Transport coefficients for rigid spherically symmetric polymers or aggregates

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Abstract. In this paper we investigate the transport properties for rigid spherically symmetric macromolecules, having a segment density distribution falling off as $r^{-\lambda}$. We calculate the rotational and translational diffusion coefficient for a spherically symmetric polymer and the shear viscosity for a dilute suspension of these molecules, starting from a continuum description based on the Debye–Brinkman equation. Instead of numerical methods for solving equations we use perturbative methods, especially methods from boundary-layer analysis. The calculations provide simple analytical formulae for the shear viscosity η, and the translational and rotational diffusion coefficients D_T and D_R. The results can also be applied to suspensions of other porous objects, such as aggregates of colloidal particles in which $D = 3 - \lambda$ is called the fractal dimension of the aggregate.

1. Introduction

Some years ago, a method was developed to calculate the transport properties for macromolecules, by applying equations from the theory of porous media [1–5]. At that time the calculations were performed for porous spheres of constant permeability [4], and for the more realistic model of Gaussian coils [2], to which the stationary Debye–Brinkman equation can be applied

$$-\nabla P + \eta_0 \Delta v - \frac{\eta_0}{k}(v - u) = 0 \tag{1a}$$

$$\text{div } v = 0 \tag{1b}$$

in which P is the average local pressure, v the average local velocity of the solvent, u the local velocity of the polymeric material, η_0 the viscosity of a pure solvent and k the (local) permeability of the polymeric material. Obviously, if we apply this equation to macromolecules, we treat the molecule as a continuum of permeability $k(r)$.

Beside the uniform porous spheres and the Gaussian coils many other types of suspended macromolecules or objects are subject to experimental and theoretical research, so it is interesting to study the permeation of the solvent into more general porous objects. In a recent paper [6] the authors discussed rigid star-like polymer molecules having a segment density distribution $n \sim 1/r^2$. The calculations for these molecules can be done exactly, but it can also be shown that perturbative approximations give much simpler results which show very reasonable agreement with the exact results. In this paper we calculate transport coefficients for a more general class of polymers with spherical symmetry, having a repeating unit distribution which has the form

$$n(r) \sim r^{-\lambda}. \tag{2}$$

This type of object occurs not only in polymer physics, but also in recent models of aggregates of colloidal particles, in which aggregates are considered to be porous structures with a fractal geometry and a power-law density distribution, characterized by a fractal dimension usually denoted by D [7]. In these models the permeability of aggregates is either neglected [8] or taken to be constant [9]. The origin of the power law in (2) is not the subject of this paper, neither do we attempt to calculate all transport properties of these suspensions of colloidal aggregates, as they can show very complex rheological behaviour as a result of the breaking up of aggregates and the formation of new aggregates, and of the interactions between aggregates. These effects can never be described with the equations (1) alone. But the one effect of permeation of the solvent into the aggregate, as calculated here, may be incorporated in more elaborate theories.

   For reasons of simplicity the type of objects which are decribed by (2) will henceforth be called power-law polymers, although the power-law polymer can be any porous object with a power-law repeating unit distribution.

   The outline of the paper is as follows. First we consider the segment distribution for a power-law polymer more specifically and try to determine the relevant dimensionless parameters. Then we calculate, respectively, the rotational diffusion coefficient, the translational diffusion coefficient and the shear viscosity for a dilute suspension, which is the order of complexity of the calculations. Each section starts with a quick review of the basic formulae of the theory on which the calculations are based, but for a detailed derivation we refer to a review of fluid flow in porous media [1]. The exact results for the special case $\lambda = 2$ will serve as a check on the results of a perturbative method.

2. The power-law polymer: dimensionless parameters

Suppose we have a macromolecule of M repeating units, where the radial-density distribution of repeating units is given by $n(r) = cr^{-\lambda}$. The exponent λ is not necessarily an integer number. In recent models aggregates of colloidal particles, for instance, are assumed to have a fractal structure with fractal dimension $D = 3 - \lambda$ between 1.5 and 3. A fractal dimension equal to 3 corresponds to a homogeneous aggregate. The proportionality factor c can be found from the normalization condition

$$\int_0^R 4\pi r^2 \frac{c}{r^\lambda}\, dr = M \tag{3}$$

yielding $c = (3 - \lambda)M/4\pi R^{3-\lambda}$.

   From the microscopic theory of Felderhof and Deutch [3] the local hydrodynamic permeability $k(r)$ for flow through a macromolecule can be found from

$$\frac{\eta_0}{k(r)} = f_{\rm T} n(r) \tag{4}$$

where $f_{\rm T}$ is the translational coefficient of friction of a single monomer. If we estimate that this coefficient is given by $f_{\rm T} = 6\pi \eta_0 a$, which is the translational friction coefficient for an impermeable sphere of radius a, the radial permeability for a molecule is found to be given by

$$\frac{1}{k(r)} = (3 - \lambda)\frac{\gamma}{R^2}\left(\frac{R}{r}\right)^\lambda \tag{5}$$

with the dimensionless parameter γ

$$\gamma = \frac{3aM}{2R}. \tag{6}$$

This definition of the parameter γ coincides with that of our previous paper [6], which considers the special case in which the exponent λ is equal to 2. The dimensionless parameters γ and λ are the only parameters in the model, beside the molecule radius R. The exponent λ is assumed to vary between 0 and 3, while the parameter γ is likely to be much greater than zero, which can be seen from its definition: the number of times the segment radius a 'fits' on the total radius R is likely to be much smaller than the total number of segments.

3. The rotational diffusion coefficient

3.1. Basic equations

Our first attention is to the rotational diffusion coefficient D_R of a power-law polymer with a hydrodynamic permeability calculated from (5). We summarize the treatment in [1]. The velocity components for a spherically symmetric polymer rotating rigidly with constant angular velocity ω_0 around the z-axis are

$$u_1 = -\omega_0 y \tag{7a}$$
$$u_2 = +\omega_0 x \tag{7b}$$
$$u_3 = 0. \tag{7c}$$

The velocity components of the solvent now have to be solved from the set of equations (1). The ansatz

$$v_1(r, \theta) = -r\omega(r) \sin\theta \sin\theta \tag{8a}$$
$$v_2(r, \theta) = +r\omega(r) \sin\theta \cos\theta \tag{8b}$$

solves (1), provided the function $\omega(r)$ satisfies

$$\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{2}{r^2} - \frac{1}{k(r)}\right) r\omega = -\frac{r\omega_0}{k(r)} \tag{9}$$

together with the boundary conditions that $\omega(\infty) = 0$ and that $\omega(0)$ is finite.

Outside the coil the permeability is infinite, and the solution of (9) is

$$\omega(r) = \frac{A_R\omega_0}{r^3} \qquad r > R. \tag{10}$$

The constant A_R must be determined by matching the 'free' solution outside the coil ($r > R$) to the solution inside the coil ($r < R$). The rotational diffusion coefficient can be found from the solution outside the coil, through the constant A_R, by the simple formula

$$D_R = \frac{k_B T}{8\pi\eta_0 A_R} \tag{11}$$

k_B being Boltzmann's constant and T the temperature.

3.2. Solutions

Inserting (5) into (9) yields the equation

$$\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{2}{r^2} - (3-\lambda)\frac{\gamma}{R^2}\left(\frac{R}{r}\right)^\lambda\right) r\omega = -r\omega_0(3-\lambda)\frac{\gamma}{R^2}\left(\frac{R}{r}\right)^\lambda. \tag{12}$$

Because of the work reported in [6], where exact results were compared to approximate results, we have chosen a perturbative approach to solve our problem.

We start by writing (12) in dimensionless form by introducing $x = r/R$ and $w(x) = r\omega(r)/R\omega_0$, yielding

$$w'' + \frac{2}{x}w' - \frac{2}{x^2}w - \frac{(3-\lambda)\gamma}{x^\lambda}w = -x\frac{(3-\lambda)\gamma}{x^\lambda} \tag{13}$$

$$w(0) = 0 \tag{14}$$

$$2w(1) + w'(1) = 0. \tag{15}$$

The prime denotes differentiation with respect to x. The second boundary condition (15) follows from (10) because w and w' have to be continuous at $x = 1$. We now introduce a small dimensionless parameter $\epsilon = [(3-\lambda)\gamma]^{-1}$ to make our problem a perturbation problem

$$\epsilon\left(w'' + \frac{2}{x}w' - \frac{2}{x^2}w\right) - \frac{1}{x^\lambda}w = -\frac{1}{x^{\lambda-1}}. \tag{16}$$

This is a singular perturbation problem because the highest derivative is multiplied by the small parameter. The zeroth-order solution $w(x) = x$ satisfies the boundary condition at $x = 0$, but can never satisfy the boundary condition at $x = 1$. This is typical for a boundary layer problem. Close to $x = 1$ the solution develops a boundary layer to meet with the boundary condition. We solve this problem using standard techniques [10]. We divide the region $x \leqslant 1$ in an 'outer' region and an 'inner' region; the latter is a small environment of the boundary $x = 1$. In fact this inner region is the outer shell of the porous coil, but it is called 'inner' by convention, because it is inside the boundary layer. For the outer solution we try an expansion of the form $w_{out} = w_0 + \epsilon w_1 + \epsilon^2 w_2 \ldots$. With this expansion the solution is found to be $w_{out} = x$ to all orders in ϵ. It is stressed that 'outer' refers to the region away from $x = 1$, but certainly *inside* the porous coil.

Inside the boundary layer, i.e. close to $x = 1$, the outer solution is not correct. We first change variables $x = 1 - \tau$ and then $X = \tau/\delta$, where δ is a small parameter that measures the width of the boundary layer. We define an inner function $W(X) = w(1 - \delta X)$ that satisfies the equation

$$\epsilon\left(\frac{1}{\delta^2}W'' - \frac{2}{\delta(1-\delta X)}W' - \frac{2}{(1-\delta X)^2}W\right) - \frac{1}{(1-\delta X)^\lambda}W = -\frac{1}{(1-\delta X)^{\lambda-1}}. \tag{17}$$

The prime now denotes differentiation with respect to the inner variable X. The reason for this substitution is that we expect that inside the boundary layer the solution varies rapidly as a function of the normal variable x, but slowly as a function of the inner variable X. Setting $\delta = \epsilon^{1/2}$ is the only choice that provides a working perturbation scheme. This choice of δ is called the distinguished limit, and renders a differential equation that is 'as rich as possible'. Thus we have a boundary layer of thickness $\epsilon^{1/2}$. We now seek solutions of the form

$$W(X) = W_0(X) + \delta W_1(X) + \delta^2 W_2(X) \ldots. \tag{18}$$

Substituting this series in (17) and comparing equal powers of δ yields the zeroth-order equation

$$W_0'' - W_0 = -1 \tag{19a}$$

$$-W_0'(0) = 0 \tag{19b}$$

which is readily solved to give

$$W_0(X) = 1 + C_0(e^X + e^{-X}). \tag{20}$$

The remaining constant C_0 must be determined from asymptotic matching of the inner solution (20) to the outer solution w_{out} in a small region of common validity, by taking the 'intermediate' limit $x \rightarrow 1$, $X \rightarrow \infty$ and $\epsilon, \delta, \epsilon X, \delta X \rightarrow 0$. Because the positive exponential in the inner solution diverges in the intermediate limit, no match can be attained unless $C_0 = 0$. Thus the zeroth-order inner solution W_0 is found to be particularly simple.

We now recall that the rotational diffusion coefficient is calculated through the constant A_R in the solution outside the coil. Because of the continuity of the solution at $x = 1$, the coefficient A_R is equal to $R^3 W(0)$, and is thus found to be given by the zeroth-order formula

$$A_R = R^3 (1 + O(\delta)).\tag{21}$$

From this equation it is seen that the zeroth-order result just equals the result for the impermeable sphere.

To obtain a more accurate formula we need to calculate higher-order solutions. The first-order inner solution must be found from

$$W_1'' - W_1 = X \tag{22a}$$

$$2 - W_1'(0) = 0 \tag{22b}$$

leading to the solution

$$W_1(X) = -X - 3\,\mathrm{e}^{-X} + C_1(\mathrm{e}^X + \mathrm{e}^{-X}).\tag{23}$$

Similar asymptotic matching of the inner and outer solutions gives us the remaining constant $C_1 = 0$, and an additional term for the coefficient A_R

$$A_R = R^3 (1 - 3\delta + O(\delta^2)).\tag{24}$$

A second-order calculation of the inner function $W_2(X)$ is straightforward and provides the next term in the series

$$A_R = R^3 \left[1 - 3\delta + (3 + \tfrac{3}{4}\lambda)\delta^2 + O(\delta^3)\right].\tag{25}$$

To check this result it should now be compared to the exact results of [6], for the special case $\lambda = 2$, so $\epsilon = \gamma^{-1}$ and $\delta = \gamma^{-1/2}$. The exact result for A_R can be written as a series in $1/\sqrt{\gamma}$

$$A_R = R^3 \frac{\sqrt{9 + 4\gamma} - 3}{\sqrt{9 + 4\gamma} + 3} = R^3 \left[1 - \frac{3}{\sqrt{\gamma}} + \frac{9}{2\gamma} + O\left(\frac{1}{\gamma\sqrt{\gamma}}\right)\right]\tag{26}$$

which is obviously in agreement with (25).

The rotational diffusion coefficient is then calculated from (11) and (25),

$$D_R = \frac{k_B T}{8\pi \eta_0 R^3 (1 - 3\delta + \tfrac{9}{2}\delta^2)}\tag{27}$$

where one should recall that $\delta = [(3 - \lambda)\gamma]^{-1/2}$, depending both on the parameter λ and the parameter γ. For large values of γ ($\delta \rightarrow 0$) one recovers the result for an impermeable sphere.

4. The translational diffusion coeffient

4.1. Basic equations

We now calculate the translational diffusion coefficient D_T, using the Debye–Brinkman equation. The coefficient of friction for an isolated particle is given by the ratio $f_T = |F/v_0|$,

where v_0 is the velocity relative to the fluid, and F the force exerted on the particle by the fluid.

We summarize the basic equations of the treatment of [1]. Consider an isolated power-law polymer fixed at the origin and a stationary fluid flow, which would have a constant pressure p_0 and a velocity field $v_0 = (0, 0, +v_0)$ in the absence of the polymer. Again, the *true velocity and pressure fields must be calculated from (1), with the boundary condition* that the fields will approach the unperturbed fields at large distances from the origin. The following ansatz due to Felderhof [4] simplifies the partial differential equation

$$v = \psi(r)v_0 - \nu(r)r \times (r \times v_0) \tag{28a}$$

$$P = p_0 - \eta_0 \xi(r)\frac{r \cdot v_0}{r} . \tag{28b}$$

The three unknown radial functions ν, ψ and ξ must be solved from three coupled equations

$$\psi'' + \frac{4}{r}\psi' - \frac{1}{k}\psi + \xi' = 0 \tag{29a}$$

$$\xi'' + \frac{2}{r}\xi' - \frac{2}{r^2}\xi - \left(\frac{1}{k}\right)'\psi = 0 \tag{29b}$$

$$\nu = \frac{1}{2r}\psi' \tag{29c}$$

and from the boundary conditions that $\psi(\infty) = 1$, $\xi(\infty) = 0$, and that $\psi(0)$ and $\xi(0)$ must be finite.

The solutions outside the coil, where $1/k$ vanishes, are readily found

$$\xi(r) = \frac{A_T}{r^2} \tag{30}$$

$$\psi(r) = 1 - \frac{A_T}{r} + \frac{B_T}{r^3} . \tag{31}$$

From the last equation and (29c) the function ν can be calculated. The constants A_T and B_T are determined by the solution inside the coil, because ξ, ψ, ψ' and ψ'' have to be continuous at $r = R$. As in the case of rotational diffusion, these solutions outside the coil determine the translational diffusion coefficient through the constant A_T by the simple relation

$$D_T = \frac{k_B T}{4\pi\eta_0 A_T} . \tag{32}$$

4.2. Solutions

In this subsection we will solve the set of (29) using methods similar to those of section (3.2). To simplify the calculations we make the substitution $\zeta = r\xi$. The equations can now be written in dimensionless form with $x = r/R$, $\psi(r) = \tilde{\psi}(x)$ and $\zeta(r) = \tilde{\zeta}(x)$. We omit the tildes as this will not cause any confusion. Inserting (5) gives the new set of equations to be solved for $x < 1$:

$$\epsilon\left(\psi'' + \frac{4}{x}\psi' + \frac{1}{x}\zeta' - \frac{1}{x^2}\zeta\right) - \frac{1}{x^\lambda}\psi = 0 \tag{33a}$$

$$\epsilon\left(\zeta'' - \frac{2}{x^2}\zeta\right) + \frac{\lambda}{x^\lambda}\psi = 0 \tag{33b}$$

with the boundary conditions that $\zeta(0) = 0$ and $\psi(0)$ remain finite, and that $\zeta(x)$, $\psi(x)$, $\psi'(x)$ and $\psi''(x)$ are continuous at $x = 1$. We have again introduced the small parameter

ϵ as $\epsilon = [(3 - \lambda)\gamma]^{-1}$. In view of the previous calculation and the exact results reported in [6] we expect a boundary layer of thickness $\epsilon^{1/2}$ for this problem. Thus we try to find outer solutions $\psi_{\text{out}}(x)$ and $\zeta_{\text{out}}(x)$ having series expansions in ϵ, and inner solutions $\Psi(X)$ and $Z(X)$ in the region close to $x = 1$ having series expansions in $\delta = \epsilon^{1/2}$.

We will first consider the outer solutions $\psi_{\text{out}}(x)$ and $\zeta_{\text{out}}(x)$. The set of (33) to zeroth order in ϵ is trivial with solution $\psi_0(x) = 0$, which is noted to satisfy the boundary conditions at $x = 0$. To find the zeroth-order solution $\zeta_0(x)$ we must consider the set of equations first order in ϵ,

$$\frac{1}{x}\zeta_0' - \frac{1}{x^2}\zeta_0 - \frac{1}{x^\lambda}\psi_1 = 0 \tag{34a}$$

$$\zeta_0'' - \frac{2}{x^2}\zeta_0 + \frac{\lambda}{x^\lambda}\psi_1 = 0. \tag{34b}$$

From this set of equations ψ_1 can be eliminated to yield an equation for ζ_0 alone

$$\zeta_0'' + \frac{\lambda}{x}\zeta_0' - \frac{2+\lambda}{x^2}\zeta_0 = 0. \tag{35}$$

This equation is solved by trying a solution of the form $\zeta_0(x) \sim x^\alpha$, giving two possible values of the exponent α,

$$\alpha = \frac{1 - \lambda \pm \sqrt{\lambda^2 + 2\lambda + 9}}{2}. \tag{36}$$

As one of the roots is negative it must be discarded because of the boundary conditions at $x = 0$, and we find the solution $\zeta_0(x) = C_{\text{out}}x^\alpha$, with α the positive root and C_{out} a constant. With more calculations the higher-order functions can be found, but we will not need those for our purposes.

To determine the inner solution, i.e. the solution in the boundary layer at the edge of the porous sphere, we make the change in variables $x = 1 - \delta X$, ($\delta = \epsilon^{1/2}$). We introduce the functions of the inner variable X as $\Psi(X) = \psi((1-x)/\delta)$ and $Z(X) = \zeta((1-x)/\delta)$, obeying the following equations:

$$\Psi'' - \frac{4\delta}{1 - \delta X}\Psi' - \frac{\delta}{1 - \delta X}Z' - \frac{\delta^2}{(1 - \delta X)^2}Z - \frac{1}{(1 - \delta X)^\lambda}\Psi = 0 \tag{37a}$$

$$Z'' - \frac{2\delta^2}{(1 - \delta X)^2}Z + \frac{\lambda}{(1 - \delta X)^\lambda}\Psi = 0. \tag{37b}$$

The functions Z and Ψ have to satisfy the boundary conditions at $x = 1$ ($X = 0$) because this point lies in their region of validity. The continuity of respectively $\zeta(r)$, $\psi(r)$, $\psi'(r)$ and $\psi''(r)$ gives

$$Z(0) = \tilde{A}_T \tag{38a}$$

$$\Psi(0) = 1 - \tilde{A}_T + \tilde{B}_T \tag{38b}$$

$$-\frac{1}{\delta}\Psi'(0) = \tilde{A}_T - 3\tilde{B}_T \tag{38c}$$

$$\frac{1}{\delta^2}\Psi''(0) = -2\tilde{A}_T + 12\tilde{B}_T \tag{38d}$$

which are obtained after rewriting the solution outside the porous coil in dimensionless form as

$$\psi(x) = 1 - \frac{\tilde{A}_T}{x} + \frac{\tilde{B}_T}{x^3} \tag{39a}$$

$$\zeta(x) = \frac{\tilde{A}_T}{x} \tag{39b}$$

with $A_T = R\tilde{A}_T$ and $B_T = R^3\tilde{B}_T$.

We seek solutions for Ψ and Z in the form of a series expansion in δ. From (38c) and (38d) it is seen that one must have $\Psi_0'(0) = 0$, $\Psi_0''(0) = 0$ and $\Psi_1''(0) = 0$ to satisfy the boundary conditions. Furthermore one has to calculate at least Ψ_2 to determine $\tilde{A}_T$ and $\tilde{B}_T$ to zeroth order. The zeroth-order functions Ψ_0 and Z_0 are found from the set of equations

$$\Psi_0'' - \Psi_0 = 0 \tag{40a}$$
$$Z_0'' + \lambda\Psi_0 = 0 \tag{40b}$$

with the zeroth-order solutions

$$\Psi_0(X) = C_0\,e^X + D_0\,e^{-X} \tag{41a}$$
$$Z_0(X) = -\lambda(C_0\,e^X + D_0\,e^{-X}) + E_0 X + F_0 \tag{41b}$$

where C_0, D_0, E_0 and F_0 are constants to be determined. These solutions must be asymptotically matched to the outer solution in the limit $x \to 1$, $X \to \infty$ and $\epsilon, \delta, \epsilon X, \delta X \to 0$. Both C_0 and E_0 must be zero because these terms diverge in the intermediate limit $X \to \infty$. Furthermore, in this limit we find that $C_{out} = F_0$. The combination of inner and outer solutions now only contains two unknown constants D_0 and F_0, which have to be determined by applying the true boundary conditions (38) at $X = 0$. The condition $\Psi'(0) = 0$ immediately gives $D_0 = 0$.

We now calculate the correction to the inner solutions to first order in δ. With $D_0 = 0$ the zeroth-order solution is very simple. Because of this simplicity the differential equations for the first-order functions $Z_1(X)$ and $\Psi_1(X)$ are precisely the same as for the zeroth-order functions, and so are the solutions

$$\Psi_1(X) = C_1\,e^X + D_1\,e^{-X} \tag{42a}$$
$$Z_1(X) = -\lambda(C_1\,e^X + D_1\,e^{-X}) + E_1 X + F_1 \tag{42b}$$

which have to be matched to the outer solution in a first-order match in the intermediate limit $x \to 1$, $X \to \infty$, but keeping terms of order δX. As again the positive exponential terms diverge in the intermediate limit, C_1 must be zero. In the intermediate limit the outer solution is written as

$$\psi(1 - \delta X) = 0 \tag{43a}$$
$$\zeta(1 - \delta X) = F_0(1 - \delta X)^\alpha \approx F_0 - \alpha F_0 \delta X. \tag{43b}$$

Comparing these solutions with the inner solution (42) in the limit $X \to \infty$ we conclude that $E_1 = -\alpha F_0$, leaving two unknown first-order constants D_1 and F_1 which have to be determined from the real boundary conditions at $x = 1$. Because $\Psi_1''(0) = 0$, we find $D_1 = 0$.

The equations second order in δ are only slightly more complicated and the solutions are

$$\Psi_2(X) = F_0(1 - \alpha) + D_2\,e^{-X} \tag{44a}$$
$$Z_2(X) = -\lambda D_2\,e^{-X} + \tfrac{1}{2}F_0(2 - \lambda + \lambda\alpha)X^2 + E_2 X + F_2. \tag{44b}$$

We now have all the solutions we need for our purposes, as will become clear shortly.

Writing the dimensionless coefficients $\tilde{A}_T$ and $\tilde{B}_T$ also as a series expansion in δ as $\tilde{A}_T = \tilde{A}_{T,0} + \delta\tilde{A}_{T,1} \ldots$ and $\tilde{B}_T = \tilde{B}_{T,0} + \delta\tilde{B}_{T,1} \ldots$, and applying the boundary conditions at $X = 0$ to zeroth order in δ yields a linear set of equations for the coefficients $\tilde{A}_{T,0}$, $\tilde{B}_{T,0}$,

D_2 and F_0

$$F_0 = \tilde{A}_{T,0} \tag{45a}$$

$$0 = 1 - \tilde{A}_{T,0} + \tilde{B}_{T,0} \tag{45b}$$

$$0 = \tilde{A}_{T,0} - 3\tilde{B}_{T,0} \tag{45c}$$

$$D_2 = -2\tilde{A}_{T,0} + 12\tilde{B}_{T,0} . \tag{45d}$$

This system of equations is easily solved and gives $D_2 = 3$, $F_0 = \frac{3}{2}$, $\tilde{A}_{T,0} = \frac{3}{2}$ and $\tilde{B}_{T,0} = \frac{1}{2}$. Similarly one can calculate the first-order correction, because the first-order coefficients $\tilde{A}_{T,1}$, $\tilde{B}_{T,1}$ are determined only by the first three equations, from which $\Phi_3''(0)$ then follows, without having to calculate the third-order function Φ_3. So we only have to solve a set of three linear equations, which yields, for the unknown first-order coefficients, $F_1 = -\frac{3}{2}$, $\tilde{A}_{T,1} = -\frac{3}{2}$ and $\tilde{B}_{T,1} = -\frac{3}{2}$.

Gathering the results we find for the important coefficient $\tilde{A}_T$ the expression

$$\tilde{A}_T = \frac{3}{2} - \frac{3}{2}\delta + O(\delta^2) \tag{46}$$

where it is again noted that δ depends on λ as $\delta = [(3 - \lambda)\gamma]^{-1/2}$. In the special case that $\lambda = 2$, equation (46) coincides with the result obtained in our previous paper [6]. Furthermore, it is noted that for the case $\lambda = 2$, (46) was found to be a reasonable approximation to the exact results for $\gamma > 5$. This is the reason why we refrain from calculations of higher-order terms in the expansion of $\tilde{A}_T$, although they can be done with a little more effort.

The translational diffusion coefficient becomes, with (32),

$$D_T = \frac{k_B T}{6\pi \eta_0 R} \frac{1}{(1 - \delta)} . \tag{47}$$

5. The shear viscosity for a dilute suspension

5.1. Basic equations

In this section we calculate the shear viscosity for a dilute suspension of power-law polymers, again following [1]. The viscosity of the pure solvent without polymers is η_0. As in the previous section we consider one polymer located at the origin of a Cartesian coordinate frame. Suppose the velocity field of the solvent without the polymer is given by a simple shear flow $v_0 = (G_0 y, 0, 0)$. Although held at the origin, the polymer will start to rotate because of the interaction with the solvent. By considering the total torque exerted by the fluid on the polymer, the velocity of the polymeric material can be calculated to be $u = (\frac{1}{2}G_0 y, -\frac{1}{2}G_0 x, 0)$. Again the actual velocity and pressure fields of the solvent must be calculated with the Debye–Brinkman equation, subject to the condition that the fields approach the unperturbed fields at large distances from the power-law polymer. To solve this problem we invoke the ansatz due to Felderhof [4]

$$v = u + \phi(v_0 - u) - \mu r \times (r \times [v_0 - u]) \tag{48a}$$

$$P = p_0 - \eta_0 \chi \frac{r \cdot v_0}{r^2} . \tag{48b}$$

We have, as before, three unknown functions of the radial distance ϕ, μ and χ, satisfying the following equations:

$$\phi'' + \frac{6}{r}\phi' - \frac{1}{k}\phi + \frac{1}{r}\chi' = 0 \tag{49a}$$

$$\chi'' + \frac{2}{r}\chi' - \frac{6}{r^2}\chi - r\left(\frac{1}{k}\right)'\phi = 0 \tag{49b}$$

$$\mu = \frac{1}{3r}\phi' \tag{49c}$$

with the boundary conditions that $\phi(\infty) = 1$, $\chi(\infty) = 0$ and that $\phi(0)$ and $\chi(0)$ are finite.
The solution outside the coil is as simple as before

$$\chi(r) = \frac{2A_V}{r^3} \tag{50}$$

$$\phi(r) = 1 - \frac{A_V}{r^3} + \frac{B_V}{r^5} \tag{51}$$

from which the function μ can be calculated. The constants A_V and B_V must be determined
by matching to the solution inside the coil, demanding that χ, ϕ, ϕ' and ϕ'' are continuous
at $r = R$. Again there is a simple relation between the solution outside the coil and the
shear viscosity of a dilute suspension of spherical polymers, first obtained by Burgers [11]

$$\frac{\eta - \eta_0}{\eta_0} = \frac{4}{3}\pi n_p A_V \tag{52}$$

where n_p is the number density of polymer coils.

5.2. Solutions

We follow the same procedure for solving the viscosity equations inside the porous coil
as we did for the translational diffusion coefficient, so we will not be as detailed. In
dimensionless perturbative form the set of equations (49) becomes

$$\epsilon\left(\phi'' + \frac{6}{x}\phi' + \frac{1}{x}\chi'\right) - \frac{1}{x^\lambda}\phi = 0 \tag{53a}$$

$$\epsilon\left(\chi'' + \frac{2}{x}\chi' - \frac{6}{x^2}\chi\right) + \frac{\lambda}{x^\lambda}\phi = 0. \tag{53b}$$

We define again an outer region and an inner region around $x = 1$. We have already seen
that it is sufficient to calculate the outer solution denoted by ϕ_{out} and χ_{out} to zeroth order
only. This gives us $\phi_0 = 0$, while χ_0 has to solved from

$$\chi_0'' + \frac{2+\lambda}{x}\chi_0' - \frac{6}{x^2}\chi_0 = 0. \tag{54}$$

However, a study of the calculation of the translational diffusion coefficient shows that it
is not necessary to solve this equation explicitly, and we immediately turn to studying the
solution in the inner region.

We must determine the inner solutions defined by $\Phi(X) = \phi((1-x)/\delta)$ and $\Xi(X) = \chi((1-x)/\delta)$, which have to be solved from the coupled equations

$$\Phi'' - \frac{6\delta}{1-\delta X}\Phi' - \frac{\delta}{1-\delta X}\Xi' - \frac{1}{(1-\delta X)^\lambda}\Phi = 0 \tag{55a}$$

$$\Xi'' - \frac{2\delta}{1-\delta X}\Xi' - \frac{6\delta^2}{(1-\delta X)^2}\Xi + \frac{\lambda}{(1-\delta X)^\lambda}\Phi = 0 \tag{55b}$$

with the set of boundary conditions

$$\Xi(0) = 2\tilde{A}_V \tag{56a}$$

$$\Phi(0) = 1 - \tilde{A}_V + \tilde{B}_V \tag{56b}$$

$$-\frac{1}{\delta}\Phi'(0) = 3\tilde{A}_V - 5\tilde{B}_V \tag{56c}$$

$$\frac{1}{\delta^2}\Phi''(0) = -12\tilde{A}_V + 30\tilde{B}_V. \tag{56d}$$

Note that we have again introduced dimensionless coefficients for the solution outside the coil through $A_V = R^3(\tilde{A}_{V,0} + \delta\tilde{A}_{V,1}\ldots)$ and $B_V = R^5(\tilde{B}_{V,0} + \delta\tilde{B}_{V,1}\ldots)$.

The zeroth-order equations are easily solved and yield

$$\Phi_0(X) = C_0\,e^X + D_0\,e^{-X} \tag{57a}$$

$$\Xi_0 = -\lambda(C_0\,e^X + D_0\,e^{-X}) + E_0 X + F_0. \tag{57b}$$

Because these inner solutions must be matched asymptotically to the outer solutions ϕ_0 and χ_0 in a zeroth-order matching procedure, one must have $C_0 = 0$ and $E_0 = 0$. Note again that 'outer' refers to the solution away from $x = 1$ but inside the porous coil. The condition $\Phi'(0) = 0$, which follows from (56c), gives $D_0 = 0$.

Solving the equations first order in δ is again very similar to solving the first-order equations for the translational diffusion coefficient. The inner solution that is capable of asymptotically matching the outer solution is

$$\Phi_1(X) = D_1\,e^{-X} \tag{58a}$$

$$\Xi_1 = -\lambda D_1\,e^{-X} + E_1 X + F_1. \tag{58b}$$

As $\Phi_1''(0)$ must be zero because of (56d), the coefficient D_1 is equal to zero. Finally the second-order solution Φ_2 is given by

$$\Phi_2(X) = E_1 + D_2\,e^{-X}. \tag{59}$$

We now apply the boundary conditions to determine the remaining unknown coefficients. Solving the set of equations (56) to zeroth order in δ gives $D_2 = 15$, $F_0 = 5$, $\tilde{A}_{V,0} = \frac{5}{2}$ and $\tilde{B}_{V,0} = \frac{3}{2}$. A first-order calculation of the remaining coefficients from the boundary conditions gives $F_1 = -15$, $\tilde{A}_{V,1} = -\frac{15}{2}$ and $\tilde{B}_{V,1} = -\frac{15}{2}$.

Combining the results, we find for the important coefficient $\tilde{A}_V$

$$\tilde{A}_V = \frac{5}{2} - \frac{15}{2}\delta + O(\delta^2). \tag{60}$$

For the shear viscosity we find with (52) and (60) the approximate formula

$$\frac{\eta - \eta_0}{\eta_0} = \frac{10}{3}\pi n_p\left(1 - 3[(3-\lambda)\gamma]^{-1/2}\right). \tag{61}$$

In the case that $\lambda = 2$, this result coincides with the (series expansion of) the exact result.

6. Discussion

In this paper we have calculated three transport coefficients for macromolecules or aggregates with a power-law repeating-unit density distribution. The calculations can be considered as classical examples of boundary-layer analysis. The physical meaning of the boundary layer in these calculations is the penetration of the velocity field of the solvent into the porous sphere, characterized by the parameter $[(3-\lambda)\gamma]^{-1/2}$. In the calculations we find no reason why the exponent λ should be positive (as is the case for a mass-density distribution that decreases with r) and the calculations seem to be valid also if the hydrodynamically impermeable core is absent, as long as γ is large enough. In the interesting limit $\lambda \to -\infty$, for γ fixed, one recovers the results for impermeable spheres. This limit corresponds to the case in which all repeating units are localized in a thin spherical

shell of radius R. The method breaks down if the exponent λ gets close to 3, because then δ is no longer a small parameter. The method is not valid for $\lambda \geqslant 3$. This results from the fact that the repeating-unit distribution cannot be normalized: all mass heaps up in the centre and the flow can penetrate easily deep into the porous polymer.

The variety of exponents for which the method is applicable suggests that the results are not sensitive to the shape of the density distribution inside the porous coil. This can also be found in the calculations: to first order in δ no property of the 'outer' solutions is retained in the final results. This suggests not only that the boundary-layer method may be succesfully applied to porous spheres with density distributions not precisely equal to a power-law distribution, but also that the present results for power-law polymers in fact cover the whole variety of mass distributions, because (almost) every density distribution function can be approximated with a power law at the edge of the porous sphere.

The results presented here may be verified in experiments directly, but the greatest advantage most probably is that the simple closed form of the diffusion coefficients, as calculated in this article, allows straightforward incorporation in more extensive models. If these models concern colloidal aggregates, some care must be applied, because colloidal aggregates are spherically symmetric only on average, while individual aggregates in general are not. The validity of models in which colloidal aggregates are treated as spheres can only be measured by their predictions. Also, in our calculation the (average) deformation due to the shear flow is neglected. Some anisotropy may be dealt with perturbatively, but, in general, taking anisotropy into account requires the finding of different ansätze, and therefore knowledge of the shape of the porous object. Following this path will be succesful probably only for a few, very specific systems, such as rigid cylinders or ellipsoids.

Finally we note that hydrodynamic permeabilities can be measured in sedimentation experiments, as is explained in the review of [1] and references therein.

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