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Brownian Motion in a Fluid in Elongational Flow

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Brownian motion of a spherical particle in stationary elongational flow is studied. We derive the Langevin equation together with the fluctuation-dissipation theorem for the particle from nonequilibrium fluctuating hydrodynamics to linear order in the elongation-rate-dependent inverse penetration depths. We then analyze how the velocity autocorrelation function as well as the mean square displacement are modified by the elongational flow. We find that for times small compared to the inverse elongation rate the behavior is similar to that found in the absence of the elongational flow. Upon approaching times comparable to the inverse elongation rate the behavior changes and one passes into a time domain where it becomes fundamentally different. In particular, we discuss the modification of the $t^{-3/2}$ long-time tail of the velocity autocorrelation function and comment on the resulting contribution to the mean square displacement. The possibility of defining a diffusion coefficient in both time domains is discussed.

KEY WORDS: Brownian motion; elongational flow; fluctuation-dissipation theorem; fluctuations around stationary states.

1. INTRODUCTION

In 1851 Stokes[1] calculated the frequency-dependent friction coefficient for an oscillating sphere in a fluid which is at rest far from the sphere. It is simple to generalize the result to a fluid which is itself in oscillatory homogeneous flow. In 1924 Faxen[2] generalized Stokes' result to the case that the fluid is in stationary but inhomogeneous flow. In ref. 3, Faxen's theorem for stationary flow was generalized to the nonstationary and inhomogeneous case. Using this generalization of Faxen's theorem in a

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fluctuating fluid, it was then possible to give an explicit expression for the random Langevin force in terms of the fluctuations of the fluid velocity. Using the fluctuation-dissipation theorem for the Navier–Stokes Langevin equation, it was then shown that the random force on the particle satisfies the usual fluctuation-dissipation theorem.[4] This verifies the well-known fact that the Brownian motion of a colloidal particle is a consequence of the fluctuations of the carrier fluid. The relevance of fluctuating hydrodynamics is clearly expressed in the study of the Brownian motion of a particle. In fact, the friction coefficient enters the expression for the velocity autocorrelation function and its frequency dependence is the origin of the long-time tail of this velocity correlation function.

The above analysis was carried out using the linearized Navier–Stokes Langevin equation in an equilibrium fluid. It is tempting to assume that the same program could be carried out when the fluid far from the particle is in stationary elongational flow. Such a program was started in a previous paper[5] (to be referred to as paper I). There we analyzed the motion of a sphere relative to a fluid in elongational flow. We concluded that the penetration depth depends on the frequency, the elongation rate, and the direction. As a consequence, we find in this case a friction tensor which also depends on the frequency, the elongation rate, and the direction expressing the symmetry breaking due to the stationary motion of the fluid.

Our main purpose in this paper is to complete the program with the study of Brownian motion. We will analyze how the dependence of the friction tensor on the elongation rate affects the behavior of the velocity autocorrelation function and of the mean square displacement. In Section 2 we discuss the validity of the Langevin equation for the Brownian particle and we derive the necessary fluctuation-dissipation theorem to the appropriate order in the elongation rate. Section 3 is devoted to the computation of the velocity autocorrelation function. We analyze its long-time behavior and we find a contribution proportional to $t^{-1/2}$ in addition to the usual $t^{-3/2}$ long-time tail. An explicit expression is given for the frequency-dependent diffusion tensor. In Section 4 we calculate the mean square displacement of the Brownian particle and discuss how the dependence of the friction coefficient on the elongation rate and the frequency modifies the results given by Foister and van de Ven.[6] Some concluding remarks are given in the final section.

2. THE LANGEVIN EQUATION AND THE FLUCTUATION-DISSIPATION THEOREM

Our purpose in this section is to derive the Langevin equation for the Brownian particle and to show that the stochastic force satisfies a fluctuation-dissipation theorem. The procedure to be followed runs closely parallel to that employed in ref. 4 to get the same results but at equilibrium.

Let us consider a spherical Brownian particle moving with respect to an incompressible fluid in elongational flow:

$$\mathbf{v}_0(\mathbf{r}) = \boldsymbol{\beta} \cdot \mathbf{r} \tag{2.1}$$

Here $\boldsymbol{\beta}$ is a symmetric traceless tensor. In paper I, where we did not consider fluctuations, we showed that the force excerted on the particle is given by

$$\mathbf{K}(\omega) = -\boldsymbol{\xi}(\omega) \cdot [\mathbf{u}(\omega) - \boldsymbol{\beta} \cdot \mathbf{R}(\omega)] \tag{2.2}$$

where $\mathbf{u}(\omega)$ and $\mathbf{R}(\omega)$ are the frequency-dependent velocity and position of the particle and $\boldsymbol{\xi}(\omega)$ is the frequency-dependent friction tensor. In the frame of reference in which $\boldsymbol{\beta}$ is diagonal, the friction tensor is found to be also diagonal

$$\xi_{ij}(\omega) = \xi_j(\omega)\, \delta_{ij} \tag{2.3}$$

and we find to linear order in $a\alpha_i$

$$\xi_j = 6\pi\eta a \left[1 + \frac{a}{10} \left(7\alpha_j + \sum_m \alpha_m \right) \right] \tag{2.4}$$

Here η is the shear viscosity and a is the radius of the sphere. The friction tensor is furthermore a function of the inverse penetration depths

$$\alpha_j = [(-i\omega + \beta_j)/\nu]^{1/2}; \qquad \operatorname{Re} \alpha_j \geqslant 0 \tag{2.5}$$

Here β_i are the eigenvalues of $\boldsymbol{\beta}$ and $\nu = \eta/\rho$ (where ρ is the density of the fluid) is the kinematic viscosity. It follows from Eqs. (2.3) and (2.4) that in the limit $\beta_j = 0$ the friction tensor reduces to the usual[1] result

$$\xi = \xi_j = 6\pi\eta a(1 + a\alpha) \tag{2.6}$$

where $\alpha = \alpha_j(\beta_j = 0) = (-i\omega/\nu)^{1/2}$, to linear order in $a\alpha$.

If the motion takes place in a fluctuating fluid, the total force exerted on the particle contains a random contribution due to the fluctuating part of the pressure tensor. The force is given by

$$\mathbf{K} = -\int_S (\mathsf{P} + \rho \mathbf{v}\mathbf{v}) \cdot \mathbf{n}\, dS \tag{2.7}$$

where P is the pressure tensor and $\mathbf{v}$ the velocity field of the fluid. S is a surface which is an infinitesimal distance outside the surface and which is not moving. The motion of the fluid is described by means of the Navier–Stokes Langevin equation

$$\rho\, \partial \mathbf{v}/\partial \mathbf{t} = -\nabla \cdot (\mathsf{P} + \rho \mathbf{v}\mathbf{v}) \tag{2.8}$$

where the pressure tensor is given by

$$P_{ij} = p\delta_{ij} + \eta(\nabla_i v_j + \nabla_j v_i) + \sigma_{ij} \tag{2.9}$$

Here p is the hydrostatic pressure and σ is a random contribution with a zero average which satisfies the following fluctuation-dissipation theorem:

$$\langle \sigma_{ij}(\mathbf{r}, t)\, \sigma_{kl}(\mathbf{r}', t') \rangle = 2k_{\mathrm{B}} T\eta(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\, \delta(\mathbf{r} - \mathbf{r}')\, \delta(t - t') \tag{2.10}$$

valid for an incompressible fluid, where $\langle \cdots \rangle$ now indicates the average in the stationary state, k_{B} is Boltzmann's constant, and T is the temperature. Notice the fact that in the context of nonequilibrium fluctuating hydrodynamics (see, for example, ref. 7) this fluctuation-dissipation theorem is assumed to be valid also in a fluid in stationary elongational flow, an assumption which is reasonable in view of the local nature of this correlation function. From Eqs. (2.7) and (2.8) it is clear that the motions of the fluid and the particle are coupled. We may now identify the random force $\mathbf{K}_R$ on the particle by writing the total force as a sum of a systematic part and a random part

$$\mathbf{K}(\omega) = -\xi(\omega) \cdot [\mathbf{u}(\omega) - \boldsymbol{\beta} \cdot \mathbf{R}(\omega)] + \mathbf{K}_R(\omega) \tag{2.11}$$

Thus, the equation of motion of the particle becomes the following stochastic differential equation:

$$-i\omega m \mathbf{u} = -\xi \cdot (\mathbf{u} - \boldsymbol{\beta} \cdot \mathbf{R}) + \mathbf{K}_R \tag{2.12}$$

We want to show that Eq. (2.12) is a Langevin equation. To this end, we need to investigate the statistical properties of the random force $\mathbf{K}_R$. It follows from the definition of $\mathbf{K}_R$ and the fact that the average of Eq. (2.11) is given by Eq. (2.2) that $\langle \mathbf{K}_R \rangle = 0$. Following a method discussed in paragraph 4 of ref. 4 to derive the fluctuation-dissipation theorem, we will compute the quantity

$$\langle \mathbf{u}(\omega) - \boldsymbol{\beta} \cdot \mathbf{R}(\omega) \rangle \cdot \langle \mathbf{K}_R(\omega)\, \mathbf{K}_R^*(\omega') \rangle \cdot \langle \mathbf{u}^*(\omega') - \boldsymbol{\beta} \cdot \mathbf{R}^*(\omega') \rangle \tag{2.13}$$

Define the fluctuation of an unspecified quantity ψ as

$$\delta\psi = \psi - \langle \psi \rangle \tag{2.14}$$

and the velocities in a coordinate frame moving along with the unperturbed fluid velocity at the center of the particle by

$$\mathbf{V} = \mathbf{v} - \boldsymbol{\beta} \cdot \mathbf{R} \qquad \text{and} \qquad \mathbf{U} = \mathbf{u} - \boldsymbol{\beta} \cdot \mathbf{R} \tag{2.15}$$

Then, using Eqs. (2.11) and (2.14) and the fact that in our case the friction tensor is symmetric, one has the identity

$$\langle \mathbf{U} \rangle \cdot \mathbf{K}_R = \langle \mathbf{U} \rangle \cdot \delta \mathbf{K} - \langle \mathbf{K} \rangle \cdot \delta \mathbf{U} \tag{2.16}$$

which also can be written as

$$\langle \mathbf{U} \rangle \cdot \mathbf{K}_R = -\int_S [\langle \mathbf{V} \rangle \cdot \delta(\mathsf{P} + \rho \mathbf{v}\mathbf{v}) - \delta \mathbf{V} \cdot \langle \mathsf{P} + \rho \mathbf{v}\mathbf{v} \rangle] \cdot \mathbf{n}\, dS \tag{2.17}$$

where we have used "stick" boundary condition at the surface of the sphere. Using Gauss' theorem and the Fourier transform of Eq. (2.8) with respect to the time, one finds from Eq. (2.17)

$$\begin{aligned} \langle \mathbf{U} \rangle \cdot \mathbf{K}_R = -\int_{V_c} & [i\omega\rho(\delta \mathbf{v} \cdot \langle \mathbf{V} \rangle - \delta \mathbf{V} \cdot \langle \mathbf{v} \rangle) \\ & + (\nabla \langle \mathbf{V} \rangle) : \delta(\mathsf{P} + \rho \mathbf{v}\mathbf{v}) - (\nabla \delta \mathbf{V}) : \langle \mathsf{P} + \rho \mathbf{v}\mathbf{v} \rangle] \end{aligned} \tag{2.18}$$

In this last expression V_c is the volume of the fluid outside the sphere. Neglecting terms of linear order in β, one may replace $\mathbf{v}$ by $\mathbf{V}$ and $\delta \mathbf{v}$ by $\delta \mathbf{V}$, so that the first term inside brackets disappears. For the same reason we may replace $\mathbf{v}$ by $\mathbf{V}$ in the convection terms, which than become of third order in $\mathbf{V}$, and may therefore also be neglected. If we subsequently substitute Eq. (2.9) for P and the analogous equation for $\delta \mathsf{P}$, use the incompressibility condition, and again replace $\mathbf{v}$ by $\mathbf{V}$ and $\delta \mathbf{v}$ by $\delta \mathbf{V}$, we obtain

$$\langle \mathbf{U} \rangle \cdot \mathbf{K}_R = -\int_{V_c} \nabla \langle \mathbf{V} \rangle : \sigma \, d\mathbf{r} \tag{2.19}$$

As in ref. 4, this last equation together with Eq. (2.10) gives

$$\begin{aligned} & \langle \mathbf{U}(\omega) \rangle \cdot \langle \mathbf{K}_R(\omega)\, \mathbf{K}_R^*(\omega') \rangle \cdot \langle \mathbf{U}^*(\omega') \rangle \\ & \quad = 4k_B T\eta \cdot 2\pi\delta(\omega - \omega') \int_{V_c} \overline{\nabla \langle \mathbf{V}(\mathbf{r}, \omega) \rangle} : \overline{\nabla \langle \mathbf{V}^*(\mathbf{r}, \omega) \rangle}\, d\mathbf{r} \end{aligned} \tag{2.20}$$

where the overbar indicates the symmetric traceless part of a tensor.

Next we also compute the quantity

$$\langle \mathbf{U} \rangle \cdot (\xi + \xi^\dagger) \cdot \langle \mathbf{U}^* \rangle = \langle \mathbf{U} \rangle \cdot \langle \mathbf{K}^* \rangle - \langle \mathbf{K} \rangle \cdot \langle \mathbf{U}^* \rangle \tag{2.21}$$

where the dagger indicates the Hermitian conjugate. Following the steps indicated above (see also ref. 4), one gets, neglecting again terms of linear and higher order in the rate of elongation,

$$\langle \mathbf{U} \rangle \cdot (\xi + \xi^\dagger) \cdot \langle \mathbf{U}^* \rangle = 2\eta \int_{V_c} \overline{\nabla \langle \mathbf{V} \rangle} : \overline{\nabla \langle \mathbf{V}^* \rangle}\, d\mathbf{r} \tag{2.22}$$

Comparing Eqs. (2.20) and (2.22), one finds the fluctuation-dissipation theorem for the random force

$$\langle \mathbf{K}_R(\omega)\, \mathbf{K}_R^*(\omega') \rangle = k_B T[\xi(\omega) + \xi^\dagger(\omega)] \cdot 2\pi\delta(\omega - \omega') \tag{2.23}$$

As is clear from our analysis above, where the terms of linear and higher order in the elongation rate have been neglected, this fluctuation-dissipation theorem is only correct to linear order in $a\alpha_i$. Notice in this context that the elongation rate is quadratic in α_i. In the limit of zero elongation rate, Eq. (2.23) reduces to the fluctuation-dissipation theorem for a fluid at equilibrium to linear order in $a\alpha$. Two important differences with the equilibrium case should be pointed out. The first one concerns the dependence of the friction tensor on the direction. This gives rise to correlations between the different components of the random force if a coordinate system is used in which the friction tensor is not diagonal. As a consequence, the velocity autocorrelation function matrix will contain analogous nondiagonal terms. The second difference originates in the fact that the friction tensor depends on the elongation rate through α_i. In the zero-frequency limit the friction tensor does not reduce to the Stokes value. The consequences for the diffusion tensor will be discussed in the next sections in more detail.

3. VELOCITY AUTOCORRELATION FUNCTION

Combining the Langevin equation (2.12) with $\mathbf{u}(\omega) = -i\omega\mathbf{R}(\omega)$, one finds as solution for the fluctuations of the velocity

$$\delta\mathbf{u}(\omega) = i\omega[m\omega^2 + \xi \cdot (i\omega + \beta)]^{-1} \cdot \mathbf{K}_R \tag{3.1}$$

Using the fluctuation-dissipation theorem (2.23), one finds for the velocity autocorrelation function

$$\langle \delta\mathbf{u}(\omega)\, \delta\mathbf{u}^*(\omega') \rangle = \mathsf{S}(\omega) \cdot 2\pi\delta(\omega - \omega') \tag{3.2}$$

where the spectral density $\mathsf{S}(\omega)$, which depends clearly on the elongation rate, is given by

$$\mathsf{S}(\omega) = k_B T\omega^2[m\omega^2 + \xi \cdot (i\omega + \beta)]^{-1} \cdot (\xi + \xi^\dagger) \cdot [m\omega^2 + (-i\omega + \beta^\dagger) \cdot \xi^\dagger]^{-1} \tag{3.3}$$

In the coordinate frame in which β is diagonal the spectral density is also diagonal and has the form

$$S_{ij}(\omega)=S_j(\omega)\,\delta_{ij} \tag{3.4}$$

where the diagonal terms are

$$S_j(\omega)=2k_{\mathrm{B}}T\omega^2[m\omega^2+\xi_j(i\omega+\beta_j)]^{-1}\,(\mathrm{Re}\,\xi_j)[m\omega^2+(-i\omega+\beta_j)\,\xi_j^*]^{-1} \tag{3.5}$$

Introducing the complex relaxation times

$$\tau_{D,j}\equiv\frac{2m}{\xi_j}\left[1+\left(1+4\frac{m\beta_j}{\xi_j}\right)^{1/2}\right]^{-1},\qquad \tau_{C,j}\equiv\frac{2m}{\xi_j}\left[1-\left(1+4\frac{m\beta_j}{\xi_j}\right)^{1/2}\right]^{-1} \tag{3.6}$$

we may write the spectral density as

$$S_j(\omega)=\frac{2k_{\mathrm{B}}T\omega^2\,\mathrm{Re}\,\xi_j}{m^2(\omega+i/\tau_{D,j})(\omega-i/\tau_{D,j}^*)(\omega+i/\tau_{C,j})(\omega-i/\tau_{C,j}^*)} \tag{3.7}$$

Using the fact that in usual experiments $\beta_i \ll |\xi_i/m|$, we find that the relaxation times reduce to

$$\tau_{D,j}=m/\xi_j,\qquad \tau_{C,j}=-\beta_j^{-1} \tag{3.8}$$

and from now on we will use these values. As a consequence, $|\tau_{D,j}| \ll |\tau_{C,j}|$ and one may therefore distinguish three regimes:

(i) $t \ll |m/\xi_j|$; this we call the inertial regime and is the regime in which inertial effects dominate the behavior.

(ii) $|m/\xi_j| \ll t \ll |\beta_j^{-1}|$; this we call the diffusion regime, as the behavior is most analogous to the usual diffusion process.

(iii) $|\beta_j^{-1}| \ll t$; this we call the convection regime.

Notice the fact that the transition times from one regime to another depend on the direction. It should be realized that the dependence of the friction coefficients on the elongation rate modifies the behavior in all three regimes. As these modifications are small and not very interesting in the inertial regime, we take $\omega \ll |\xi_j/m|$, so that Eq. (3.7) reduces to

$$S_j(\omega)=2k_{\mathrm{B}}T\,\mathrm{Re}\,\frac{1}{\xi_j}\,\frac{\omega^2}{(\omega-i\beta_j)(\omega+i\beta_j)} \tag{3.9}$$

Using Eq. (2.4), we have to linear order in α_i

$$\frac{1}{\xi_j}=\frac{1}{6\pi\eta a}\left[1+\frac{a}{10}\left(7\alpha_j+\sum_m \alpha_m\right)\right]^{-1}\cong\frac{1}{6\pi\eta a}\left[1-\frac{a}{10}\left(7\alpha_j+\sum_m \alpha_m\right)\right] \quad (3.10)$$

In the diffusion regime, $\omega \gg |\beta_j|$ and one obtains to linear order in β_j

$$\alpha_j=(-i\omega/\nu)^{1/2}\,(1+i\beta_j/2\omega)=\alpha(1+i\beta_j/2\omega) \quad (3.11)$$

Substituting this expression in Eq. (3.10) then gives, using the fact that $\boldsymbol{\beta}$ is traceless,

$$1/\xi_j=(1/6\pi\eta a)[1-\alpha a(1+7i\beta_j/20\omega)] \quad (3.12)$$

Upon substitution of this equation in Eq. (3.9), we obtain

$$S_j(\omega)=\frac{k_{\mathrm{B}}T}{3\pi\eta a}\,\mathrm{Re}\left[1-\alpha a\left(1+\frac{7i\beta_j}{20\omega}\right)\right]\mathrm{Re}\left(1-\frac{\beta_j}{i\omega+\beta_j}\right) \quad (3.13)$$

The 1 inside the square brackets corresponds to the contribution which is found if one uses the Stokes friction coefficient. If one neglects the term proportional to $a\alpha$, the description reduces to the one used, e.g., by Foister and van de Ven.[6] The term proportional to $a\alpha$ is the term which for $\beta_j=0$ gives the $t^{-3/2}$ long-time tail of the velocity autocorrelation function. The β_j dependence outside the brackets modifies the contribution from the Stokes term as well as the long-time tail. As we have expanded $1/\xi_j$ in β_j/ω, we should in fact also expand the last term. While this is convenient for the purpose of calculating the modification of the long-time tail, it is not convenient for the modification of the other term and we thus use

$$S_j(\omega)=\frac{k_{\mathrm{B}}T}{3\pi\eta a}\,\mathrm{Re}\left[1-\frac{\beta_j}{i\omega+\beta_j}-a\alpha\left(1+\frac{7i\beta_j}{20\omega}\right)\right] \quad (3.14)$$

Inverse Fourier transformation[3] of this expression gives

$$S_j(t)=\frac{k_{\mathrm{B}}T}{6\pi\eta a}\left[2\delta(t)+\beta_j e^{\beta_j t}+a(4\pi\nu)^{-1/2}\,t^{-3/2}\left(1-\frac{7}{10}\beta_j t\right)\right] \quad (3.15a)$$

$$=\frac{k_{\mathrm{B}}T}{6\pi\eta a}\left[2\delta(t)+\beta_j+a(4\pi\nu)^{-1/2}\,t^{-3/2}\left(1-\frac{7}{10}\beta_j t\right)\right] \quad (3.15b)$$

where we used $|\beta_j t| \ll 1$ in the last identity. Equations (3.15) show how the velocity autocorrelation function in the diffusion regime is modified by the

[3] One must be careful with the choice of the contour in the complex ω plane in order to assure the proper causal nature of the Green's function.

shear gradient to linear order in β_j. Because of the traceless nature of $\boldsymbol{\beta}$, the trace of the velocity autocorrelation function

$$\operatorname{Tr} \mathsf{S}(t) = \sum_j S_j(t) = \frac{k_B T}{2\pi\eta a} [\delta(t) + a(4\pi\nu)^{-1/2} t^{-3/2}] \tag{3.16}$$

is not modified to linear order in β_j in the diffusion regime. When one approaches the convection regime, $\beta_j t$ becomes comparable to 1, and higher powers of $\beta_j t$ should also be taken into account.

In the convection regime one has $\omega \ll |\beta_j|$, so that Eq. (3.9) reduces to

$$S_j(\omega) = 2k_B T(\omega/\beta_j)^2 \operatorname{Re}[1/\xi_j(\omega = 0)] \tag{3.17}$$

This expression would seem to imply that $S_j(t)$ has decayed to zero in this regime. While this conclusion is essentially correct in directions where $\beta_j < 0$, it is incorrect in directions for which $\beta_j > 0$. In these directions, as is clear from Eq. (3.15a), the velocity autocorrelation function diverges. In fact, if one uses the Stokes friction, one has

$$S_j(t) = \frac{k_B T}{6\pi\eta a} [2\delta(t) + \beta_j e^{\beta_j t}] \tag{3.18}$$

which is valid in both the diffusion and convection regimes in this case. We have not calculated the modified behavior of the long-time tail in the convection regime, but it seems clear that it will also contain factors proportional to $\exp(\beta_j t)$ and will thus have similar convergence problems.

Because of the rather complex behavior of the velocity autocorrelation function, it is not really clear how a frequency-independent diffusion coefficient should be defined in the two regimes. We will postpone the discussion of a possible definition of such a quantity to the next section, where we study the mean square displacement.

Of course one may always define a frequency-dependent diffusion tensor using

$$\mathsf{D}(\omega) = \frac{1}{2} \mathsf{S}(\omega) = \int_0^\infty dt \, \langle \delta \mathbf{u}(t) \, \delta \mathbf{u}(0) \rangle \cos \omega t \tag{3.19}$$

If one then restricts the value of the frequency to the diffusion regime where $|\beta_j| \ll \omega$, the above expression together with Eq. (3.9) gives

$$D_{ij}(\omega) = D_j(\omega) \, \delta_{ij} = k_B T \operatorname{Re}[1/\xi_j(\omega)] \, \delta_{ij} \tag{3.20}$$

which is the familiar expression in terms of the frequency-dependent friction coefficient. In the convection regime where $\omega \ll |\beta_j|$ one obtains

$$D_j(\omega) = k_B T(\omega/\beta_j)^2 \operatorname{Re}[1/\xi_j(\omega = 0)] \tag{3.21}$$

which is rather different from the expression in the diffusion regime.

4. MEAN SQUARE DISPLACEMENT

In order to clarify the subsequent discussion we will first consider the special case in which the friction tensor is given by the Stokes value

$$\xi_{ij}(\omega) = 6\pi\eta a \delta_{ij} \tag{4.1}$$

Substituting in Eq. (2.12), Fourier transforming back, and using $\mathbf{u}(t) = d\mathbf{R}(t)/dt$ gives

$$m\, d^2\mathbf{R}(t)/dt^2 = -6\pi\eta a[d\mathbf{R}(t)/dt - \boldsymbol{\beta}\cdot\mathbf{R}(t)] + \mathbf{K}_R(t) \tag{4.2}$$

It is easy to solve this expression explicitly and one obtains

$$R_j(t) = [m(-1/\tau_{C,j} + 1/\tau_{D,j})]^{-1} \int_0^t dt' \, \{\exp[-(t-t')/\tau_{C,j}] - \exp[-(t-t')/\tau_{D,j}]\} \, K_{R,j}(t') \tag{4.3}$$

where $\tau_{C,j}$ and $\tau_{D,j}$ are given by Eq. (3.8), where one should substitute $6\pi\eta a$ instead of ξ_j. Note the fact that we took not only $R_j(0) = 0$ but also $u_j(0) = 0$. Using again the fact that $|\beta_i| \ll 6\pi\eta a/m$, one may use in this case

$$\tau_{D,j} = m/6\pi\eta a, \qquad \tau_{C,j} = -\beta_j^{-1} \tag{4.4}$$

Substituting these simplifications in Eq. (4.3), one finds

$$R_j(t) = (1/6\pi\eta a) \int_0^t dt' \, \{\exp[\beta_j(t-t')] - \exp[-6\pi\eta a(t-t')/m]\} \, K_{R,j}(t') \tag{4.5}$$

Notice the fact that both in Eq. (4.3) and in Eq. (4.5) the initial condition for the particle sets the position as well as the velocity equal to zero at $t = 0$ so that the random force only contributes to $\delta R_j(t)$ after $t = 0$. Using the above equations and the fluctuation-dissipation theorem for the random force we find for the mean square displacement

$$\langle R_j^2(t)\rangle = D_0\{[\exp(2\beta_j t) - 1]/\beta_j - 4[\exp(\beta_j - 6\pi\eta a/m)t - 1]\} \times \{(\beta_j - 6\pi\eta a/m) - [\exp(-12\pi\eta a t/m) - 1](m/6\pi\eta a)\}^{-1} \tag{4.6}$$

where $D_0 \equiv k_B T/6\pi\eta a$ is the Stokes–Einstein diffusion coefficient. Beyond the inertial regime, i.e., $t \gg m/6\pi\eta a$, the mean square displacement reduces to

$$\langle R_j^2(t)\rangle = D_0[\exp(2\beta_j t) - 1]/\beta_j \tag{4.7}$$

This expression is the same as the one given by Foister and van de Ven[6] if one uses a coordinate frame rotated 45° with respect to the one they use in their solution. In the diffusion regime the above equation gives

$$\langle R_j^2(t)\rangle = 2D_0 t(1+\beta_j t+\cdots) \tag{4.8}$$

Since in the diffusion regime $|\beta_j t| \ll 1$, it follows from Eq. (4.8) that the diffusion coefficient is most appropriately defined by D_0. When one approaches the convection regime this definition is no longer correct, however. In the convection regime Eq. (4.7) shows that the mean square displacement diverges exponentially if $\beta_j > 0$, gives the diffusive value $2D_0 t$ if $\beta_j = 0$, and approaches $|D_0/\beta_j|$ if $\beta_j < 0$. It is clear that no diffusion coefficient can be defined in the convection regime for directions where $\beta_j \neq 0$.

In order to analyze how these results are modified by using $\xi_j(\omega)$ instead of the Stokes value, we use the identity

$$\langle R_j^2(t)\rangle = 2\int_0^t dt' \int_0^{t'} dt'' \, \langle u_j(t'')\, u_j(0)\rangle = 2\int_0^t dt' \int_0^{t'} dt'' \, S_j(t'') \tag{4.9}$$

It is important to realize that the mean square displacement depends on the initial condition for the velocity of the particle. In deriving Eq. (4.6) we took $u_j(0) = 0$, whereas in the derivation of both the explicit expressions for $S_j(t)$ in the previous section and the above identity the possible values of $u_j(0)$ are given by a Maxwell distribution. Substitution of Eq. (3.15b) into Eq. (4.9) gives for the mean square displacement in the diffusion regime

$$\langle R_j^2(t)\rangle = 2D_0\left[t\left(1+\frac{1}{2}\beta_j t\right) + a(4\pi\nu)^{-1/2}\int_{\tau_s}^t dt' \int_{\tau_s}^{t'} dt'' \, (t'')^{-3/2}\left(1-\frac{7}{10}\beta_j t''\right)\right] \tag{4.10}$$

where $\tau_s \equiv m/6\pi\eta a$. This lower cutoff in the integration is used to account for the fact that Eq. (3.15b) is only valid for times larger than τ_s and is necessary to eliminate a divergence. Keeping only the largest power of t due to the long-time tail and its correction linear in β_j, we obtain

$$\langle R_j^2(t)\rangle = 2D_0\left[t\left(1+\frac{1}{2}\beta_j t\right) + 2a(\pi\nu)^{-1/2}\, t^{-1/2}\left(1+\frac{7}{30}\beta_j t\right)\right] \tag{4.11}$$

It is clear that for small values of $\beta_j t$ the mean square displacement is the same as in the absence of shear. When $|\beta_j t|$ increases, the elongational flow modifies the Stokes–Einstein term as well as the term due to the long-time tail. The difference of 1/2 in the modification of the Stokes–Einstein term is due to the different initial conditions used. Given the size of the various contributions in Eq. (4.11), it is most appropriate to identify the Stokes–Einstein value D_0 as the time-independent diffusion coefficient in the diffusion regime also for a system in elongational flow. For longer times when one passes into the convection regime D_0 can no longer be identified as the diffusion coefficient. In fact, the time dependence of the mean square displacement, like the time dependence of the velocity autocorrelation function, becomes such that its typical behavior is no longer diffusionlike.

5. CONCLUSIONS

We have shown that it is possible to extend the validity of the fluctuation-dissipation theorem to linear order in the inverse penetration depths. Using this extension, we were then able to discuss how the velocity autocorrelation function and the mean square displacement are modified by the dependence of the friction coefficients in the various directions on the rate of elongation. We have not been able to prove the validity of the fluctuation-dissipation theorem to higher order in the inverse penetration depths. In fact, this theorem may very well not be valid to higher order in these inverse penetration depths, as the validity of such a theorem in this nonequilibrium situation is certainly not self-evident.

In elongational flow the motion of the Brownian particle in the convection regime, i.e., for times larger than the inverse elongation rate, is in general not diffusive. The occurrence of Taylor diffusion in the convection regime, for instance, for Poiseuille flow, is due in part to the presence of boundaries which eliminate divergences like those found above in this regime.

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