1$ g cm $^{-3}$. For the sphere we shall assume a mass (m) of 1 g and a radius (σ) of 1.74×10^{-4} cm. If we now insert all these numerical values into (4.6), (4.8) and (4.9) and evaluate the ratios $D(t)/D_{NS}(t)$, $D(t)/D_{BB}(t)$, we obtain the curves plotted in figures 1 and 2 respectively.

5. Discussion

For the data chosen for E_1 and S_2 we obtain practically the same values for $D(t)/D_{NS}(t)$, as shown in figure 1. It is clear from this curve that, for any value of t , $D(t) > D_{NS}(t)$, which indicates that for the Maxwell fluids the mean square displacement (MSD) of the spheres is always *greater* than for a Newtonian fluid described by the Stokes approximation for the drag. Thus, as a function of time, the decay of the viscoelastic MSD is *slower* than for the Newtonian fluid and so the spheres diffuse (on average) over *larger* distances during the same time interval. But as (4.6) shows, this behaviour is analytic; algebraic decays of the type $t^{-n/2}$ (n integer) do not appear for this model. Note that for the chosen values of the parameters involved, figure 1 shows that $D(t)$ may be somewhat larger than $D_{NS}(t)$ over long time intervals, so correlations persist more in a Maxwell fluid than in a Newtonian one. On the other hand, $D(t) < D_{BB}(t)$ for any t , either for E_1 or S_2 (figure 2). This means that the decay of the MSD for the viscoelastic fluid is *faster* than for a Newtonian one with Boussinesq–Basset corrections and Brownian particles diffuse over *shorter* distances in this case.

So, the time behaviour of $D(t)$ is between that of $D_{NS}(t)$ and $D_{BB}(t)$. Yet, being always analytic, it is closer to that of $D_{NS}(t)$ where all the memory effects in the drag have been completely neglected. Thus, in the limit of Maxwell, elasticity does not appreciably modify the time-dependence of the drag and of $D(t)$, although its magnitude may be considerably larger than that of $D_{NS}(t)$. Long time tails do not show up in spite of the existence of a memory in the stochastic dynamics. Therefore a wide separation of timescales between microscopic and macroscopic processes exists for this model.

The time-dependent diffusion coefficient $D(t)$ may be also defined as the long time limit of the ratio $\langle \Delta R_i^2(t) \rangle / t$, where $\langle \Delta R_i^2(t) \rangle$ stands for the mean-square displacement of the particle. This may be rewritten as

$$D(t) = \frac{1}{3} \int_0^t ds (1 - s/t) \langle \mathbf{U}(0) \cdot \mathbf{U}(s) \rangle \quad (5.1a)$$

where, according to (4.5),

$$\langle \mathbf{U}(0) \cdot \mathbf{U}(s) \rangle = \int_{-\infty}^{\infty} d\mathbf{R} G_{ii}(\mathbf{R}, s). \quad (5.1b)$$

The question thus arises as to whether (4.5) and (5.1a) lead to the same results for a viscoelastic fluid. It is well known that for a Markovian-Brownian motion in a Newtonian fluid both definitions become identical if $\langle \mathbf{U}(0) \cdot \mathbf{U}(s) \rangle \rightarrow 0$ as $t \rightarrow \infty$, so that for times long compared to the velocity correlation time (5.1a) reduces to (4.5) (Berne and Pecora 1975). A similar argument holds for the viscoelastic case. Indeed, note that substitution of (4.4) into (5.1b) yields

$$\langle \mathbf{U}(0) \cdot \mathbf{U}(t) \rangle = 3\kappa_B T m^{-1} M(t) \quad (5.2)$$

where the Green function $M(t)$ is given by (3.2) and vanishes as $t \rightarrow \infty$, since $a > 0$, $b < 0$ (3.3). a^{-1} and b^{-1} thus measure the decay rate (correlation time) of the velocity correlation function and they should be smaller than the diffusion times if (5.1a) is going to be equivalent to (4.5). This is readily checked for E_1 , the most elastic of the fluids considered, by inserting the values of its parameters given in the previous section into (3.3). One finds that $b = 0.5$ s and $a = 5 \times 10^{-4}$ s, which are indeed much smaller than the times considered in figure 1.

It is worth pointing out that a similar conclusion is reached when the effects of elasticity on the drag coefficient for the creeping flow around a sphere (Acharya *et al* 1976, Kato *et al* 1972) indicate that this influence is not significant and that a Maxwell fluid behaves similarly to a Newtonian fluid. Whether the same conclusions are applicable to other properties of viscoelastic fluids remains to be assessed.

Finally it should be stressed that the relaxation model used for the viscoelastic flow is an approximation; perhaps when a more realistic model of viscoelasticity is used $D(t)$ will show long-time-tail effects.

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References

- Acharya A, Mashelkar R A and Ulbrecht J 1976 *Rheol. Acta* **15** 454
- Astarita G and Marrucci G 1974 *Principles of Non-Newtonian Fluid Mechanics* (New York: McGraw-Hill)
- Berne B J, Boom J P and Rice S A 1966 *J. Chem. Phys.* **45** 1086
- Berne B J and Pecora R 1975 *Dynamic Light Scattering* (New York: Wiley)
- Bird R B, Armstrong R C and Hassager D 1977 *Dynamics of Polymeric Liquids* vol 1 (New York: Wiley)
- Case K M 1971 *Phys. Fluids* **14** 2091
- Chandrasekhar S 1943 *Rev. Mod. Phys.* **25** 1
- Chhabra R P, Uhlherr P H T and Boger D V 1980 *J. Non-Newtonian Fluid Mech.* **6** 187
- Chow T S and Hermans J J 1972 *J. Chem. Phys.* **56** 3150
- Dufty J W 1974 *Phys. Fluids* **17** 328
- Fox R F and Uhlenbeck G 1970 *Phys. Fluids* **13** 1893
- Hauge E H and Martin-Löf A 1973 *J. Stat. Phys.* **7** 259
- Kato H, Tachibana M and Ockawa K 1972 *Bull. JSME* **15** 1556
- Kubo R, Toda M and Hashitsume N 1985 *Statistical Physics II* (Berlin: Springer) § 1.6
- Landau L D and Lifshitz E M 1960 *Fluid Mechanics* (Reading, MA: Addison-Wesley)
- van Hove L 1954 *Phys. Rev.* **95** 249
- Volkov V S and Pokrovsky V N 1983 *J. Math. Phys.* **24** 267
- Volkov V S and Vinogradov G V 1984 *J. Non-Newtonian Fluid Mech.* **15** 29
- Zwanzig R 1964 *J. Res. NBS B* **64** 143
- 1965 *Ann. Rev. Phys. Chem.* **16** 67
- Zwanzig R and Bixon M 1970 *J. Fluid Mech.* **69** 21