Notes

Translational Friction Coefficient of Hydrodynamically Screened Rodlike Macromolecules

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Muthukumar and Edwards[1] have calculated the hydrodynamic screening length ξ in a semidilute solution of rods at concentrations below the onset of entanglement.[2,3] They also derived the reduced viscosity of the suspension. Here we give an elementary derivation of ξ in the spirit of Brinkman's approach[4] instead of the Freed–Edwards theory.[5] Along the way we calculate the translational friction coefficient Ξ by applying arguments similar to those of Yamakawa and Fujii[6] but with the use of a straightforward variational principle.

We consider a test rod moving through a relatively dense swarm of other rodlike macromolecules. Let us assume the suspension may be viewed as a practically unbounded porous medium described by a combination of Darcy's law and the inertialess Navier–Stokes equation[4]

$$\eta_0 \Delta \mathbf{v} - (\eta_0/\xi^2)\mathbf{v} = \nabla p \tag{1}$$

where $\mathbf{v}$ is the average fluid velocity, η_0 is the solvent viscosity, p the pressure, and ξ is a screening length.

The fluid is incompressible

$$\nabla \cdot \mathbf{v} = 0 \tag{2}$$

The test rod translates uniformly with velocity $\mathbf{U}$ through this effective medium. Thus there is a force distribution on the macromolecular surface acting on the surrounding fluid. Since eq 1 and 2 are linear we can try solving them by superposing solutions caused by the action of fundamental singularities (see for instance the polymer literature[6-8,14] but also the work of hydrodynamicists[9-13]). First of all, we replace the force distribution on the surface of the rod by a superposition of stokeslets, and perhaps other singularities, distributed along the center line of the rod. A point force $\mathbf{F}\delta(\mathbf{R})$ (or "stokeslet") proportional to the δ function $\delta(\mathbf{R})$ acting on the effective medium at the origin induces the velocity field

$$\mathbf{v}_s(\boldsymbol{R}) = \mathbf{T}^{\text{eff}}(\mathbf{R})\cdot\mathbf{F} \tag{3}$$

with

$$T^{\text{eff}} = (e^{-R/\xi} + h(R/\xi))\frac{\mathbf{I}}{4\pi\eta_0 R} - (e^{-R/\xi} + 3h(R/\xi))\frac{\mathbf{RR}}{4\pi\eta_0 R^3} \tag{4}$$

where $h(z) = z^{-2}[e^{-z}(1+z) - 1]$. If $\xi \to \infty$, we simply regain the usual Oseen tensor. We shall disregard higher order source terms, which is a good approximation for the purpose of this calculation.

Next, we specify the force distribution $\mathbf{f}(s)$ along the center line, which is indexed by the distance s from one end. In view of eq 3 this leads to a superpostion of velocity fields, and it is clear that the total sum of these velocities must match as closely as possible to the constant velocity $\mathbf{U}$ of the polymer surface (if we require a stick boundary condition). Higher order source terms would be needed to do the matching exactly. However, it can be argued that a smoothing procedure like taking cross-sectional averages before matching enables us to accommodate the stick boundary condition rather well.[6,7] Hence, the force distribution is given by

$$\mathbf{U} = \int_0^L \langle \mathbf{T}^{\text{eff}}(-\mathbf{X} + \mathbf{r})\rangle_{\mathbf{r}} \cdot \mathbf{f}(s)\, ds \tag{5}$$

Here $\mathbf{X}$ is the vector from some point t on the center line to point s, $\mathbf{r}$ is the vector from t to some point on the surface, the brackets denote a cross-sectional average, and L is the length of the rod.

Keeping in line with the level of approximation adopted, we now conveniently preaverage the screened Oseen tensor (eq 4). Hence, we have to solve the following integral equation:

$$\int_0^L K(|t-s|)\psi(s)\, ds = 1 \tag{6}$$

where

$$6\pi\eta_0\psi(s)\mathbf{U} \equiv \mathbf{f}(s) \tag{7}$$

and

$$K(x) = \frac{\exp(-(x^2 + a^2)^{1/2}/\xi)}{(x^2 + a^2)^{1/2}} \tag{8}$$

The radius of the rod is a. In order to derive ξ and Ξ explicitly we first need to calculate the force $\mathbf{F}$ on the rod in terms of ξ. By definition the force is given by

$$\mathbf{F} = \int_0^L \mathbf{f}(s)\, ds = 6\pi\eta_0\mathbf{U}\int_0^L \psi(s)\, ds \tag{9}$$

The friction coefficient Ξ, which is already orientationally averaged because of the preaveraging of $\mathbf{T}^{\text{eff}}$, can be written as

$$\mathbf{F} \equiv \Xi\mathbf{U} \tag{10}$$

$$\Xi = 6\pi\eta_0\int_0^L \psi(s)\, ds \tag{11}$$

Equations analogous to eq 6 are often solved in the Kirkwood–Riseman approximation. However, we only need an integral of ψ so that it is expedient to use a variational principle as is nowadays increasingly done (see, e.g., ref 15 and 16). The kernel K is symmetric and positive definite; a lower bound to Ξ can be found in standard texts[17]

$$\Xi = \frac{6\pi\eta_0\left[\int_0^L \alpha(s)\, ds\right]^2}{\int_0^L\int_0^L \alpha(s)K(|s-t|)\alpha(t)\, ds\, dt} \tag{12}$$

where $\alpha(s)$ is a trial function. A zero-order choice for $\alpha(s)$, one which is in fact quite realistic, is just to set it equal to a constant. This immediately yields an expression analogous to the one derived without screening[6]

$$\Xi = 6\pi\eta_0 L^2\left[\int_0^L\int_0^L K(|s-t|)\, ds\, dt\right]^{-1} \tag{13}$$

When $L \gg \xi$, Ξ reduces to

$$\Xi = 3\pi\eta_0 L K_0^{-1}(a/\xi) \tag{14}$$

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with Bessel function

$$K_0(z) = \int_0^\infty \frac{e^{-z(x^2+1)^{1/2}}\,dx}{(x^2+1)^{1/2}} \tag{15}$$

which for small z becomes

$$z = -\ln z + \ln 2 - \gamma + \mathcal{O}(z^2 \ln z) \tag{16}$$

Finally we employ Brinkman's reasoning[4] to obtain ξ. In eq 1 the macroscopic flow is dominated by the screening term so that the pressure difference Δp on a column of the suspension of length l and cross-section A is given by Darcy's law

$$\Delta p/l = \eta_0 v_0/\xi^2 \tag{17}$$

where v_0 is the average fluid velocity with respect to the rods. Hence, the total force on the particles enclosed in volume $V = Al$ is

$$A\Delta p = V\eta_0 v_0/\xi^2 \tag{18}$$

The total force exerted on the N rods in the same volume can also be calculated with the help of eq 10 and 14

$$A\Delta p = 3\pi\eta_0 L v_0 N K_0^{-1}(a/\xi) \tag{19}$$

Self-consistency demands that

$$K_0(a/\xi)\xi^{-2} = 3\pi cL \tag{20}$$

where we have introduced the number density $c = N/V$. The friction coefficient for $a \ll \xi \ll L$ becomes

$$\Xi = \frac{3\pi\eta_0 L}{\ln(\xi/a) + \ln 2 - \gamma} \tag{21}$$

Equation 20 is all but identical to the result of ref 1. The slight disparity would disappear if one were to use the same short-distance cut-offs.

Several comments on the validity of these calculations are in order. As in ref 1 we have assumed the background is a uniform, isotropic medium acting on the probe only hydrodynamically and not mechanically. Taking the coupling between rods along would modify the numerical coefficients in eq 13 and 21. Note that there is some numerical evidence[3] that rods in semidilute solutions may overlap substantially with only minor entanglement.

Another difficulty is the nature of hydrodynamic screening. This seems plausible for a particle diffusing through a fixed network, the perturbed fluid being slowed down by the network just as it is by walls of a vessel in Poiseuille flow.[18,19] The existence of hydrodynamic screening for swarms of moving particles is often doubted. Brinkman[4] simply wrote down eq 1 ad hoc. Freed and Edwards[5] developed an elaborate though still not rigorous theory in which they replaced a complicated tensor depending on many-particle interactions by an averaged one. Finally, Lekkerkerker and Bedeaux[20] have pointed out that the interpretation of eq 1 may be difficult because the amount of screening depends on the reference frame since eq 1 is not Galilean invariant. This problem does not arise here because the noninvariant terms are of the same order as those deleted in the slender-body approximation.

In summary, these calculations could be useful for a rod moving through a gel or through a swarm of much longer rods (which can be considered fixed on the diffusion time scale of the probe rod) as long as mechanical entanglement can be assumed negligible. The application to other cases (e.g., all rods of equal length) is speculative and probably much more approximate.

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Comparison of Predicted Rouse-Zimm Dynamics with Observations for a 2311 Base Pair DNA Fragment

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In this work we use estimates of the radius of gyration and the translational diffusion constant of a 2311 base pair (bp) DNA fragment (1.53×10^6 molecular weight)[1] in solution to calculate the decay times predicted by the Rouse–Zimm model[2,3] for a flexible polymer. These calculations, when combined with previous electric birefringence measurements,[4] allow us to determine the degree to which the dynamics of this DNA fragment fit the predictions of the Rouse–Zimm model.

Radius of Gyration and Translational Diffusion Constant

Assuming a rise per base pair of 3.36 Å[5] the contour length of the 2311-bp DNA fragment would be 7760 Å. We will assume that the effects of excluded volume may be neglected for a DNA of this length and use a well-known formula for the radius of gyration of a wormlike coil[6]

$$R_g^2 = \frac{LP}{3} - P^2 + \frac{2P^3}{L} - \frac{2P^4}{L^2}(1 - e^{-L/P}) \tag{1}$$

where L is the contour length of the molecule and P is the persistence length. Many different measurements have been made of the persistence length of DNA in both high- and low-ionic-strength buffers[7-11] and the reported values show some variation. We will assume the persistence length in high-ionic-strength buffer (containing 100 mM Na^+) to be 500 Å. Although we note that there is some disagreement in the literature over the effect of ionic strength on the persistence length,[7-12] we will follow the recent work of Cairney and Harrington[8] and assume the persistence length to be 1000 Å in the low-ionic-strength buffer used for electric birefringence measurements.[4] Using these values in eq 1, we would predict a radius of

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