Dynamics of Rodlike Polymers in Dilute Solution

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ABSTRACT: In this paper we calculate the translational and rotational friction coefficients for a suspended rigid rod as well as its contribution to the viscosity in the dilute limit as a function of the aspect ratio. In the long rod limit the asymptotic behavior is found to be identical to Yamakawa's expressions. For finite rods, our results, in particular those for the translational friction coefficient, reproduce numerical values obtained by Tirado et al. and differ from the values obtained by Broersma using the Oseen-Burgers approximation and from the values obtained later using the slender body theory.

1. Introduction

In a wide variety of physico-chemical problems, one has to deal with suspensions of rodlike particles. There are many characteristics of the system that make its study rather complicated. For instance, one can mention the anisotropy of the particles which makes them more easily oriented by external fields and the elongated form that makes the entanglement effect in semidilute suspensions much more noticeable than for flexible polymers, and furthermore, in sufficiently concentrated suspensions the system exhibits a liquid crystalline phase. In dilute solutions the main source of complication is the interaction of the rod with the solvent. The different parts of the particle cause disturbances in the velocity field that affect the whole motion of the polymer. These are the so-called hydrodynamic interactions which take place between any surface element of the suspended particles. In the case of a single sphere, one can compute the friction coefficients rather easily due to its simple geometrical form and exact results have been known for dilute suspensions for a long time.[1,2] In the case of elongated particles, however, calculations are much more difficult and there are only exact results for ellipsoids[3] and spheroids.[4,5] The problem of computing the friction coefficients for other elongated particles has been attempted by several authors. Kirkwood et al.,[6] modeled the particle as a line of touching spheres ("shish-kebab" model) and considered the hydrodynamic interactions between the different spheres. Broersma[7] used a cylinder-like model and solved the hydrodynamic problem by using an extended version of the Oseen-Burgers[8] procedure and, in this way, obtained expressions for the translational and rotational friction coefficients. In the Oseen-Burgers procedure, the force of the particle on the fluid is located along the symmetry axis of the particle. Yamakawa[9] also used this procedure to get the reduced viscosity in the long cylinder limit. Further developments of the "slender body" theory initiated by Burgers were given by Cox[10,11] and Batchelor.[12] A different approach was followed by Youngren et al.[13] and Tirado et al.[14] In Tirado et al.'s work the surface of the cylinder is modeled by a stack of rings, all of which are composed by small touching spheres. The hydrodynamic problem is reduced to the consideration of the friction of the spheres and the hydrodynamic interaction between all the spheres. In the analysis of Youngren et al. a rather similar technique was used in which the surface is subdivided into a collection of finite elements in which the force density is then assumed to be constant. They restrict themselves to translational motion parallel to the axis, for which they find the same results as Tirado et al. within the error Youngren et al. quote. Note in this respect that the error they quote is relative to the friction coefficient and leads to a much larger error in the coefficient $\gamma_\parallel$ plotted by Tirado et al.[14] From the experimental point of view, the expressions given by Broersma[7,15,16] and Tirado et al.[14,17,18] are widely used in fitting experimental data.[18,19] Tirado et al.'s expressions turn out to be most useful in this respect.

In this paper we model the cylindrical particle using a force distribution on the surface of the cylinder which is chosen to be uniformly distributed around the axis. This implies, on the one hand, that any force distribution which does not have this symmetry is replaced by a distribution which is uniform for rotation of the cylinder around its axis. On the other hand, this procedure places a possible force distribution at the end plates on the circumference of the cylinder near its extremes. Our analysis goes beyond the slender body theory in the sense that the force distribution is located on the surface of the cylinder rather than on its axis. The solvent is taken as a continuum whose dynamic properties are described by the Navier-Stokes equation.[20] In our description we have also included thermal noise in the bulk of the solvent, which is responsible for the spontaneous fluctuations of the velocity field. These fluctuations are, for instance, the cause of the Brownian motion performed by the suspended particles. In section 2 we derive the Langevin equation containing all the dynamic features of the coupling between the motion of the particle and the solvent. In section 3 we use the results of section 2 to compute the expressions of the translational and rotational diffusion coefficients and the reduced viscosity in the long rod limit and reproduce the expressions given by Yamakawa.[9] Murakami, who used essentially the same kind of force distribution, was not able to reproduce the correct asymptotic behavior.[21] In section 4 we take finite-size effects into account in the evaluation of the values of these transport coefficients. The results are compared with the analytical calculations of Broersma[7,15,16] and with the numerical data of Tirado et al.[14,17,18] We find that our analytical calculation reproduces the values given by Tirado et al.[14] for the translational friction coefficient for motion along the axis and, for motion in the direction orthogonal to the axis, is very close, unlike those given by

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Broersma.[16] For the rotational friction coefficient our result is about as much above the values given by Tirado et al. as Broersma's values are below. Furthermore, we also give the viscosity which was until now only given in the long cylinder limit by Yamakawa.[9] In the last section, a discussion of these results is given.

2. Equation of Motion of the Rod

Our purpose in this section is to derive the equation of motion of the polymer, following the line of reasoning given in refs 22 and 23. Thus, the motion of the fluid will be governed by the linearized Navier–Stokes equation with appropriate stochastic sources accounting for the presence of fluctuations in the fluid. One has

$$\rho\frac{\partial\vec{v}(\vec{r},t)}{\partial t} = -\nabla\cdot\vec{\vec{P}}(\vec{r},t) \qquad (2.1)$$

together with the incompressibility condition

$$\nabla\cdot\vec{v} = 0 \qquad (2.2)$$

In eqs 2.1 and 2.2 ρ is the density, $\vec{v}(\vec{r},t)$ is the velocity field, and $\vec{\vec{P}}(\vec{r},t)$ is the pressure tensor. This quantity is given by

$$P_{\alpha\beta} = p\delta_{\alpha\beta} - \eta\left(\frac{\partial v_\beta}{\partial r_\alpha} + \frac{\partial v_\alpha}{\partial r_\beta}\right) + \Pi^{R}_{\alpha\beta} = P^{s}_{\alpha\beta} + \Pi^{R}_{\alpha\beta} \qquad (2.3)$$

where p is the hydrostatic pressure and η the shear viscosity. Furthermore, $\Pi^{R}_{\alpha\beta}$ is the random pressure tensor. According to fluctuating hydrodynamics,[20] the random pressure tensor is a Gaussian white noise with

$$\langle\vec{\vec{\Pi}}^{R}(\vec{r},t)\rangle = 0 \qquad (2.4)$$

$$\langle\Pi^{R}_{\alpha\beta}(\vec{r},t)\Pi^{R}_{\gamma\mu}(\vec{r}\,',t')\rangle = 2k_{B}T\eta\Delta_{\alpha\beta\gamma\mu}\delta(\vec{r}-\vec{r}\,')\delta(t-t') \qquad (2.5)$$

where use has been made of the fourth-rank traceless symmetric unit tensor

$$\Delta_{\alpha\beta\gamma\mu} \equiv \delta_{\alpha\gamma}\delta_{\beta\mu} + \delta_{\alpha\mu}\delta_{\beta\gamma} - \frac{2}{3}\delta_{\alpha\beta}\delta_{\gamma\mu} \qquad (2.6)$$

In the presence of suspended particles one may also extend the validity of eq 2.1 inside the particles by the introduction of induced force densities.[24] The perturbations caused by the motion of the particles are then introduced through the induced forces. In dilute solution one can consider the presence of only one particle which, in our case, will be a cylinder of length L and radius a with the aspect ratio $\epsilon \equiv a/L < 1$. We will assume that the perturbations of the fluid decay instantaneously and will, therefore, use the so-called creeping flow approximation for the fluid dynamics from now on. Taking this into consideration, we can write the equation of motion of the whole system as

$$0 = -\nabla p(\vec{r},t) + \eta\nabla^2\vec{v}(\vec{r},t) + \vec{F}(\vec{r},t) - \nabla\cdot\vec{\vec{\Pi}}^{R}(\vec{r},t) \qquad (2.7)$$

where $\vec{F}(\vec{r},t)$ is the induced force density.

It is convenient here to introduce a comoving coordinate frame attached to the cylinder. Let us assume that the center of the cylinder is at the space point $\vec{R}$. We can choose a coordinate frame whose origin is placed at $\vec{R}(t)$ and whose z-axis coincides with the cylinder's axis which is pointing in the $\hat{s}(t)$ and corotates with the cylinder. A position in this frame will be given using cylindrical coordinates s, $r_\perp$, and φ where s is the distance along the axis of the cylinder from its center, $r_\perp$ is the distance orthogonal to the cylinder's axis, and φ is the azimutal angle around this axis. In this way, the surface of the cylinder is defined by $r_\perp = a$ and $|s| \le L/2$.

The induced force density is chosen such that the hydrostatic pressure inside the cylinder is zero,

$$p(\vec{r},t) = 0 \qquad r_\perp < a, |s| \le L/2 \qquad (2.8)$$

and the velocity field inside the cylinder is equal to the velocity of the cylinder at that point

$$\vec{v}(\vec{r},t) = \vec{u}(r_\perp,s,\varphi,t) \qquad r_\perp \le a, |s| \le L/2 \qquad (2.9)$$

On the surface of the cylinder we use stick boundary conditions so that the extended velocity field is continuous at the surface of the cylinder. In the quasistatic approximation used in this paper, the induced force density is only unequal to zero on the surface of the cylinder and can therefore be written as

$$\vec{F}(\vec{r},t) = \vec{F}^{(s)}(s,\varphi,t)\delta(r_\perp - a)\theta(L/2 - |s|) \qquad (2.10)$$

In this equation we have neglected the induced forces due to the end surfaces. In this paper we shall furthermore assume that the dependence of $\vec{F}^{(s)}(s,\varphi,t)$ on φ is not important for the properties that we want to describe so that, as a good approximation, one can take

$$\vec{F}^{(s)}(\varphi,s,t) \simeq \vec{f}(s,t)/2\pi a \qquad (2.11)$$

with $\vec{f}(s,t)$ being the induced force density per unit length. Both approximations are most appropriate for the long rod limit. We shall discuss the role of these approximations in the conclusion. Clearly, under such an approximation, rotations around the axis cannot be taken into account.

In order to explicitly solve eq 2.7, it is convenient to introduce the Fourier transform of the fields with respect to position. For instance, one has for the velocity field

$$\vec{v}(\vec{k},t) = \int d\vec{r}\,\exp(-i\vec{k}\cdot\vec{r})\vec{v}(\vec{r},t) \qquad (2.12)$$

In this representation we can obtain, using the incompressible nature of the fluid (2.2), from eq 2.7, the formal solution for the velocity field[24]

$$\vec{v}(\vec{k},t) = \vec{v}_0(\vec{k},t) + \frac{(\vec{\vec{1}} - \hat{k}\hat{k})}{\eta k^2}\cdot[\vec{F}(\vec{k},t) - i\vec{k}\cdot\vec{\vec{\Pi}}^{R}(\vec{k},t)] \qquad (2.13)$$

where $\vec{v}_0(\vec{k},t)$ is the velocity field due to sources at infinity and $\hat{k} \equiv \vec{k}/k$. This formal solution can also be expressed in real space giving

$$\vec{v}(\vec{r},t) = \vec{v}_0(\vec{r},t) + \int d\vec{r}\,'\,\vec{\vec{T}}(\vec{r}-\vec{r}\,')\cdot[\vec{F}(\vec{r}\,',t) - \nabla\cdot\vec{\vec{\Pi}}^{R}(\vec{r}\,',t)] \qquad (2.14)$$

Here, $\vec{\vec{T}}(\vec{r})$ is the Oseen tensor which corresponds to the Green function of the linearized quasistatic Navier–Stokes equation and is given by

$$\vec{\vec{T}}(\vec{r}) = \int d\vec{r}\,\exp(-i\vec{k}\cdot\vec{r})\frac{(\vec{\vec{1}} - \hat{k}\hat{k})}{\eta k^2} = \frac{1}{8\pi\eta r}(\vec{\vec{1}} + \hat{r}\hat{r}) \qquad (2.15)$$

Using stick boundary conditions, the average of the velocity field over the contour of a transverse section of the cylinder is equal to the velocity of the corresponding point on the axis. If we denote the position vector of a point of the $\hat{s}$-axis by $\vec{c}(s,t) = \vec{R} + s\hat{s}$, we have for the velocity of the corresponding point in the cylinder

$$\vec{u}(s,t) = \frac{1}{2\pi a}\int_0^{2\pi} d\varphi\,\vec{u}(r_\perp = a,s,\varphi,t) = \frac{1}{2\pi a}\int d\vec{r}\,'\,\delta(r'_\perp - a)\delta(s' - s)\vec{v}(\vec{r}\,',t) \qquad (2.16)$$

for $|s| \le L/2$. Using now the formal solution given in eq

2.13, one arrives at

$$\vec{u}(s,t) = \frac{1}{2\pi a}\int d\vec{r}'\ \delta(r'_{\perp} - a)\delta(s' - s) \times \{\vec{v}_0(\vec{r}',t) + \int d\vec{r}''\ \vec{\vec{T}}(\vec{r}' - \vec{r}'')\cdot[\vec{F}(\vec{r}'',t) - \nabla\cdot\vec{\vec{\Pi}}^{R}(\vec{r}'',t)]\} \quad (2.17)$$

By assuming that the flow in the absence of the polymer is homogeneous and given by $\vec{v}_0(\vec{r},t) = \vec{r}\cdot\vec{\vec{\beta}}$, the first integral of the right-hand side of eq 2.17 simply gives $\vec{c}(s,t)\cdot\vec{\vec{\beta}}$. Using eq 2.11 and the integral representation of the Oseen tensor given in eq 2.15, the term which contains the induced force density in eq 2.17 can be expressed as

$$\int_{-L/2}^{L/2} ds' \left\{\int \frac{d\vec{k}}{(2\pi)^3} \exp[ik_{\parallel}(s - s')]J_0^2(k_{\perp}a)\frac{\vec{\vec{1}} - \hat{k}\hat{k}}{\eta k^2}\right\}\cdot\vec{f}(s') \quad (2.18)$$

where $k_{\parallel}$ and $k_{\perp}$ are the components of the wavevector $\vec{k}$ parallel and perpendicular to the direction of the axis of the cylinder, respectively, and $J_0(x)$ is the Bessel function of first kind and order 0. We can then identify the mobility kernel

$$\vec{\vec{\mu}}(s - s') = \int \frac{d\vec{k}}{(2\pi)^3} \exp[ik_{\parallel}(s - s')]J_0^2(k_{\perp}a)\frac{\vec{\vec{1}} - \hat{k}\hat{k}}{\eta k^2} \quad (2.19)$$

The random part of the velocity field is written as

$$\vec{v}^{R}(s,t) = -\frac{1}{2\pi a}\int d\vec{r}'\ \delta(r'_{\perp} - a)\delta(s' - s)\int d\vec{r}''\ \vec{\vec{T}}(\vec{r}' - \vec{r}'')\cdot[\nabla\cdot\vec{\vec{\Pi}}^{R}(\vec{r}'',t)]$$
$$= -\int \frac{d\vec{k}}{(2\pi)^3} \exp(ik_{\parallel}s)J_0(k_{\perp}a)\frac{\vec{\vec{1}} - \hat{k}\hat{k}}{\eta k^2}\cdot\{i\vec{k}\cdot\vec{\vec{\Pi}}^{R}(\vec{k},t)\} \quad (2.20)$$

The properties of the part of the velocity follow from the ones of the random pressure tensor given in eqs 2.4 and 2.5 and are given by, cf. appendix A,

$$\langle \vec{v}^{R}(s,t)\rangle = 0 \quad (2.21)$$

After some algebra, one gets

$$\langle \vec{v}^{R}(s,t)\vec{v}^{R}(s',t')\rangle = 2k_BT\vec{\vec{\mu}}(s - s')\delta(t - t') \quad (2.22)$$

It should be noted in this context that the time rate of change of the position and orientations of the polymer are slow compared to the relaxation time of the velocity. As a result of this, and in accordance with the linearization of the Navier–Stokes equation, the stochastic properties of $\vec{v}^{R}$ given above are (and may be) calculated at any instant in time as if the position and orientation of the polymer were momentarily frozen.

In view of these considerations, we can obtain an equation relating the velocity of a given point of the cylinder axis with the induced force density, that is

$$\vec{u}(s,t) = \vec{c}(s,t)\cdot\vec{\vec{\beta}} + \int_{-L/2}^{L/2} ds'\ \vec{\vec{\mu}}(s - s')\cdot\vec{f}(s',t) + \vec{v}^{R}(s,t) \quad (2.23)$$

In the description of the fluid motion we have neglected acceleration. Similarly, we will neglect the acceleration of the polymer. This implies that the force exerted by the fluid on each segment of the cylinder is balanced by external and internal forces on this segment. As the force exerted on the particle by the fluid equals minus the force exerted by the fluid on the particle, we thus have

$$\vec{f}(s,t) = \vec{f}^{\,int}(s,t) + \vec{f}^{\,ext}(s,t) \quad (2.24)$$

where $\vec{f}^{\,int}$ is the force per unit length due to interactions with neighboring segments which, in this case, has to be considered as a force due to the rigid constraints, i.e. the force distribution necessary to assure that the rod neither bends nor stretches. Moreover, $\vec{f}^{\,ext}$ is the force per unit length due to external fields. Substituting $\vec{f}$ for $\vec{f}^{\,int} + \vec{f}^{\,ext}$ in eq 2.23 one obtains

$$\vec{u}(s,t) = \vec{c}(s,t)\cdot\vec{\vec{\beta}} + \int_{-L/2}^{L/2} ds'\ \vec{\vec{\mu}}(s - s')\cdot[\vec{f}^{\,int}(s',t) + \vec{f}^{\,ext}(s',t)] + \vec{v}^{R}(s,t) \quad (2.25)$$

This equation together with the stochastic properties of $\vec{v}^{R}$ given in eqs 2.21 and 2.22 describes the dynamics of the polymer including the effect due to the fluctuations of the fluid.

To go further, we will expand the variables of eq 2.25 in terms of Legendre polynomials which will be used in the next section to obtain certain explicit results. For an unspecified quantity $\phi(x,t)$, one has

$$\phi(x,t) = \sum_{l=0}^{\infty}\phi_l(t)P_l(x) \quad (2.26)$$

where $-1 < x < 1$ and $P_l(x)$ is the normalized Legendre polynomial of order l which follows from the formula

$$P_l(x) = \left(\frac{2l + 1}{2}\right)^{1/2}\frac{1}{2^l l!}\frac{d}{dx^l}(x^2 - 1)^l \quad (2.27)$$

The Legendre polynomials form a complete orthonormal set so that

$$\int_{-1}^{1} dx\ P_l(x)P_q(x) = \delta_{lq} \quad (2.28)$$

and

$$\phi_l = \int_{-1}^{1} dx\ \phi(x)P_l(x) \quad (2.29)$$

Now, we introduce the dimensionless variable $x \equiv 2s/L$ and expand $\vec{f}^{\,int}(x,t)$ and $\vec{f}^{\,ext}(x,t)$ in the sense of eq 2.26. Then, we multiply both sides of eq 2.25 by $P_l(x)$ and, after integration over x, we get

$$\vec{u}_l(t) = \vec{c}_l(t)\cdot\vec{\vec{\beta}} + \sum_{q=0}^{\infty}\vec{\vec{\mu}}_{lq}\frac{L}{2}[\vec{f}_q^{\,int}(t) + \vec{f}_q^{\,ext}(t)] + \vec{v}_l^{R}(t) \quad (2.30)$$

where use has been made of the orthogonality property of the Legendre polynomials. In this last equation we have introduced the mobility matrices $\vec{\vec{\mu}}_{lq}$

$$\vec{\vec{\mu}}_{lq} \equiv \int_{-1}^{1} dx\ dx'\ P_l(x)\vec{\vec{\mu}}(x - x')P_q(x') \quad (2.31)$$

In view of eqs 2.21, 2.22, and 2.29, the random term satisfies

$$\langle \vec{v}_l^{R}(t)\rangle = 0 \quad (2.32)$$

$$\langle \vec{v}_l^{R}(t)\vec{v}_q^{R}(t')\rangle = 2k_BT\vec{\vec{\mu}}_{lq}\delta(t - t') \quad (2.33)$$

Using the symmetry of $\vec{\vec{\mu}}(x - x')$ for interchange between x and x', it follows that

$$\vec{\vec{\mu}}_{ij} = \vec{\vec{\mu}}_{ji} \quad (2.34)$$

It is shown in appendix E that

$$\vec{\vec{\mu}}_{ij} = 0 \quad \text{if } i + j \text{ is odd} \quad (2.35)$$

This property is a consequence of the fact that the cylinder has an inversion center. The last relation is very useful because it results in a decoupling of translation and rotation. Furthermore, according to eq B.1, due to the symmetry of the system for rotations around the axis, the mobility matrices take the general form

$$\vec{\vec{\mu}}_{ij} \equiv \mu_{ij}^{\perp}(\vec{\vec{1}} - \hat{s}\hat{s}) + \mu_{ij}^{\parallel}\hat{s}\hat{s} \tag{2.36}$$

Due to the fact that $\vec{c}(s,t) = \vec{R}(t) + s\hat{s}(t)$, we straightforwardly get

$$\vec{c}_0(t) = \sqrt{2}\vec{R}(t) \tag{2.37}$$

$$\vec{c}_1(t) = \frac{L}{\sqrt{6}}\hat{s}(t) \tag{2.38}$$

$$\vec{c}_q(t) = 0 \quad \text{for } q \geq 2 \tag{2.39}$$

Differentiating $\vec{c}(s,t)$ with respect to time, one finds

$$\vec{u}_0(t) = \sqrt{2}\dot{\vec{R}}(t) \tag{2.40}$$

$$\vec{u}_1(t) = \frac{L}{\sqrt{6}}\dot{\hat{s}}(t) = \frac{L}{\sqrt{6}}\vec{\omega}(t) \times \hat{s}(t) \tag{2.41}$$

$$\vec{u}_q(t) = 0 \quad \text{for } q \geq 2 \tag{2.42}$$

where $\vec{\omega}$ is the angular velocity whose components are always orthogonal to $\hat{s}$. Note that the motion of the particle is represented by the first two components of $\vec{c}(s,t)$ in its representation in terms of Legendre polynomials only. It should be noted, however, that the mobility kernel is not diagonal in l and q so that the motion of the particle will be influenced by all the moments of the force distribution through its nondiagonal terms. One can also see that the zeroth order moment of the forces is proportional to the total force, $\vec{K}$, while the first order moment is related to the total torque $\vec{T}$, that is

$$\vec{K}(t) = \int_{-L/2}^{L/2} \mathrm{d}s\, \vec{f}(s,t) = \frac{L}{\sqrt{2}}\vec{f}_0(t) \tag{2.43}$$

$$\vec{T}(t) = \int_{-L/2}^{L/2} \mathrm{d}s\, s\hat{s}(t) \times \vec{f}(s,t) = \frac{L^2}{2\sqrt{6}}\hat{s}(t) \times \vec{f}_1(t) \tag{2.44}$$

Notice the fact that the higher order moments do not necessarily vanish. It is interesting to see that the random velocity is also different from zero for $l \geq 2$. In this way, we will show that random perturbations of higher order influence the motion of the particles due to the nondiagonal elements of the mobility kernel.

3. Polymer Dynamics

We proceed in this section to the analysis of the dynamics using the equation of motion (2.30) for the velocity of the particle. The representation in terms of Legendre polynomials given in this equation will permit us to analyze the motion of the center of mass and the rotational motion and to compute the viscosity. In this section we will consider the long cylinder limit, $\epsilon \to 0$, in which case it is justified to neglect the off-diagonal elements of the mobility kernel. It is found that this approximation leads to the results given by Yamakawa.[9] In the following section we will discuss the modification of these results when finite-size effects are taken into account.

3.1. Diffusion Coefficients. When the coupling due to the nondiagonal elements in the representation of the mobility kernel is neglected, the relevant equations are those of eq 2.30 where $l = 0, 1$. One has

$$\vec{u}_0(t) = \vec{c}_0(t)\cdot\vec{\vec{\beta}} - \vec{\vec{\mu}}_{00}\cdot\frac{L}{2}[\vec{f}_0^{\,\mathrm{int}}(t) + \vec{f}_0^{\,\mathrm{ext}}(t)] + \vec{v}_0^{\mathrm{R}} \tag{3.1}$$

$$\vec{u}_1(t) = \vec{c}_1(t)\cdot\vec{\vec{\beta}} - \vec{\vec{\mu}}_{11}\cdot\frac{L}{2}[\vec{f}_1^{\,\mathrm{int}}(t) + \vec{f}_1^{\,\mathrm{ext}}(t)] + \vec{v}_1^{\mathrm{R}} \tag{3.2}$$

The mobility matrices $\vec{\vec{\mu}}_{00}$ and $\vec{\vec{\mu}}_{11}$ are explicitly calculated in appendix B in the long rod limit neglecting terms of the order a/L.

We can then use eq 3.1 to calculate the center of mass diffusion coefficient. For this purpose we may take the external forces acting on the particle and the velocity gradients equal to zero. Furthermore, $\vec{f}_0^{\,\mathrm{int}}$ vanishes due to the fact that the total force due to interactions between neighboring segments is zero. Consequently, eq 3.1 simply reads

$$\vec{u}_0(t) = \vec{v}_0^{\mathrm{R}}(t) \tag{3.3}$$

Then, one has the center of mass velocity correlation function

$$\langle \vec{u}_0(t)\vec{u}_0(t')\rangle = \langle \vec{v}_0^{\mathrm{R}}(t)\vec{v}_0^{\mathrm{R}}(t')\rangle = 2k_{\mathrm{B}}T\vec{\vec{\mu}}_{00}\delta(t-t') \tag{3.4}$$

where the mobility tensor $\vec{\vec{\mu}}_{00}$ is given by (cf. appendix B)

$$\vec{\vec{\mu}}_{00} = \frac{1}{2\pi\eta L}\left\{2\left[\ln\frac{L}{2a} + 2\ln 2 - \frac{3}{2}\right]\hat{s}\hat{s} + \left[\ln\frac{L}{2a} + 2\ln 2 - \frac{1}{2}\right](\vec{\vec{1}} - \hat{s}\hat{s})\right\} \tag{3.5}$$

which depends on the orientation of the rod. In order to calculate the diffusion coefficient, we use the Green–Kubo formula

$$D_{\mathrm{G}} = \frac{1}{3}\int_0^\infty \mathrm{d}t'\, \langle \dot{\vec{R}}(t)\cdot\dot{\vec{R}}(t')\rangle_{\mathrm{eq}} \tag{3.6}$$

The average is now over the full equilibrium ensemble and, therefore, also over the slowly varying position and orientation of the rod. The average used in eq 3.4 differs in this respect. See also the remark below eq 2.22. Thus, using the relation $\vec{u}_0 = \sqrt{2}\dot{\vec{R}}$ and eq 3.6, one finds

$$D_{\mathrm{G}} = \frac{k_{\mathrm{B}}T}{3}\mathrm{tr}(\vec{\vec{\mu}}_{00}) \tag{3.7}$$

where the symbol $\mathrm{tr}(\vec{\vec{\mu}}_{00})$ stands for the trace of the tensor $\vec{\vec{\mu}}_{00}$. Making use of eq 3.5 is this last equation, one arrives at

$$D_{\mathrm{G}} = \frac{k_{\mathrm{B}}T}{3\pi\eta L}\left[\ln\frac{L}{2a} + 2\ln 2 - 1\right] \tag{3.8}$$

which is the result given by Yamakawa.[9]

The rotational motion can be analyzed in a similar way. Setting again $\vec{\vec{\beta}} = 0$ and $\vec{f}^{\,\mathrm{ext}} = 0$ in eq 3.2 and using $\dot{\hat{s}} = \vec{\omega} \times \hat{s}$, we get

$$\vec{u}_1(t) = \frac{L}{\sqrt{6}}\vec{\omega}(t) \times \hat{s}(t) = \vec{\vec{\mu}}_{11}\cdot\frac{L}{2}\vec{f}_1^{\,\mathrm{int}}(t) + \vec{v}_1^{\mathrm{R}}(t) \tag{3.9}$$

We multiply both sides of this last eq by $\hat{s}\times$ which leads us to

$$\frac{L}{\sqrt{6}}\hat{s} \times (\vec{\omega} \times \hat{s}) = \hat{s} \times \vec{v}_1^{\mathrm{R}} \tag{3.10}$$

where use has been made of the fact that $\vec{f}_1^{\,\mathrm{int}}$ is parallel to $\hat{s}$ and, therefore, $\hat{s} \times \vec{f}_1^{\,\mathrm{int}} = 0$. Furthermore, using the fact that $\vec{\omega}$ is orthogonal to $\hat{s}$, eq 3.10 can finally be written as

$$\vec{\omega} = \frac{\sqrt{6}}{L}\hat{s} \times \vec{v}_1^{\mathrm{R}} \tag{3.11}$$

Thus, the angular velocity correlation function is

$$\langle \vec{\omega}(t)\vec{\omega}(t')\rangle = \frac{12k_{\mathrm{B}}T}{L^2}\mu_{11}^{\perp}(\vec{\vec{1}} - \hat{s}\hat{s}) \tag{3.12}$$

where we have employed eq 2.33 with $l = q = 1$ and eq 2.36.

The mobility matrix $\overleftrightarrow{\mu}_{11}$ is, cf. appendix B,

$$\overleftrightarrow{\mu}_{11} = \frac{1}{2\pi\eta L}\left\{2\left[\ln\frac{L}{2a} + 2\ln 2 - \frac{17}{6}\right]\hat{s}\hat{s} + \left[\ln\frac{L}{2a} + 2\ln 2 - \frac{11}{6}\right](\overleftrightarrow{1} - \hat{s}\hat{s})\right\} \quad (3.13)$$

The rotational diffusion coefficient then follows from the corresponding Green–Kubo formula

$$D_r = \frac{1}{2}\int_0^\infty \mathrm{d}t\ \langle\vec{\omega}(t)\cdot\vec{\omega}(0)\rangle_{\mathrm{eq}} = \frac{3k_BT}{\pi\eta L^3}\left[\ln\frac{L}{2a} + 2\ln 2 - \frac{11}{6}\right] \quad (3.14)$$

which is again the result given by Yamakawa.[9] It should be noted that in obtaining eq 3.12 from eq 3.11, we assumed that $\langle\vec{\omega}\rangle = 0$. Of course one knows that $\langle\vec{\omega}\rangle_{\mathrm{eq}} = 0$ but is not obvious that the average in the restricted ensemble is also zero. The reason for this is that the rate of change of $\hat{s}(t)$ is caused by $\vec{v}_1^{\mathrm{R}}(t)$ and this could in principle make $\langle\hat{s}(t) \times \vec{v}_1^{\mathrm{R}}(t)\rangle \neq 0$. In appendix C we will show that this term is zero.

3.2. Viscosity. To derive the expression for the linear viscosity we will start from the corresponding Green–Kubo formula[25]

$$[\eta] = \frac{N_A}{Mk_BT}\int_0^\infty \mathrm{d}t\ \langle J_{xy}(t)J_{xy}(0)\rangle_{\mathrm{eq}} \quad (3.15)$$

where N_A is the Avogadro number and M, the molecular weight. Furthermore, the quantity $J_{\alpha\beta}(t)$ is the $\alpha\beta$ element of the tensor (we will use Green indices to denote the components of tensors and vectors and summation over repeated indices will be understood)

$$\overleftrightarrow{J} \equiv -\sum_m \vec{R}_m\vec{F}_m \quad (3.16)$$

with $\vec{R}_m$ being the position of the mth segment of the polymer with respect to the center of mass and $\vec{F}_m$, the sum of the internal and the external forces acting on the mth segment. According to this definition, in the case of our continuous rod, $\overleftrightarrow{J}$ is given by

$$\overleftrightarrow{J} = -\int_{-L/2}^{L/2}\mathrm{d}s\ s\hat{s}\vec{f}(s) = -\frac{L^2}{\sqrt{24}}\hat{s}\vec{f}_1 \quad (3.17)$$

where $\vec{f}_1 = \vec{f}_1^{\mathrm{int}} + \vec{f}_1^{\mathrm{ext}}$. According to our previous analysis, $\vec{f}_1$ is precisely the induced force, that is, the force that the particle exerts on the fluid. In deriving the above equation, we have substituted the sum over m by an integration over the contour length, replaced the force by force density per unit length, and used the definition of $\vec{f}_1$.

The fluid is in equilibrium and there are no external fields acting on the system. Due to the fact that, in the absence of external fields, $\vec{f}_1$ is parallel to the polymer axis, we find from eq 3.9 that

$$\frac{L}{2}\vec{f}_1 = \frac{L}{2}\vec{f}_1^{\mathrm{int}} = -\xi^{\parallel}\hat{s}\hat{s}\cdot\vec{v}_1^{\mathrm{R}} \quad (3.18)$$

where $\xi^{\parallel}$ is the parallel part of the friction matrix which is defined as the inverse of the mobility matrix $\overleftrightarrow{\mu}_{11}$. Making use of eq 2.36, then the friction matrix simply reads

$$\overleftrightarrow{\xi}_{11} \equiv \xi^{\perp}(\overleftrightarrow{1} - \hat{s}\hat{s}) + \xi^{\parallel}\hat{s}\hat{s} \quad (3.19)$$

with $\xi^{\parallel} = 1/\mu_{11}^{\parallel}$ and $\xi^{\perp} = 1/\mu_{11}^{\perp}$. Substitution of eq 3.18 into eq 3.17 gives

$$\overleftrightarrow{J} = \frac{L}{\sqrt{6}}\xi^{\parallel}\hat{s}\hat{s}\hat{s}\cdot\vec{v}_1^{\mathrm{R}} \quad (3.20)$$

Now, we will proceed to calculate the time-correlation function of $\overleftrightarrow{J}$. Neglecting for the time being the contribution due to correlations between $\hat{s}\hat{s}\hat{s}$ and $\vec{v}_1^{\mathrm{R}}$, one has

$$\langle J_{\alpha\beta}(t)J_{\gamma\nu}(0)\rangle = \frac{L^2}{6}(\xi^{\parallel})^2\hat{s}_\alpha\hat{s}_\beta\hat{s}_\mu\langle v_\mu^{\mathrm{R}}v_\delta^{\mathrm{R}}\rangle\hat{s}_\delta\hat{s}_\gamma\hat{s}_\nu = 2k_BT\frac{L^2}{6}\xi^{\parallel}\hat{s}_\alpha\hat{s}_\beta\hat{s}_\gamma\hat{s}_\nu\delta(t) \quad (3.21)$$

Averaging with respect to the equilibrium configurational distribution function, one then finds

$$\langle J_{\alpha\beta}(t)J_{\gamma\nu}(0)\rangle_{\mathrm{eq}} = 2k_BT\frac{L^2}{6}\xi^{\parallel}\delta(t)\int\frac{\mathrm{d}\hat{s}}{4\pi}\hat{s}_\alpha\hat{s}_\beta\hat{s}_\gamma\hat{s}_\nu = 2k_BT\frac{L^2}{6}\xi^{\parallel}\delta(t)\frac{1}{15}(\delta_{\alpha\beta}\delta_{\gamma\nu} + \delta_{\alpha\gamma}\delta_{\beta\nu} + \delta_{\alpha\nu}\delta_{\beta\gamma}) \quad (3.22)$$

This will give the so-called viscous contribution to the viscosity.[26]

Our next step will be to calculate the contribution to the stress tensor due to correlations between $\hat{s}$ and $\vec{v}_1^{\mathrm{R}}$. To this end, we have to consider that the configuration is not frozen and, consequently, there is some coupling between the random velocity and the orientational vector. We can then average $\overleftrightarrow{J}$ with respect to $\vec{v}_1^{\mathrm{R}}$ to obtain a slow contribution to the correlation function. However, one should realize that, since the configuration cannot be considered as frozen in this context, the Langevin equation for $\hat{s}$ becomes nonlinear. Using Stratonovich's interpretation rule of this Langevin equation, we have that $\langle\overleftrightarrow{J}\rangle_{\mathrm{eq}} = \langle\hat{s}\vec{f}_1^{\mathrm{int}}\rangle_{\mathrm{eq}} \neq 0$ for a system in equilibrium, which is clearly incorrect. The origin of this problem is the nonlinear nature of the Langevin equation. At this point one should add, as it is commonly done,[26] the Brownian force

$$\vec{f}_1^{\mathrm{B}} \equiv \frac{2}{L}\overleftrightarrow{\xi}_{11}\cdot\vec{v}_1^{\mathrm{R}} \quad (3.23)$$

to the induced (internal) force. Consequently, the velocity-averaged $\overleftrightarrow{J}$ should be written as

$$\langle\overleftrightarrow{J}\rangle = -\frac{L^2}{\sqrt{24}}\langle\hat{s}(\vec{f}_1 + \vec{f}_1^{\mathrm{B}})\rangle = -\frac{L}{\sqrt{6}}\xi^{\perp}\langle\hat{s}(\overleftrightarrow{1} - \hat{s}\hat{s})\cdot\vec{v}^{\mathrm{R}}\rangle = 3k_BT\left(\hat{s}\hat{s} - \frac{\overleftrightarrow{1}}{3}\right) \quad (3.24)$$

This term will end up giving the contribution to the viscosity due to rotational motion. We have explicitly performed this average in appendix C. Note that the tensor $(\hat{s}\hat{s} - \overleftrightarrow{1}/3)$ is the irreducible tensor of second rank[27] whose equilibrium average is zero so that $\langle\overleftrightarrow{J}\rangle_{\mathrm{eq}} = 0$.

In appendix D we show that

$$\langle\langle J_{\alpha\beta}\rangle(t)\langle J_{\gamma\nu}\rangle(0)\rangle_{\mathrm{eq}} = 9(k_BT)^2\exp(-6D_rt)\frac{1}{15}\left(\delta_{\alpha\gamma}\delta_{\beta\nu} + \delta_{\alpha\nu}\delta_{\beta\gamma} - \frac{2}{3}\delta_{\alpha\beta}\delta_{\gamma\nu}\right) \quad (3.25)$$

This will give the so-called elastic contribution to the viscosity.

Substituting the contributions given in eqs 3.22 and 3.25 into eq 3.15, for the viscosity we get

$$[\eta] = \frac{N_A}{Mk_BT}\int_0^\infty dt\left[2k_BT\frac{L^2}{6}\xi^{\parallel}\delta(t)\frac{1}{15} + 9(k_BT)^2\exp(-6D_rt)\frac{1}{15}\right] = \frac{N_AL^2}{90M}\left[\frac{1}{\mu_{11}^{\parallel}} + \frac{3}{2\mu_{11}^{\perp}}\right] \quad (3.26)$$

Making use of eq 3.13 we arrive at

$$[\eta] = \frac{N_A\eta\pi L^3}{90M}\left[\frac{1}{\ln(L/2a) + 2\ln 2 - {}^{17}/_6} + \frac{3}{\ln(L/2a) + 2\ln 2 - {}^{11}/_6}\right] \simeq \frac{2\pi N_A\eta L^3}{45M}\frac{1}{\ln(L/2a) + 2\ln 2 - {}^{25}/_{12}} \quad (3.27)$$

which is in agreement with the result given by Yamakawa.[9]

4. Finite-Size Effects

In the analysis of the finite-size cylinder two aspects have to be considered. On the one hand, one has to obtain expressions for the mobility matrices $\overleftrightarrow{\mu}_{ij}$ as functions of the aspect ratio ϵ from the mobility kernel given in eq 2.19. It is no longer correct to use the values obtained in the long rod limit as was done in the previous section. On the other hand, higher order moments of the force distribution are now coupled with translational and rotational motion through mobility matrices $\overleftrightarrow{\mu}_{ij}$ for $i \neq j$. In the previous section this coupling was neglected by using the fact that the diagonal elements, $i = j$, diverge logarithmically in the long rod limit while the off-diagonal elements remain constant. We find that only the first few of these higher order moments of the force distribution play a relevant role in the determination of the transport coefficients. Thus we will restrict our analysis to $l = 0$, 2, and 4 for the translational motion and to $l = 1$, 3, and 5 for the rotational motion and the viscosity. The results do not significantly change when moments of order 6 and 7 are respectively included in the description.

We will now first consider translational motion for which one then has, cf. eqs 2.24 and 2.30,

$$\begin{aligned} \vec{u}_0(t) - \vec{c}_0(t)\cdot\overleftrightarrow{\beta} &= \overleftrightarrow{\mu}_{00}\cdot\frac{L}{2}\vec{f}_0(t) + \overleftrightarrow{\mu}_{02}\cdot\frac{L}{2}\vec{f}_2(t) + \overleftrightarrow{\mu}_{04}\cdot\frac{L}{2}\vec{f}_4(t) + \vec{v}_0^{R} \\ 0 &= \overleftrightarrow{\mu}_{20}\cdot\frac{L}{2}\vec{f}_0(t) + \overleftrightarrow{\mu}_{22}\cdot\frac{L}{2}\vec{f}_2(t) + \overleftrightarrow{\mu}_{24}\cdot\frac{L}{2}\vec{f}_4(t) + \vec{v}_2^{R} \\ 0 &= \overleftrightarrow{\mu}_{40}\cdot\frac{L}{2}\vec{f}_0(t) + \overleftrightarrow{\mu}_{42}\cdot\frac{L}{2}\vec{f}_2(t) + \overleftrightarrow{\mu}_{44}\cdot\frac{L}{2}\vec{f}_4(t) + \vec{v}_4^{R} \end{aligned} \quad (4.1)$$

The expressions for the mobility matrices as functions of the aspect ratio ϵ are computed in appendix E. The mobility matrices satisfy $\overleftrightarrow{\mu}_{ij} = \overleftrightarrow{\mu}_{ji}$, cf. eq 2.34, and can be written as

$$\overleftrightarrow{\mu}_{ij} = \mu_{ij}^{\perp}(\overleftrightarrow{1} - \hat{s}\hat{s}) + \mu_{ij}^{\parallel}\hat{s}\hat{s} \quad (4.2)$$

according to eq 2.36.

The moments of the induced force density may be solved from eq 4.1, and one may then show that

$$\vec{u}_0(t) - \vec{c}_0(t)\cdot\overleftrightarrow{\beta} = \overleftrightarrow{\mu}^*_{00}\cdot\frac{L}{2}\vec{f}_0(t) + \vec{v}_0^* \quad (4.3)$$

where parallel and orthogonal components of the effective mobility and the effective random velocity are defined as

$$\mu_{00}^* = \mu_{00} + \frac{\mu_{02}(\mu_{24}\mu_{04} - \mu_{44}\mu_{02})}{\mu_{22}\mu_{44} - \mu_{24}^2} + \frac{\mu_{04}(\mu_{24}\mu_{02} - \mu_{22}\mu_{04})}{\mu_{22}\mu_{44} - \mu_{24}^2} \quad (4.4)$$

$$v_0^* = v_0^R + \frac{\mu_{02}(\mu_{24}v_4^R - \mu_{44}v_2^R)}{\mu_{22}\mu_{44} - \mu_{24}^2} + \frac{\mu_{04}(\mu_{24}v_2^R - \mu_{22}v_4^R)}{\mu_{22}\mu_{44} - \mu_{24}^2} \quad (4.5)$$

where we did not explicitly write the superscripts $\perp$ and $\parallel$ in both formulas since the components are not mixed. From eqs 2.33, 4.4, and 4.5, one may verify that

$$\langle\vec{v}_0^*(t)\vec{v}_0^*(t')\rangle = 2k_BT\overleftrightarrow{\mu}_{00}^*\delta(t - t') \quad (4.6)$$

Following the same procedure for the rotational motion, one arrives at

$$\vec{u}_1(t) - \vec{c}_1(t)\cdot\overleftrightarrow{\beta} = \overleftrightarrow{\mu}_{11}^*\cdot\frac{L}{2}\vec{f}_1(t) + \vec{v}_1^* \quad (4.7)$$

where the effective quantities now read

$$\mu_{11}^* = \mu_{11} + \frac{\mu_{13}(\mu_{35}\mu_{15} - \mu_{55}\mu_{13})}{\mu_{33}\mu_{55} - \mu_{35}^2} + \frac{\mu_{15}(\mu_{35}\mu_{13} - \mu_{33}\mu_{15})}{\mu_{33}\mu_{55} - \mu_{35}^2} \quad (4.8)$$

$$v_1^* = v_1^R + \frac{\mu_{13}(\mu_{35}v_5^R - \mu_{55}v_3^R)}{\mu_{33}\mu_{55} - \mu_{35}^2} + \frac{\mu_{15}(\mu_{35}v_3^R - \mu_{33}v_5^R)}{\mu_{33}\mu_{55} - \mu_{35}^2} \quad (4.9)$$

where we again omitted the superscripts $\perp$ and $\parallel$ explicitly in these formulas. From eqs 2.33, 4.8, and 4.9, one may now verify that

$$\langle\vec{v}_1^*(t)\vec{v}_1^*(t')\rangle = 2k_BT\overleftrightarrow{\mu}_{11}^*\delta(t - t') \quad (4.10)$$

In order to compare our results with other approximate results and with numerical data, it is convenient to write the mobilities given in eqs 4.4 and 4.8 in the following way

$$\overleftrightarrow{\mu}_{00}^* \equiv \frac{1}{2\pi\eta L}\left\{\left[\ln\left(\frac{L}{2a}\right) + \gamma_{00}^{\perp}(\epsilon)\right](\overleftrightarrow{1} - \hat{s}\hat{s}) + 2\left[\ln\left(\frac{L}{2a}\right) + \gamma_{00}^{\parallel}(\epsilon)\right]\hat{s}\hat{s}\right\} \quad (4.11)$$

and

$$\overleftrightarrow{\mu}_{11}^* \equiv \frac{1}{2\pi\eta L}\left\{\left[\ln\left(\frac{L}{2a}\right) + \gamma_{11}^{\perp}(\epsilon)\right](\overleftrightarrow{1} - \hat{s}\hat{s}) + 2\left[\ln\left(\frac{L}{2a}\right) + \gamma_{11}^{\parallel}(\epsilon)\right]\hat{s}\hat{s}\right\} \quad (4.12)$$

The functions $\gamma_{00}^{\perp,\parallel}(\epsilon)$ and $\gamma_{11}^{\perp,\parallel}(\epsilon)$, which are in fact defined by these formulas, are rather complex functions of ϵ involving logarithms and powers of ϵ. In Figures 1–4 we plot these functions compared with the numerical data of Tirado et al.[14,17,18] and the analytical calculations of Broersma.[7,15,16] The former modeled the cylinder by a stack of rings of touching beads and numerically solved the hydrodynamic problem of taking into account the hydrodynamic interaction between all the beads. The latter used the so-called Oseen–Burgers procedure described elsewhere. For a comparison with other results in the context of the slender body theory[12] and those of Youngren et al.,[13] we refer to Tirado et al.[14] As we showed in the preceding section, we recover the asymptotic values of Yamakawa,[9] who also used the Oseen–Burgers procedure in the $\epsilon \to 0$ limit. Broersma finds these values in this limit as well. The calculations of Tirado et al. do not reach this limiting value for small ϵ. For finite values of ϵ our results and, in particular those for $\gamma_{00}^{\parallel}$, agree very well with those obtained by Tirado et al. This is the case even for small values of ϵ. Nevertheless, our result increases for even smaller values of ϵ than those considered by Tirado et al. to the asymptotic value 2 ln 2 − $^3/_2$ given by

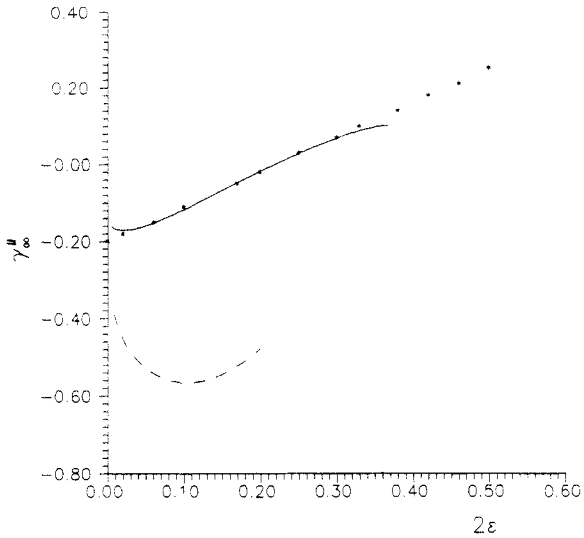

Figure 1. $\gamma_{00}^{\parallel}(\epsilon)$. The solid line corresponds to the present calculation. The dashed line corresponds to the calculation of Broersma.[16] * stands for the numerical data of Tirado et al.[14]

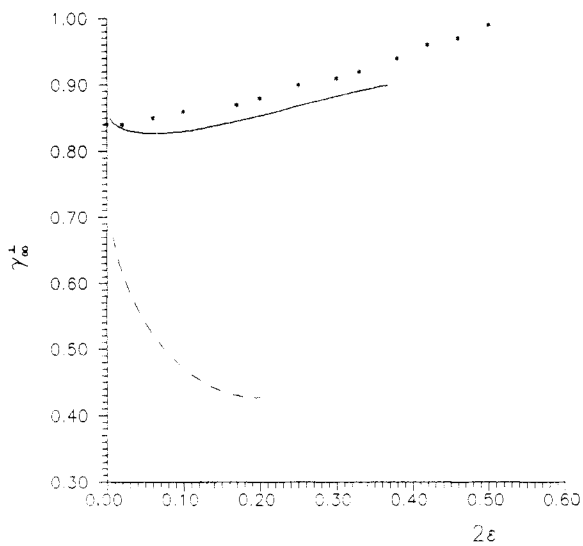

Figure 2. $\gamma_{00}^{\perp}(\epsilon)$. The solid line corresponds to the present calculation. The dashed line corresponds to the calculation of Broersma.[16] * stands for the numerical data of Tirado et al.[14]

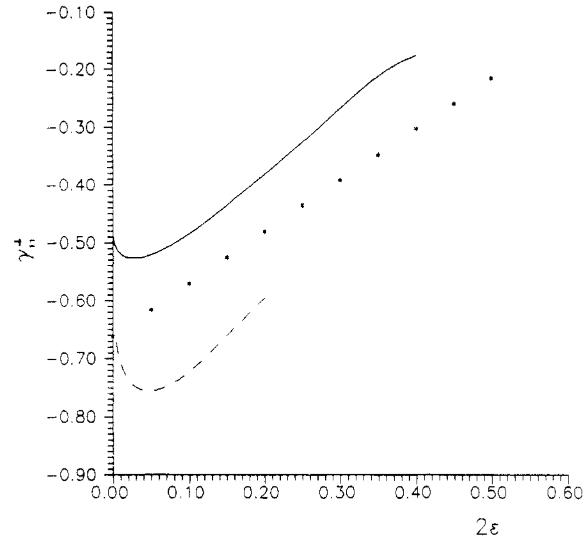

Figure 3. $\gamma_{11}^{\perp}(\epsilon)$. The solid line corresponds to the present calculation. The dashed line corresponds to the calculation of Broersma.[16] * stands for the numerical data of Tirado et al.[17]

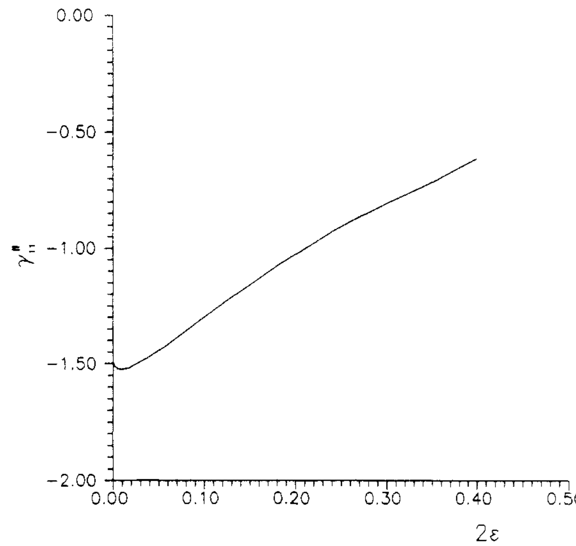

Figure 4. $\gamma_{11}^{\parallel}(\epsilon)$. The solid line corresponds to the present calculation.

Yamakawa.[9] This shows that Tirado et al. have not as yet reached the asymptotic regime. The values given by Broersma are much too small for finite ϵ. The reason for this is the fact that his use of the Oseen–Burgers procedure,[15] in which the induced force is placed on the central line, turns out to correspond to an expansion in $1/\ln \epsilon$ and to neglect powers of ϵ in the expressions of the mobility matrices which is only valid for ϵ vanishingly small. It is clear that this approach based on the Oseen–Burgers method is unsatisfactory for finite values of ϵ. The main difference between the Oseen–Burgers procedure and our procedure is the fact that, in the former, some force distribution is placed at the axis of the cylinder and is adjusted so that the velocity field satisfies the required boundary conditions at the surface. The other results in the context of the slender body theory[12] are similarly found to be insatisfactory for finite ϵ.[14] In our case, however, we locate the force on the surface which leads to a much more accurate description. In fact, this approach has been used before[21] but, in that case, the proper asymptotic behavior was not reproduced.

In Figures 3 and 4 we show $\gamma_{11}^{\perp}$ and $\gamma_{11}^{\parallel}$ as functions of ϵ. In the first one our results are compared again with the numerical data of Tirado et al.[17] and the calculations of Broersma,[7,18] while there are no values from these authors for the second quantity. Our values now are larger than the numerical values whereas Broersma's values are smaller. The discrepancies are probably due to the fact that for the rotational motion the inhomogeneities of the induced force distribution around the axis and the effect of the end plates play a more important role than for the translational motion.

The transport coefficients for finite ϵ can be obtained in the same way as in the preceding section since eqs 3.1 and 3.2 are formally identical to eqs 4.3 and 4.7, substituting $\overleftrightarrow{\mu}_{ii}$ by $\overleftrightarrow{\mu}_{ii}^{*}$. In Figure 5 we plot our results for the viscosity compared with the curves obtained from the asymptotic analysis. As in the case of the rotational friction coefficient, the asymptotic behavior agrees with Yamakawa.[9] For larger values of ϵ there are no other results to compare with.

5. Discussion

As we discussed above, the translational friction coefficient for translation parallel to the axis of the cylinder calculated by using our method agrees very well with the values obtained by Tirado et al.[14] In fact, it agrees better

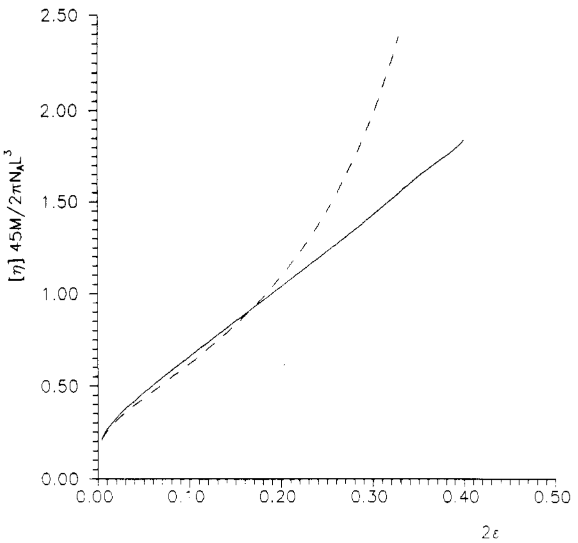

Figure 5. $[\eta](\epsilon)$. The dashed line corresponds to the reduced viscosity calculated from eq 3.27 with $\mu^{\perp}_{11}$ and $\mu^{\parallel}_{11}$ given by eq 3.13. The solid line corresponds to the same quantity by using $\mu^{\perp *}_{11}$ and $\mu^{\parallel *}_{11}$ given by eq 4.12 in eq 3.27.

than the other coefficients. It seems clear that this is related to the fact that for this coefficient the force distribution will be symmetric around the axis of the cylinder, which is not true for the other coefficients. The only source of error is, therefore, related to the end plates. If the aspect ratio is small ($\epsilon < 0.15$) this error is clearly negligible. For larger aspect ratios the influence of the end plates will become more important and our method is no longer appropriate. Comparing our results with Broersma,[7,16] we conclude that the use of the Oseen–Burgers procedure, in which the force is placed along the axis of the cylinder, is less accurate than our approximation, in which the force is located on the lateral surface. Concerning the other translational friction coefficient, our procedure still gives a considerably better agreement with Tirado et al. than with Broersma's results. In that case, the error in our results is not only due to the end plates but may also be due to the fact that the real force distribution is no longer symmetric around the axis of the cylinder. This is even more pronounced for the rotational friction coefficient where our results deviate considerably from those of Tirado et al.[17]

We find that for aspect ratios smaller than 0.01 the behavior of the friction coefficients goes over to the asymptotic behavior given by Yamakawa.[9] For larger values of the aspect ratio the qualitative behavior of our results resembles the behavior found by Tirado et al. much better than those obtained by Broersma. For the viscosity there are no numerical results which make a sensitive comparison possible. The asymptotic formula given by Yamakawa, however, agrees rather well with our results up to an aspect ratio of 0.1. Our general conclusion is that the calculation using a force distribution on the lateral surface of the cylinder, which is symmetric around the axis, leads to a considerable improvement over the use of a force distribution along the central line for a finite cylinder.

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A. Fluctuation-Dissipation Theorem

Here, we will derive the stochastic properties followed by the random velocity $\vec{v}^R(s,t)$ as well as the fluctuation-dissipation theorem. To this end, we introduce the Fourier transforms of eqs 2.4 and 2.5. One gets

$$\langle \vec{\vec{\Pi}}^R(\vec{k},t)\rangle = 0 \qquad (A.1)$$

$$\langle \Pi^R_{\alpha\beta}(\vec{k},t)\Pi^R_{\gamma\mu}(\vec{k}'',t')\rangle = 2(2\pi)^3 k_B T\eta\Delta_{\alpha\beta\gamma\mu}\delta(\vec{k}+\vec{k}'')\delta(t-t') \qquad (A.2)$$

Let us now consider eq 2.20. As far as the configuration (i.e. the orientation) of the system can be taken as frozen, the averages will affect only the random pressure tensor. According to this, we have

$$\langle \vec{v}^R(\vec{r},t)\rangle = -\int \frac{d\vec{k}}{(2\pi)^3}\exp(ik_\parallel s)J_0(k_\perp a)\frac{\vec{\vec{1}}-\hat{k}\hat{k}}{\eta k^2}\cdot\{i\vec{k}\cdot\langle\vec{\vec{\Pi}}^R(\vec{k},t)\rangle\} = 0 \qquad (A.3)$$

where, in deriving the last line, use has been made of eq A.1. We make use again of eq 2.20 to compute $\langle \vec{v}^R(s,t)\vec{v}^R(s',t')\rangle$, yielding

$$\langle \vec{v}^R(s,t)\vec{v}^R(s',t')\rangle = \int\frac{d\vec{k}}{(2\pi)^3}\int\frac{d\vec{k}'}{(2\pi)^3}\exp(ik_\parallel s)J_0(k_\perp a)\exp(ik'_\parallel s')J_0(k'_\perp a)\times \frac{\vec{\vec{1}}-\hat{k}\hat{k}}{\eta k^2}\cdot\{i\vec{k}\cdot\langle\vec{\vec{\Pi}}^R(\vec{k},t)\vec{\vec{\Pi}}^R(\vec{k}',t')\rangle\cdot(i\vec{k}')\}\cdot\frac{\vec{\vec{1}}-\hat{k}'\hat{k}'}{\eta k'^2} \qquad (A.4)$$

Substituting eq A.2 into eq A.4 and performing the integration over $\vec{k}'$, one arrives at

$$\langle \vec{v}^R(s,t)\vec{v}^R(s',t')\rangle = 2k_B T\delta(t-t')\int\frac{d\vec{k}}{(2\pi)^3}\times \exp[ik_\parallel(s-s')]J_0^2(k_\perp a)\frac{\vec{\vec{1}}-\hat{k}\hat{k}}{\eta k^2} = 2k_B T\delta(t-t')\vec{\vec{\mu}}(s-s') \qquad (A.5)$$

where the last equality follows from eq 2.19 and agrees with eq 2.22.

B. Mobility Matrices in the Long Rod Limit

Our purpose in this appendix will be to compute some mobility matrices which correspond to moments of the mobility kernel. Performing the integration with respect to $\vec{k}_\perp$ in eq 2.19, one gets

$$(8\pi^2\eta)\vec{\vec{\mu}}(x-x') = \int_{-\infty}^{\infty}dk\,\exp[ikL(x-x')/2]\times \left\{(\vec{\vec{1}}-\hat{s}\hat{s})\left(1-\frac{k}{2}\frac{d}{dk}\right)+2\hat{s}\hat{s}\left(1+\frac{k}{2}\frac{d}{dk}\right)\right\}I_0(|ka|)K_0(|ka|) \qquad (B.1)$$

where we have written k instead of $k_\parallel$ for simplicity's sake. I_0 and K_0 are modified Bessel functions of the first and second kind, respectively. We introduce the dimensionless quantity $\chi \equiv kL/2$. For convenience we also rewrite the mobility kernel as

$$\vec{\vec{\mu}}(x) = (\vec{\vec{1}}-\hat{s}\hat{s})A^\perp(x)+2\hat{s}\hat{s}A^\parallel(x) \qquad (B.2)$$

where

$$(8\pi^2\eta)A^{\perp,\parallel}(x) = \frac{2}{L}\int_{-\infty}^{\infty}d\chi\,\exp(i\chi x)\left(1+\alpha^{\perp,\parallel}\frac{\chi}{2}\frac{d}{d\chi}\right)I_0(2|\epsilon\chi|)K_0(2|\epsilon\chi|) \qquad (B.3)$$

Here, $\alpha^\perp = -1$ and $\alpha^\parallel = 1$. The long rod limit is obtained by considering $\epsilon \rightarrow 0$. We then expand the integrand in powers of ϵ by neglecting terms of second order and higher.

One gets

$$(8\pi^2\eta)A(x) \simeq \frac{2}{L}\int_{-\infty}^{\infty}\mathrm{d}\chi\ \exp(i\chi x)[-\ln|\epsilon\chi| - (C + \alpha/2)] \quad (B.4)$$

where C is Euler's constant and we have omitted the superscripts $\perp$ and $\|$ since it is clear enough. Note that there are no terms linear in ϵ. This approximation is not valid for $\chi > (2\epsilon)^{-1}$ which introduces a cutoff value for χ. If one considers, however, the limits of the integral as infinite, this leads us to convergent results. By inspection of eq B.4 one sees that the integral represents the Fourier transform of the expression between brackets. However, such a transform is only defined as a distribution.[28] One can skip the use of the distribution theory because the mobility matrices defined in eq 2.31 can be directly computed by introducing the expression (B.4) into eq 2.31 and performing first the integration will respect to x and x'. We will, however, compute the integral in (B.4) because the calculation of the mobility matrices is easier once the expression for the mobility kernel as a distribution is obtained. Firstly, we consider the integral

$$\frac{2}{L}\int_{-\infty}^{\infty}\mathrm{d}\chi\ \exp(i\chi x)[-\ln\epsilon - (C + \alpha/2)] = -\frac{4\pi}{L}\delta(x)[\ln\epsilon + (C + \alpha/2)] \quad (B.5)$$

The remaining integral gives the distribution

$$\frac{2}{L}\int_{-\infty}^{\infty}\mathrm{d}\chi\ \exp(i\chi x)[-\ln|\chi|] = \frac{2\pi}{L}\left[\frac{\mathrm{d}}{\mathrm{d}x}(Sign(x)\ln|x|) + C'\delta(x)\right] \quad (B.6)$$

where C' is a constant to be determined below and the function $Sign(x)$ is equal to 1 if $x > 0$ and to -1 if $x < 0$. Putting together all these results, we get

$$A(x) = \frac{1}{4\pi\eta L}\left[\frac{\mathrm{d}}{\mathrm{d}x}(Sign(x)\ln|x|) - 2(\ln\epsilon + (C + \alpha/2) - C'/2)\delta(x)\right] \quad (B.7)$$

The undetermined constant can be fixed by computing one of the moments of $A(x)$ directly from the integral expression (B.4) and comparing it with the result obtained after using eq B.6. On one hand, if we take $l = q = 0$, we get

$$\begin{aligned} A_{00} &= \int_{-1}^{1}\mathrm{d}x\ \mathrm{d}x'\ P_0(x)A(x-x')P_0(x') \\ &= \frac{1}{\pi^2\eta L}\int_{-\infty}^{\infty}\mathrm{d}\chi\left(\frac{\sin\chi}{\chi}\right)^2[-\ln|\epsilon\chi| - (C + \alpha/2)] \\ &= \frac{1}{2\pi\eta L}[\ln(2/\epsilon) - 1 + \alpha/2] \end{aligned} \quad (B.8)$$

where we have interchanged the order of the integration. On the other hand, if one uses the distribution shown in eq B.6, the same quantity gives

$$\begin{aligned} A_{00} &= \int_{-\infty}^{\infty}\frac{\mathrm{d}x\ \mathrm{d}x'}{4\pi\eta L}\left[\frac{\mathrm{d}}{\mathrm{d}x}(Sign(x-x')\ln|x-x'|) - 2(\ln\epsilon + (C + \alpha/2) - C'/2)\delta(x-x')\right] \\ &= \frac{1}{2\pi\eta L}[\ln(2/\epsilon) - 1 + \alpha/2 - (C - C'/2)] \end{aligned} \quad (B.9)$$

Comparing eqs B.8 and B.9, one finds $C' = 2C$. Consequently, the final expression for the kernel A in our approximation reads

$$A(x) = \frac{1}{4\pi\eta L}\left[\frac{\mathrm{d}}{\mathrm{d}x}(Sign(x)\ln|x|) - 2(\ln\epsilon + \alpha/2)\delta(x)\right] \quad (B.10)$$

Once we have arrived at this last equation, the calculation of the mobility matrices is straightforward. We will give here the expressions for the mobility matrices that are used in section 4 and in appendix E.

$$(2\pi\eta L)\overset{=}{\mu}_{00} = \left[\ln\left(\frac{2L}{a}\right) - \frac{1}{2}\right](\overset{=}{1} - \hat{s}\hat{s}) + 2\left[\ln\left(\frac{2L}{a}\right) - \frac{3}{2}\right](\hat{s}\hat{s}) \quad (B.11)$$

$$(2\pi\eta L)\overset{=}{\mu}_{22} = \left[\ln\left(\frac{2L}{a}\right) - \frac{71}{30}\right](\overset{=}{1} - \hat{s}\hat{s}) + 2\left[\ln\left(\frac{2L}{a}\right) - \frac{101}{30}\right](\hat{s}\hat{s}) \quad (B.12)$$

$$(2\pi\eta L)\overset{=}{\mu}_{44} = \left[\ln\left(\frac{2L}{a}\right) - \frac{1867}{630}\right](\overset{=}{1} - \hat{s}\hat{s}) + 2\left[\ln\left(\frac{2L}{a}\right) - \frac{2497}{630}\right](\hat{s}\hat{s}) \quad (B.13)$$

$$(2\pi\eta L)\overset{=}{\mu}_{02} = -\frac{\sqrt{5}}{6}[(\overset{=}{1} - \hat{s}\hat{s}) + 2(\hat{s}\hat{s})] \quad (B.14)$$

$$(2\pi\eta L)\overset{=}{\mu}_{04} = -\frac{3}{20}[(\overset{=}{1} - \hat{s}\hat{s}) + 2(\hat{s}\hat{s})] \quad (B.15)$$

$$(2\pi\eta L)\overset{=}{\mu}_{24} = -\frac{3\sqrt{5}}{14}[(\overset{=}{1} - \hat{s}\hat{s}) + 2(\hat{s}\hat{s})] \quad (B.16)$$

$$(2\pi\eta L)\overset{=}{\mu}_{11} = \left[\ln\left(\frac{2L}{a}\right) - \frac{11}{6}\right](\overset{=}{1} - \hat{s}\hat{s}) + 2\left[\ln\left(\frac{2L}{a}\right) - \frac{17}{6}\right](\hat{s}\hat{s}) \quad (B.17)$$

$$(2\pi\eta L)\overset{=}{\mu}_{33} = \left[\ln\left(\frac{2L}{a}\right) - \frac{569}{210}\right](\overset{=}{1} - \hat{s}\hat{s}) + 2\left[\ln\left(\frac{2L}{a}\right) - \frac{779}{210}\right](\hat{s}\hat{s}) \quad (B.18)$$

$$(2\pi\eta L)\overset{=}{\mu}_{55} = \left[\ln\left(\frac{2L}{a}\right) - \frac{21937}{6930}\right](\overset{=}{1} - \hat{s}\hat{s}) + 2\left[\ln\left(\frac{2L}{a}\right) - \frac{28867}{6930}\right](\hat{s}\hat{s}) \quad (B.19)$$

$$(2\pi\eta L)\overset{=}{\mu}_{13} = -\frac{\sqrt{21}}{10}[(\overset{=}{1} - \hat{s}\hat{s}) + 2(\hat{s}\hat{s})] \quad (B.20)$$

$$(2\pi\eta L)\overset{=}{\mu}_{15} = -\frac{\sqrt{33}}{28}[(\overset{=}{1} - \hat{s}\hat{s}) + 2(\hat{s}\hat{s})] \quad (B.21)$$

$$(2\pi\eta L)\overset{=}{\mu}_{35} = -\frac{\sqrt{77}}{18}[(\overset{=}{1} - \hat{s}\hat{s}) + 2(\hat{s}\hat{s})] \quad (B.22)$$

C. Contribution of Brownian Motion to the Stress Tensor

To obtain the result given in eq 3.24, we will use the method of functional derivatives.[29] In our case, the random velocity is Gaussian and white which enables us to write (Furutsu–Novikov result)

$$\langle\hat{s}_\alpha(\delta_{\beta\gamma} - \hat{s}_\beta\hat{s}_\gamma)v_\gamma^{\mathrm{R}}\rangle = \int_{-\infty}^{t}\mathrm{d}t'\ \langle v_\gamma^{\mathrm{R}}(t)v_\nu^{\mathrm{R}}(t')\rangle\left\langle\frac{\delta}{\delta v_\nu^{\mathrm{R}}(t')}[\hat{s}_\alpha(\delta_{\beta\gamma} - \hat{s}_\beta\hat{s}_\gamma)](t)\right\rangle \quad (C.1)$$

where $t \geq t'$ due to causality. If one now uses eq 2.33 and performs the integral, one gets

$$\langle\hat{s}_\alpha(\delta_{\beta\gamma} - \hat{s}_\beta\hat{s}_\gamma)v_\gamma^{\mathrm{R}}\rangle = k_{\mathrm{B}}T\mu_{\gamma\nu}\left\langle\frac{\delta}{\delta v_\nu^{\mathrm{R}}(t)}[\hat{s}_\alpha(\delta_{\beta\gamma} - \hat{s}_\beta\hat{s}_\gamma)](t)\right\rangle \quad (C.2)$$

where use has been made of the fact that, due to causality, the integral of the δ-function is $^1/_2$. Now we have to obtain the functional derivative of $\hat{s}$ to perform the average in eq C.2. To this end, we have to use the Langevin equation (3.2), in which we substitute eq 3.18 and obtain after integration and subsequent functional differentiation

$$\frac{\delta \hat{s}_\alpha}{\delta v_\nu^{\mathrm{R}}} = \frac{\sqrt{6}}{L}(\delta_{\alpha\nu} - \hat{s}_\alpha \hat{s}_\nu) \quad \text{(C.3)}$$

Using eq C.3 in eq C.2, we arrive at

$$\langle \hat{s}_\alpha(\delta_{\beta\gamma} - \hat{s}_\beta \hat{s}_\gamma) v_\gamma^{\mathrm{R}} \rangle = -3k_{\mathrm{B}}T(\hat{s}_\alpha \hat{s}_\beta - \delta_{\alpha\beta}/3)\mu^{\perp}\frac{\sqrt{6}}{L} \quad \text{(C.4)}$$

Now, with use of eq C.4 in eq 3.24, the last equality is satisfied.

Taking advantage of these results, we can also prove that $\langle \hat{s} \times \vec{v}_1^{\mathrm{R}} \rangle = 0$. In this case, as in eq 2.2, we can write

$$\epsilon_{\alpha\beta\gamma}\langle \hat{s}_\beta v_\gamma^{\mathrm{R}} \rangle = k_{\mathrm{B}}T\epsilon_{\alpha\beta\gamma}\mu_{\gamma\nu}\left\langle \frac{\delta}{\delta v_\nu^{\mathrm{R}}(t)}\hat{s}_\beta(t) \right\rangle \quad \text{(C.5)}$$

where $\epsilon_{\alpha\beta\gamma}$ is the Levi–Civita tensor. Making use of eq C.3 to eliminate the functional derivative in eq C.5, we find that the right-hand side of this equation is proportional to

$$\epsilon_{\alpha\beta\gamma}(\delta_{\beta\gamma} - \hat{s}_\beta \hat{s}_\gamma) = 0 \quad \text{(C.6)}$$

which is obviously zero.

D. Calculation of $\langle \langle J_{\alpha\beta} \rangle (t) \langle J_{\gamma\nu} \rangle (0) \rangle_{\mathrm{eq}}$

Let us now calculate the correlation function of $\langle \vec{J} \rangle$. Once the velocity is removed, we have to use the probability distribution function for the different orientations of the particle. This probability distribution function satisfies the Smoluchowski equation[26]

$$\frac{\partial}{\partial t}\psi(\hat{s},t) = D_{\mathrm{r}}\mathcal{R}^2\psi(\hat{s},t) \quad \text{(D.1)}$$

where D_{r} is the rotational diffusion coefficient given in eq 3.14 and the rotational operator $\vec{\mathcal{R}}$ is defined as

$$\vec{\mathcal{R}} \equiv \hat{s} \times \frac{\partial}{\partial \hat{s}} \quad \text{(D.2)}$$

One can see that the conditional probability $\mathcal{G}(\hat{s},t|\hat{s}',t_0)$, which follows from the formula

$$\psi(\hat{s},t) = \int \mathrm{d}\hat{s}'\, \mathcal{G}(\hat{s},t|\hat{s}',t_0)\psi(\hat{s}',t_0) \quad \text{(D.3)}$$

also satisfies the Smoluchowski equation, that is

$$\frac{\partial}{\partial t}\mathcal{G}(\hat{s},t|\hat{s}',t_0) = D_{\mathrm{r}}\mathcal{R}^2\mathcal{G}(\hat{s},t|\hat{s}',t_0) \quad \text{(D.4)}$$

The operator $\mathcal{R}^2$ acts only on the $\hat{s}$ dependence of $\mathcal{G}$. Let us rewrite the elastic contribution to the stress tensor as

$$\langle J_{\alpha\beta} \rangle \equiv 3k_{\mathrm{B}}TS_{\alpha\beta} \quad \text{(D.5)}$$

where we have introduced the phase space variable

$$S_{\alpha\beta} \equiv (\hat{s}_\alpha \hat{s}_\beta - \delta_{\alpha\beta}/3) \quad \text{(D.6)}$$

The correlation function of this last quantity is then

$$\langle S_{\alpha\beta}(t)S_{\gamma\nu}(0) \rangle_{\mathrm{eq}} = \int \mathrm{d}\hat{s} \int \mathrm{d}\hat{s}'\, (\hat{s}_\alpha \hat{s}_\beta - \delta_{\alpha\beta}/3) \times \mathcal{G}(\hat{s},t|\hat{s}',0)\psi(\hat{s}',0)(\hat{s}'_\gamma \hat{s}'_\nu - \delta_{\gamma\nu}/3) \quad \text{(D.7)}$$

Deriving this equation with respect to time and using the evolution equation for the transition probability given in eq D.4, we get

$$\frac{\partial}{\partial t}\langle S_{\alpha\beta}(t)S_{\gamma\nu}(0) \rangle_{\mathrm{eq}} = \int \mathrm{d}\hat{s} \int \mathrm{d}\hat{s}'\, S_{\alpha\beta}D_{\mathrm{r}}[\mathcal{R}^2\mathcal{G}(\hat{s},t|\hat{s}',0)]\psi(\hat{s}',0)S'_{\gamma\nu} \quad \text{(D.8)}$$

where $S'_{\gamma\nu} = (\hat{s}'_\gamma \hat{s}'_\nu - \delta_{\gamma\nu}/3)$. Making use of the fact that the rotational operator satisfies

$$\int \mathrm{d}\hat{s}\, A(\hat{s})[\mathcal{R}^2 B(\hat{s})] = \int \mathrm{d}\hat{s}\, [\mathcal{R}^2 A(\hat{s})]B(\hat{s}) \quad \text{(D.9)}$$

and

$$\mathcal{R}^2 S_{\alpha\beta} = -6S_{\alpha\beta} \quad \text{(D.10)}$$

we finally arrive at

$$\frac{\partial}{\partial t}\langle S_{\alpha\beta}(t)S_{\gamma\nu}(0) \rangle_{\mathrm{eq}} = -6D_{\mathrm{r}}\langle S_{\alpha\beta}(t)S_{\gamma\nu}(0) \rangle_{\mathrm{eq}} \quad \text{(D.11)}$$

Therefore,

$$\langle S_{\alpha\beta}(t)S_{\gamma\nu}(0) \rangle_{\mathrm{eq}} = \exp(-6D_{\mathrm{r}}t)\langle S_{\alpha\beta}(0)S_{\gamma\nu}(0) \rangle_{\mathrm{eq}} \quad \text{(D.12)}$$

where the quantity $\langle S_{\alpha\beta}(0)S_{\gamma\nu}(0) \rangle_{\mathrm{eq}}$ has to be calculated by means of the initial distribution function which, in our case, is the equilibrium distribution function. This leads us to

$$\langle S_{\alpha\beta}(t)S_{\gamma\nu}(0) \rangle_{\mathrm{eq}} = \exp(-6D_{\mathrm{r}}t)\int \frac{\mathrm{d}\hat{s}}{4\pi}S_{\alpha\beta}S_{\gamma\nu} = \exp(-6D_{\mathrm{r}}t)\frac{1}{15}\left(\delta_{\alpha\gamma}\delta_{\beta\nu} + \delta_{\alpha\nu}\delta_{\beta\gamma} - \frac{2}{3}\delta_{\alpha\beta}\delta_{\gamma\nu}\right) \quad \text{(D.13)}$$

Now, making use of eqs D.5 and D.13, one arrives at eq 3.25.

E. Mobility Matrices for the Finite Cylinder

Let us consider again eq B.3. To simplify the calculations, note that if $g(\epsilon x)$ is an arbitrary function, one can write

$$x\frac{\mathrm{d}}{\mathrm{d}x}g(\epsilon x) = \epsilon\frac{\mathrm{d}}{\mathrm{d}\epsilon}g(\epsilon x) \quad \text{(E.1)}$$

Then, eq B.3 can be written as

$$A(x - x') = \frac{1}{4\pi^2\eta L}\left(1 + \frac{\alpha\epsilon}{2}\frac{\mathrm{d}}{\mathrm{d}\epsilon}\right) \times \int_{-\infty}^{\infty}\mathrm{d}\chi\, \exp[i\chi(x - x')]I_0(2|\epsilon\chi|)K_0(2|\epsilon\chi|) \quad \text{(E.2)}$$

It is now convenient to expand the exponential function of the integrand of this last equation in terms of the normalized Legendre polynomials. That is[30]

$$\exp(i\chi x) = \sqrt{\frac{\pi}{\chi}}\sum_{n=0}^{\infty}\sqrt{2n + 1}\,i^n j_{n+1/2}(\chi)P_n(x) \quad \text{(E.3)}$$

where $J_{n+1/2}(x)$ is the Bessel function of first kind and order $n + {}^1/_2$. By means of this expansion, the kernel $A(x - x')$ can be written as

$$A(x - x') = \frac{1}{4\pi\eta L}\sum_{n,m}\sqrt{(2n + 1)(2m + 1)}\,i^{n-m}P_n(x)P_m(x') \times \left(1 + \frac{\alpha\epsilon}{2}\frac{\mathrm{d}}{\mathrm{d}\epsilon}\right)\int_{-\infty}^{\infty}\mathrm{d}\chi\, \frac{1}{\chi}J_{n+1/2}(\chi)J_{m+1/2}(\chi)I_0(2|\epsilon\chi|)K_0(2|\epsilon\chi|) \quad \text{(E.4)}$$

Table I. Coefficients of the Polynomial Fit for the Functions $h_{ij}^{\perp,\parallel}$ [a]

	ϵ	ϵ^2	ϵ^3	ϵ^4	ϵ^5	ϵ^6	ϵ^7	ϵ^8	ϵ^9	ϵ^{10}
$h_{00}^{\parallel}$	1.9075	−0.9699								
$h_{22}^{\parallel}$	9.4650	−22.3152	16.6738							
$h_{44}^{\parallel}$	16.8810	−69.3611	185.3248	−208.9894						
$h_{02}^{\parallel}$	4.0195	−33.5164	235.7469	−1239.7866	4052.1465	−5901.7101				
$h_{04}^{\parallel}$	5.3199	−133.5052	2794.3170	−46583.6100	581345.7	−5172166.8	31265938.5	−120591900	265713000	−253383000
$h_{24}^{\parallel}$	12.0451	−232.6888	4142.5943	−65207.4317	812676.4339	−7290209.3827	44054787.6859	−168370552.1426	366338370.8558	−345610020.7043
$h_{00}^{\perp}$	0.6377	−0.0108								
$h_{22}^{\perp}$	3.207	−0.7483	−16.6738							
$h_{44}^{\perp}$	5.5605	4.0251	−82.7231	208.9894						
$h_{02}^{\perp}$	1.3106	3.0341	−117.4311	1036.9331	−4052.1465	5901.7101				
$h_{04}^{\perp}$	1.7799	4.8844	−996.813	29733.69	−485949.3	4880773.2	−30898861.5	120591900	−265713000	253383000
$h_{24}^{\perp}$	3.9438	19.9247	−1992.5479	51381.8234	−764583.3075	7222117.7587	−44054787.6859	168370552.1429	−366338370.8558	345610020.7043
$h_{11}^{\parallel}$	5.6575	−7.7021	4.7963							
$h_{33}^{\parallel}$	13.2382	−44.3031	100.9065	−99.2981						
$h_{55}^{\parallel}$	20.9018	−114.2289	477.6772	−1189.3838	1264.1145					
$h_{13}^{\parallel}$	8.2912	−125.8840	2243.3316	−42245.1385	625305.2573	−6309679.7357	41318106.3672	−167747474.6017	383339330.7466	−376586905.4601
$h_{15}^{\parallel}$	10.1121	−337.9658	8724.0835	−165067.3651	2193884.09100	−20033432.6703	122478878.0786	−477261366.7382	1068092277.4335	−1042009090.7369
$h_{35}^{\parallel}$	15.7926	−391.1164	8552.1768	−153621.8098	2070687.1387	−19655479.7245	124922640.2871	−500611718.3007	1136691336.8140	−1111072828.2850
$h_{11}^{\perp}$	1.8519	0.8588	−4.7963							
$h_{33}^{\perp}$	4.3773	1.9505	−41.9761	99.2981						
$h_{55}^{\perp}$	6.9618	1.6109	−134.8468	696.9622	−1264.1145					
$h_{13}^{\perp}$	2.6457	21.9109	−1524.9662	39415.4438	−620761.2302	6309679.7357	−41318106.3672	167747474.6017	−383339330.7466	376586905.4601
$h_{15}^{\perp}$	3.5095	−6.3759	−2031.9782	76609.2577	−1454303.8198	16326776.6009	−112355396.1743	465702847.12836	−1068092277.4334	1042009090.7368
$h_{35}^{\perp}$	5.3081	15.0969	−3222.6846	102683.4925	−1777450.6438	18747976.4176	−123767747.9193	500611718.3007	−1136691336.814	1111072828.285

[a] A given coefficient corresponds to the power in ϵ indicated in the first row.

Due to the fact that

$$\frac{1}{\chi}J_{n+1/2}(\chi)J_{m+1/2}(\chi) = (-1)^{n+m+2}\frac{1}{(-\chi)}J_{n+1/2}(-\chi)J_{m+1/2}(-\chi) \quad (E.5)$$

it is found that the integral vanishes if $n + m$ is odd which agrees with what we stated in eq 2.38. Therefore, we can finally write

$$A(x - x') = \frac{1}{2\pi\eta L}\sum_{n,m}\sqrt{(2n + 1)(2m + 1)}i^{n-m}P_n(x)P_m(x') \times \left(1 + \frac{\alpha\epsilon}{2}\frac{d}{d\epsilon}\right)\int_0^\infty d\chi \frac{1}{\chi}J_{n+1/2}(\chi)J_{m+1/2}(\chi)I_0(2\epsilon\chi)K_0(2\epsilon\chi) \quad (E.6)$$

From this expression we can directly obtain the moments of the scalar kernel A

$$A_{n,m} = \frac{1}{2\pi\eta L}\sqrt{(2n + 1)(2m + 1)}i^{n-m} \times \left(1 + \frac{\alpha\epsilon}{2}\frac{d}{d\epsilon}\right)\int_0^\infty d\chi \frac{1}{\chi}J_{n+1/2}(\chi)J_{m+1/2}(\chi)I_0(2\epsilon\chi)K_0(2\epsilon\chi) \quad (E.7)$$

From this last equation one can compute the mobility matrices which, of course, coincide with the results given in appendix B for these quantities when $\epsilon \to 0$. We have numerically evaluated this integral and substract the value that is obtained by means of the asymptotic kernel given in appendix B which contains the nonanaliticities. The remaining function is smooth and we have computed a polynomial approximation in powers of ϵ which fits very well with the numerical data. Then, in general we will have

$$\overleftrightarrow{\mu}_{ij}(\epsilon) = \left[\mu_{ij}^{\perp}(\epsilon \to 0) + \frac{1}{2\pi\eta L}h_{ij}^{\perp}(\epsilon)\right](\overleftrightarrow{1} - \hat{s}\hat{s}) + \left[\mu_{ij}^{\parallel}(\epsilon \to 0) + \frac{1}{\pi\eta L}h_{ij}^{\parallel}(\epsilon)\right]\hat{s}\hat{s} \quad (E.8)$$

where $\mu_{ij}^{\perp,\parallel}(\epsilon \to 0)$ are the values for the mobility matrices given in appendix B. For the functions $h_{ij}^{\perp,\parallel}(\epsilon)$ we report polynomial fits valid in the interval $0 < \epsilon \leq 0.2$. The coefficients of these polynomial fits are given in Table I.

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