Frictional properties of dilute polymer solutions. I. Rotational friction coefficient*

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The theory of Debye and Bueche for the frictional properties of dilute polymer solutions is placed on a microscopic basis. It is shown that the microscopic foundations for the theories of Debye–Bueche and Kirkwood–Riseman are identical, but that the theories differ in their statistical analysis. The Debye–Bueche equations are applied to the rotational friction coefficient of a spherically symmetric polymer with arbitrary radial density distribution. An exact result is derived for a Gaussian distribution of low density. A variational principle of minimum energy dissipation is formulated which is suitable for numerical work.

I. INTRODUCTION

The theory of the nonequilibrium properties of dilute polymer solutions was significantly advanced in 1946 when Debye[1] pointed out that the reason for the failure of the older theories to account for the experimental data was due to the neglect of hydrodynamic interactions between different parts of the polymer. In fact, when a polymer is subjected to an external flow, each segment will move in a local fluid velocity field which is the superposition of the external flow and the disturbances of the flow due to all the other segments. Debye analysed the effect of these hydrodynamic interactions by studying a simple continuum model, consisting of a uniform sphere which is permeable to the flow and exerts a friction proportional to the local relative velocity of polymer and fluid. Debye calculated the intrinsic viscosity for a dilute solution of such spheres, and Bueche calculated the translational friction coefficient. They published their results in a joint paper[2] in 1948. Independently similar calculations for the same model were made by Brinkman.[3]

At the same time Kirkwood and Riseman[4] presented a theory based on Debye's idea of hydrodynamic interactions between polymer segments but starting at a microscopic level. They restricted themselves to linear chains and used the knowledge of the conformational statistics of such chains. Hence the Kirkwood–Riseman (KR) theory is based on a much more detailed picture of the polymer than the Debye–Bueche theory. Although the results of the two theories were qualitatively the same, the Kirkwood–Riseman theory appeared to be more trustworthy quantitatively, and their theory has been the basis of much of the later work.[5] A serious drawback of the KR theory is that, although starting at a microscopic level, it contains several *ad hoc* assumptions about statistical averages which are made purely for computational convenience. In our view the statistical treatment of the KR theory is strongly biased by the fact that it is formulated for linear chains (or at most branched chains, see Ref. 5, p. 317).

The relation between the Debye–Bueche and Kirkwood–Riseman theories seems not to have been clearly understood.[6] It is one of the objects of this paper to demonstrate that the microscopic basis of the two theories is identical. In fact, we show that starting from the same microscopic equations as Kirkwood–Riseman one can derive the basic macroscopic equations of Debye–Bueche by a simple mean field approximation. Thus the difference between the two theories rests solely on the difference in statistical treatment. We feel that the Debye–Bueche equations, once placed on such a microscopic basis, have the appeal of simplicity and truth. Moreover one has the advantage that the theory allows one to avoid the "preaveraging" which is required as a practical matter in the KR approach. From a statistical point of view the mean field approximation is a natural starting point. In any case it is straightforward to correct for correlations between segments as will be shown in a later paper.

The basic equations of our theory are the linear Navier-Stokes equations for incompressible, stationary flow, with added friction terms, and are identical to those used by Debye and Bueche. We differ in that we aim to treat more general density distributions than the uniform sphere. This will make a quantitative difference. In this article we present the general formulation and apply the theory to the rotational friction coefficient, which is the simplest frictional property of spherically symmetric polymers. To our knowledge this transport coefficient has not been treated in the Debye–Bueche theory. Throughout we adhere in our notation as closely as possible to the monograph by Yamakawa.[5]

In later articles we shall deal with the translational drag coefficient and the intrinsic viscosity; numerical work will also be presented. We believe that the quantitative numerical results based on the present theory will be more reliable than those following from the KR theory.

The present work should be seen in perspective of other important developments following the KR and Debye–Bueche theories. These developments include explicit consideration of the internal polymer segment dynamics in order to investigate such phenomena as the frequency dependent intrinsic viscosity. The most famous model for dealing with such dynamical effects is associated with the names of Rouse,[7a] Bueche,[7b] and Zimm.[7c] An alternative approach is based on the more fundamental Kirkwood[7d] diffusion equation. These developments are reviewed by Yamakawa[5] and we note the recent contributions by Bixon[7e] and by Zwanzig[7f] that investigate the relationship between the two approaches.

There, of course, have been several different attacks on the approximation of preaveraging the hydrodynamic interaction. In addition to the formal investigation of Fixman and co-workers,[8a] there have been some exact results by Zwanzig and co-workers[8b] and by Paul and Mazo,[8c] most notably for plane polygons, that avoid the preaveraging approximation. These latter results may prove useful for assessing the consequences of the approximation of neglecting correlations in the theory presented here.

II. BASIC EQUATIONS

The frictional properties of dilute polymer solutions are usually studied on the basis of the following simplified model. The solvent in the absence of polymers is assumed to satisfy the Navier–Stokes equations for an incompressible fluid in stationary flow with neglect of inertial effects

$$\eta_0\nabla^2\mathbf{v}_0 - \nabla p_0 = 0, \quad \nabla\cdot\mathbf{v}_0 = 0, \tag{2.1}$$

where $\mathbf{v}_0(\mathbf{r})$ is the flow velocity, $p_0(\mathbf{r})$ is the pressure, and η_0 is the solvent viscosity. The presence of polymers disturbs the flow and hence affects the transport properties of the fluid. For low concentrations we need only consider the effect of a single polymer. Moreover we neglect non-Newtonian behavior and regard the polymer as a rigid structure in each of the many conformations it may adopt. We consider the usual simple model of a polymer consisting of segments connected by rigid bonds whose effect on the flow is negligible. We shall allow cross linking between segments, so that the polymer is not necessarily a linear chain. Provided the segments are sufficiently small the effect of each segment on the flow is given by the Oseen fields, i.e., if $-\mathbf{F}_j$ is the force on segment j then the flow disturbance is given by

$$\delta_j\mathbf{v}(\mathbf{r}) = \mathbf{T}(\mathbf{r}-\mathbf{r}_j)\cdot\mathbf{F}_j, \quad \delta_j p(\mathbf{r}) = \mathbf{Q}(\mathbf{r}-\mathbf{r}_j)\cdot\mathbf{F}_j \tag{2.2}$$

where the Oseen tensor $\mathbf{T}(\mathbf{R})$ and the Oseen vector $\mathbf{Q}(\mathbf{R})$ are given by

$$\mathbf{T}(\mathbf{R}) = \frac{1}{8\pi\eta_0}\left(\frac{\mathbf{I}}{R} + \frac{\mathbf{RR}}{R^3}\right), \quad \mathbf{Q}(\mathbf{R}) = \frac{1}{4\pi}\frac{\mathbf{R}}{R^3}. \tag{2.3}$$

where $\mathbf{I}$ is the unit tensor. The Oseen fields satisfy

$$\eta_0\nabla_R^2\mathbf{T} - \nabla_R\mathbf{Q} = -\mathbf{I}\delta(\mathbf{R}), \quad \nabla_R\cdot\mathbf{T} = 0. \tag{2.4}$$

In the Appendix it is shown that the pair $(\mathbf{T}, \mathbf{Q})$ can be regarded as the Green solution to the linear Navier–Stokes equations (2.1).

The microscopic fluid flow field and pressure are given by summing the contributions (2.2) from all n segments

$$\mathbf{v}(\mathbf{r}) = \mathbf{v}_0(\mathbf{r}) + \sum_{j=1}^{n}\delta_j\mathbf{v}(\mathbf{r}), \tag{2.5a}$$

$$p(\mathbf{r}) = p_0(\mathbf{r}) + \sum_{j=1}^{n}\delta_j p(\mathbf{r}). \tag{2.5b}$$

By construction $\mathbf{v}(\mathbf{r})$ and $p(\mathbf{r})$ satisfy

$$\eta_0\nabla^2\mathbf{v} - \nabla p = -\mathbf{f}(\mathbf{r}), \quad \nabla\cdot\mathbf{v} = 0 \tag{2.6}$$

where $\mathbf{f}(\mathbf{r})$ is the microscopic force density defined by

$$\mathbf{f}(\mathbf{r};\{\mathbf{r}_j\}) = \sum_{j=1}^{n}\mathbf{F}_j\delta(\mathbf{r}-\mathbf{r}_j). \tag{2.7}$$

Since we have assumed the polymer to be a rigid structure the polymer velocity field $\mathbf{u}(\mathbf{r})$ is given by

$$\mathbf{u}(\mathbf{r}) = \mathbf{u}_0 + \boldsymbol{\omega}\times(\mathbf{r}-\mathbf{R}_m), \tag{2.8}$$

where $\mathbf{u}_0$ is the translational speed and the second term describes the rotation about the center of mass position $\mathbf{R}_m$. The force $-\mathbf{F}_j$ on the jth segment is given by

$$\mathbf{F}_j = \zeta[\mathbf{u}(\mathbf{r}_j) - \mathbf{v}'(\mathbf{r}_j)], \tag{2.9}$$

where ζ is the friction constant of the segment, and $\mathbf{v}'(\mathbf{r}_j)$ is the fluid flow velocity (2.5a) at the location of the segment with exclusion of the self-contribution. Hence the hydrodynamic interactions between all segments of the polymer are described by the set of equations

$$\mathbf{F}_j = \zeta[\mathbf{u}(\mathbf{r}_j) - \mathbf{v}_0(\mathbf{r}_j)] - \zeta\sum_{\substack{k=1\\k\neq j}}^{n}\mathbf{T}_{jk}\cdot\mathbf{F}_k \quad (j=1,\cdots,n), \tag{2.10}$$

where $\mathbf{T}_{jk} \equiv \mathbf{T}(\mathbf{r}_j - \mathbf{r}_k)$. For simplicity we suppose that all segments have the same friction constant ζ; the extension to heterogeneous polymer chains is immediate.

We shall assume that the polymer structure has a certain randomness which is given in terms of a known statistical distribution of the segment positions $\mathcal{P}(\mathbf{r}_1,\cdots,\mathbf{r}_n)$ In order to extract useful information from the microscopic equations obtained so far we must average over this distribution. In carrying out the averaging procedure explicitly one is forced to make approximations of a statistical nature. The KR theory[4] of the frictional properties of linear chain polymers makes in its formulation and approximations strong use of the linearity of the molecule. In addition, practical application of the KR theory requires preaveraging of the Oseen tensor. Thus we propose a different averaging procedure which has the added advantages that it is not limited to linear chains but allows cross linking, and that it does not require preaveraging.

We define the average flow velocity, average pressure and average force density by

$$\mathbf{V}(\mathbf{r}) = \langle\mathbf{v}(\mathbf{r})\rangle, \quad P(\mathbf{r}) = \langle p(\mathbf{r})\rangle, \quad \mathbf{F}(\mathbf{r}) = \langle\mathbf{f}(\mathbf{r})\rangle, \tag{2.11}$$

where the average is over the statistical distribution $\mathcal{P}(\mathbf{r}_1,\cdots,\mathbf{r}_n)$. Averaging Eqs. (2.6) one finds

$$\eta_0\nabla^2\mathbf{V} - \nabla P = -\mathbf{F}(\mathbf{r}), \quad \nabla\cdot\mathbf{V} = 0, \tag{2.12}$$

where now the functions vary relatively slowly in space. In order to use these equations one needs a further relation between $\mathbf{F}$ and $\mathbf{V}$ which must be obtained by averaging the force equations (2.10). Before performing this average it is convenient to rewrite the equations in a continuum description. We can drop the restriction

$k \neq j$ in (2.10) by slightly modifying the Oseen tensor $\mathbf{T}(\mathbf{R})$ by cutting out a small sphere of infinitesimal radius ϵ about $R=0$. In the final equations (2.15) and (2.16) we take the limit $\epsilon \to 0$. We define the microscopic number density $\nu(\mathbf{r})$ and its statistical average $\rho(\mathbf{r})$ by

$$\nu(\mathbf{r};\{\mathbf{r}_j\}) = \sum_{j=1}^{n} \delta(\mathbf{r}-\mathbf{r}_j), \quad \rho(\mathbf{r}) = \langle \nu(\mathbf{r};\{\mathbf{r}_j\})\rangle. \tag{2.13}$$

Multiplying (2.10) by $\delta(\mathbf{r}-\mathbf{r}_j)$ and summing over j one finds the exact microscopic equation

$$\mathbf{f}(\mathbf{r}) = \zeta\nu(\mathbf{r})[\mathbf{u}(\mathbf{r})-\mathbf{v}_0(\mathbf{r})] - \zeta\nu(\mathbf{r})\int \mathsf{T}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{f}(\mathbf{r}')\,d\mathbf{r}'. \tag{2.14}$$

Hence one has for the average force field the exact equation

$$\mathbf{F}(\mathbf{r}) = \zeta\rho(\mathbf{r})[\mathbf{u}(\mathbf{r})-\mathbf{v}_0(\mathbf{r})] - \zeta\left\langle \nu(\mathbf{r})\int \mathsf{T}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{f}(\mathbf{r}')\,d\mathbf{r}'\right\rangle. \tag{2.15}$$

As the next step we make a mean field approximation and simply break the average on the right hand side.[9] Then $\mathbf{F}(\mathbf{r})$ satisfies the closed integral equation

$$\mathbf{F}(\mathbf{r}) = \zeta\rho(\mathbf{r})[\mathbf{u}(\mathbf{r})-\mathbf{v}_0(\mathbf{r})] - \zeta\rho(\mathbf{r})\int \mathsf{T}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{F}(\mathbf{r}')\,d\mathbf{r}'. \tag{2.16}$$

This can be written in the abbreviated form

$$\mathbf{F}(\mathbf{r}) = \zeta\rho(\mathbf{r})[\mathbf{u}(\mathbf{r})-\mathbf{V}(\mathbf{r})], \tag{2.17}$$

where $\mathbf{V}(\mathbf{r})$ satisfies the integral equation

$$\mathbf{V}(\mathbf{r}) = \mathbf{v}_0(\mathbf{r}) - \zeta\int \mathsf{T}(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}')[\mathbf{V}(\mathbf{r}')-\mathbf{u}(\mathbf{r}')]\,d\mathbf{r}'. \tag{2.18}$$

Averaging the defining equation (2.5b) for the pressure one finds

$$P(\mathbf{r}) = p_0(\mathbf{r}) + \frac{1}{4\pi}\int \frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^3}\cdot\mathbf{F}(\mathbf{r}')\,d\mathbf{r}'. \tag{2.19}$$

It is shown in the Appendix that (2.17–19) are consistent with Eqs. (2.12). By substitution of the constitutive equation (2.17) we can now write (2.12) in the form

$$\eta_0\nabla^2\mathbf{V} - \zeta\rho(\mathbf{r})[\mathbf{V}(\mathbf{r})-\mathbf{u}(\mathbf{r})] - \nabla P = 0, \quad \nabla\cdot\mathbf{V} = 0. \tag{2.20}$$

These are the starting equations of Debye and Bueche.[2] Hence we have shown that the microscopic foundations for the theories of Kirkwood–Riseman and Debye–Bueche are identical. The relation between these two theories has not always been clearly understood.[6]

When the first term in (2.20) is omitted and $\mathbf{u}(\mathbf{r})$ is put equal to zero one obtains $\zeta\rho\mathbf{V} = -\nabla P$ which is known as Darcy's law[10] for a porous medium. The product $[\zeta\rho(\mathbf{r})]^{-1}$ is called the permeability. Thus in adopting Eqs. (2.20) one essentially considers the polymer as a porous body. In this and following papers we shall carry the analysis of Eqs. (2.20) much further than it was taken by Debye and Bueche, and make a careful comparison with the results of the Kirkwood–Riseman theory.

III. ROTATORY FRICTION OF A SPHERICALLY SYMMETRIC POLYMER

The simplest frictional property of a spherical polymer is the rotational drag. It is convenient to choose a coordinate system in which the polymer is at rest with center of mass at the origin. Then $\mathbf{u}(\mathbf{r}) = 0$, and our basic equations (2.20) can be written

$$\nabla^2\mathbf{V} - \kappa^2(r)\mathbf{V} - \eta_0^{-1}\nabla P = 0, \quad \nabla\cdot\mathbf{V} = 0, \tag{3.1}$$

where $\kappa^2(r) = \zeta\rho(r)/\eta_0$ has the dimension $(\text{length})^{-2}$.

For rotation the unperturbed flow is given by

$$\mathbf{v}_0(\mathbf{r}) = \boldsymbol{\omega}\times\mathbf{r}, \quad p_0 = \text{constant}. \tag{3.2}$$

We introduce spherical coordinates (r, θ, φ) and corresponding unit vectors $(\mathbf{e}_r, \mathbf{e}_\theta, \mathbf{e}_\varphi)$. Choosing the z axis along the direction of ω we attempt to solve (3.1) by $(\mathbf{V}, P)$ of the form

$$\mathbf{V}(\mathbf{r}) = \omega r\phi(r)\sin\theta\,\mathbf{e}_\varphi, \quad P(\mathbf{r}) = p_0. \tag{3.3}$$

The unperturbed flow is of this form with $\phi(r) = 1$. One easily checks that $\nabla\cdot\mathbf{V} = 0$ is automatically satisfied. Substituting in (3.1) one finds that the ansatz (3.3) works provided $\phi(r)$ satisfies

$$r^2\phi'' + 4r\phi' - \kappa^2(r)r^2\phi = 0, \tag{3.4}$$

where a prime indicates differentiation with respect to r. At large distances $\kappa^2(r)$ tends to zero rapidly and (3.4) becomes a free field equation with independent solutions 1 and $1/r^3$. Fitting to the unperturbed flow we can therefore write the asymptotic behavior

$$\phi(r) \approx 1 - A/r^3 \text{ as } r\to\infty, \tag{3.5}$$

where A is a constant to be determined. The rotatory friction coefficient f_r can be expressed directly in terms of this constant. We shall show that the total torque about the origin exerted on the fluid is given by

$$\mathscr{T} = -8\pi\eta_0 A\omega. \tag{3.6}$$

Since on the other hand $\mathscr{T} = -f_r\boldsymbol{\omega}$ we have

$$f_r = 8\pi\eta_0 A = 8\pi\eta_0 a^3 \tag{3.7}$$

where a is an *effective radius* defined by $A = a^3$. For a hard sphere a would coincide with the sphere radius.

In order to derive (3.6) we introduce the stress tensor

$$\boldsymbol{\sigma} = \eta_0(\nabla\mathbf{V})_s - P\mathbf{I}, \tag{3.8}$$

where $(\nabla\mathbf{V})_{s,\alpha\beta} \equiv (\partial V_\alpha/\partial x_\beta) + (\partial V_\beta/\partial x_\alpha)$. Then (3.1) can be written

$$\nabla\cdot\boldsymbol{\sigma} = \eta_0\kappa^2\mathbf{V}, \quad \nabla\cdot\mathbf{V} = 0, \tag{3.9}$$

and one can easily show the identity

$$\frac{\partial}{\partial x_\beta}(\sigma_{\alpha\beta}x_\gamma - \sigma_{\gamma\beta}x_\alpha) = -(F_\alpha x_\gamma - F_\gamma x_\alpha). \tag{3.10}$$

Integrating both sides over a volume Ω bounded by a surface Σ and applying Gauss's theorem one finds

$$-\int_\Sigma \mathbf{r}\times(\boldsymbol{\sigma}\cdot\mathbf{n})\,dS = \int_\Omega \mathbf{r}\times\mathbf{F}(\mathbf{r})\,d\mathbf{r}. \tag{3.11}$$

This shows the equality of two alternative expressions for the torque exerted on the fluid in Ω. The total torque is found by extending the integral on the right over all space,

$$\mathscr{T} = \int \mathbf{r}\times\mathbf{F}(\mathbf{r})\,d\mathbf{r} = -\zeta\int \mathbf{r}\times\mathbf{V}(\mathbf{r})\rho(r)\,d\mathbf{r}. \tag{3.12}$$

Substituting (3.3) one finds

$$\mathscr{T} = -\omega \frac{8\pi}{3} \zeta \int_0^\infty r^4 \phi(r) \rho(r)\, dr. \tag{3.13}$$

From the left-hand side of (3.11) and the asymptotic behavior (3.5) one finds $\mathscr{T} = -8\pi\eta_0 A\omega$, which is (3.6). Thus we have two expressions for the rotatory friction coefficient, viz., (3.7) $f_r = 8\pi\eta_0 A$ and

$$f_r = \frac{8\pi}{3} \zeta \int_0^\infty r^4 \phi(r) \rho(r)\, dr. \tag{3.14}$$

The problem of calculating the rotatory friction coefficient amounts to solving the differential equation (3.4) for $\phi(r)$ with the conditions that $\phi(r)$ behave asymptotically as given in (3.5) and be regular at the origin. To explore the latter condition we note that for the flow (3.3) one has

$$(\nabla \mathbf{V})_s = \omega r \phi' \sin\theta (\mathbf{e}_r \mathbf{e}_\varphi + \mathbf{e}_\varphi \mathbf{e}_r). \tag{3.15}$$

Hence the condition that $\phi(r)$ tend to a constant at $r = 0$ is sufficient for the stress tensor to be regular at the origin. Note that (3.4) is identical to the Schrödinger equation for the radial wave function (divided by r) of a particle scattering with angular momentum $l = 1$ from the potential $\kappa^2(r)$ at zero energy. Henceforth we shall call $\kappa^2(r)$ the potential, in analogy to the quantummechanical problem.

IV. EXPLICIT SOLUTIONS FOR UNIFORM SPHERE AND SPHERICAL SHELL

For sufficiently simple potentials $\kappa^2(r)$ the differential equation (3.4) can be solved explicitly. We consider first the *uniform sphere* for which

$$\begin{aligned} \kappa^2(r) &= \kappa^2 \text{ constant for } 0 \le r < R, \\ &= 0 \qquad\quad \text{for } R < r < \infty. \end{aligned} \tag{4.1}$$

Then one has in the two regions

$$\begin{aligned} \phi(r) &= B\left(\frac{\cosh\kappa r}{r^2} - \frac{\sinh\kappa r}{\kappa r^3}\right) \text{for } 0 \le r < R, \\ \phi(r) &= 1 - A/r^3 \qquad\qquad \text{for } R < r < \infty, \end{aligned} \tag{4.2}$$

where the constants A and B must be found by fitting the solutions at $r = R$. The boundary conditions for the original problem are that all components of $\mathbf{V}$ and the normal–normal and tangential–normal components of $\boldsymbol{\sigma}$ are continuous at the boundary surface. These conditions are satisfied when $\phi(r)$ and $\phi'(r)$ are continuous at $r = R$. Hence one finds for A and B

$$\begin{aligned} A &= R^3[1 + 3/\sigma^2 - (3/\sigma)\coth\sigma], \\ B &= 3R^2/(\sigma \sinh\sigma), \end{aligned} \tag{4.3}$$

where $\sigma = \kappa R$ is Debye's shielding ratio.[2] Thus we find that

$$f_r = 8\pi\eta_0 R^3 [1 + 3/\sigma^2 - (3/\sigma)\coth\sigma]. \tag{4.4}$$

Note that with a proper interpretation of constants the same expression gives the magnetic moment of a superconducting sphere in the London theory of superconductivity.[11]

In the limit of strong potential $\kappa \to \infty$, one obtains for the effective radius $a = R$, which is the hard sphere result. For soft potentials $\kappa \approx 0$ one has

$$a^3 = R^3[\tfrac{1}{15}\sigma^2 - \tfrac{2}{315}\sigma^4 + O(\sigma^6)], \qquad \kappa \to 0. \tag{4.5}$$

The first term gives the free draining limit for the friction coefficient. Using $f_r = 8\pi\eta_0 a^3$ and $n = \frac{4}{3}\pi R^3 \rho$ one finds

$$f_r = \tfrac{2}{5} n \zeta R^2 \quad \text{(free draining)}. \tag{4.6}$$

The free draining limit can also be obtained from (3.14) by using for ϕ the unperturbed value $\phi(r) = 1$. Hence one finds for any spherically symmetric density distribution

$$f_r = \tfrac{2}{3} n \zeta \langle r^2 \rangle \quad \text{(free draining)}, \tag{4.7}$$

where $\langle r^2 \rangle = n^{-1} \int r^2 \rho(r)\, d\mathbf{r}$. For a uniform sphere $\langle r^2 \rangle = \frac{3}{5} R^2$, which agrees with (4.6).

When the segments are distributed in a *spherical shell* of radius R one has

$$\kappa^2(r) = \mu\delta(r - R) \tag{4.8}$$

where $\mu = \zeta\tau/\eta_0$ and τ is the uniform surface density, $\tau = n/4\pi R^2$. The solutions in the regions $r < R$ and $r > R$ are

$$\begin{aligned} \phi(r) &= B & 0 \le r < R, \\ \phi(r) &= 1 - A/r^3 & R < r < \infty. \end{aligned} \tag{4.9}$$

The jump conditions for the original problem are that $\mathbf{V}$ must be continuous at $r = R$, while the tangential–normal components of the stress tensor jump by $[\sigma_{\theta r}] = \eta_0 \mu V_\theta$ and $[\sigma_{\varphi r}] = \eta_0 \mu V_\varphi$. The normal–normal component of σ is just $-P$, which is constant throughout. V_φ is the only nonvanishing component of $\mathbf{V}$ and one easily finds the conditions that ϕ must be continuous at $r = R$ while $\phi'(r)$ must jump by $\phi'_+ - \phi'_- = \mu\phi(R)$. Hence one obtains

$$\begin{aligned} A &= R^3\ \mu R/(3 + \mu R), \\ B &= 3/(3 + \mu R). \end{aligned} \tag{4.10}$$

In the limit $\mu \to \infty$ one finds again the hard sphere result $a = R$, while the free draining limit ($\mu \to 0$) is $A \approx \mu R^4/3$ which implies $f_r = \frac{2}{3} n \zeta R^2$, in agreement with (4.7). From Eq. (4.10) one finds that the rotatory friction coefficient of the shell may be expressed as

$$f_r = 8\pi\eta_0 R^3\ \mu R/(3 + \mu R) = 8\pi\eta_0 R^3\ \sigma^2/(9 + \sigma^2), \tag{4.11}$$

where $\sigma^2 = 3\mu R = 3n\zeta/4\pi\eta_0 R$, as in the case of the uniform sphere.

V. ENERGY DISSIPATION AND VARIATIONAL PRINCIPLE

The differential equation (3.4) can be solved only for a few special cases and hence we are obliged to look for perturbation methods allowing us to handle more realistic density distributions, e.g., a Gaussian. In this section we show that a study of the energy dissipation leads to a variational principle which will be useful in numerical work. This variation principle is not related to the very powerful variational principle introduced by Rotne and Pragner[12] to study the consequences of the hydrodynamic interaction in the Kirkwood diffusion equation.

From (3.9) one easily shows the identity

$$\nabla \cdot (\mathbf{V} \cdot \boldsymbol{\sigma}) = \tfrac{1}{2}\eta_0 (\nabla \mathbf{V})_s^2 + \eta_0 \kappa^2 \mathbf{V}^2. \tag{5.1}$$

Integrating this over a volume Ω bounded by a surface Σ

and using Gauss's theorem one finds

$$\int_\Sigma \mathbf{V}\cdot\sigma\cdot\mathbf{n}\,dS=\eta_0\int_\Omega\left[\tfrac{1}{2}(\nabla\mathbf{V})_s^2+\kappa^2\mathbf{V}^2\right]d\mathbf{r}\,. \tag{5.2}$$

The left hand side of this equation represents the work done on the fluid in Ω from the outside, so that the right hand side gives the energy dissipated in Ω. The energy dissipation is the sum of the usual viscous dissipation in the fluid and the dissipation due to friction between fluid and polymer. The friction term can also be written $\eta_0\kappa^2\mathbf{V}^2=-\mathbf{F}\cdot\mathbf{V}$. The total energy dissipation is given by the integral over all space

$$W=\eta_0\int\left[\tfrac{1}{2}(\nabla\mathbf{V})_s^2+\kappa^2\mathbf{V}^2\right]d\mathbf{r}\,. \tag{5.3}$$

For the case of rotational flow one can substitute (3.3) and (3.15). Performing the angular integrations one finds

$$W=\frac{8\pi}{3}\eta_0\omega^2\int_0^\infty\left[\phi'^2+\kappa^2\phi^2\right]r^4\,dr\,. \tag{5.4}$$

Integrating by parts one can transform this to

$$W=\frac{8\pi}{3}\eta_0\omega^2\left[(r^4\phi\phi')\Big|_0^\infty-\int_0^\infty\phi(L\phi)r^2\,dr\right], \tag{5.5}$$

where L is the linear operator

$$L=r^2\frac{d^2}{dr^2}+4r\frac{d}{dr}-\kappa^2(r)r^2\,. \tag{5.6}$$

We note that the equation $L\phi=0$ is identical to (3.4). Hence the integral in (5.5) vanishes. The first term in (5.5) can be calculated from the asymptotic behavior (3.5). This yields

$$W=8\pi\eta_0A\omega^2=f_r\omega^2\,, \tag{5.7}$$

as was to be expected.

Another important observation is that $L\phi=0$ is also the Euler equation for the functional W as given in (5.4) upon variation of ϕ. This shows that the energy dissipation is stationary for the actual flow. Somewhat more explicitly we calculate $W[\phi]$ to second order in variations $\phi\to\phi+\delta\phi$,

$$W[\phi+\delta\phi]-W[\phi]\approx\frac{8\pi}{3}\eta_0\omega^2\left[(2r^4\phi'\delta\phi)\Big|_0^\infty-2\right.$$
$$\left.\times\int_0^\infty(\delta\phi)(L\phi)r^2\,dr+\int_0^\infty\left[(\delta\phi')^2+\kappa^2(\delta\phi)^2\right]r^4\,dr\right]. \tag{5.8}$$

The first line shows that W is stationary when $L\phi=0$ for variations $\delta\phi$ for which the boundary terms vanish. The expression in the second line is positive definite. Hence the stationary point is actually a minimum. This principle of minimum energy dissipation can be traced back to the same principle valid for the general form of W given in (5.3). Since we do not need the more general formulation in this article we shall be satisfied with the simple form (5.8).

Suppose one considers a trial function $\phi_t(r)=\phi+\delta\phi$, which is regular at the origin and has asymptotic behavior

$$\phi_t(r)\approx 1-a_t^3/r^3\text{ as }r\to\infty\,, \tag{5.9}$$

with a trial value a_t for the effective radius. If ϕ is the desired exact solution of $L\phi=0$ with asymptotic behavior (3.5), then the first line in (5.8) vanishes and one has $W[\phi]\leqslant W[\phi_t]$. This can be expressed in two ways, using either (5.4) or (5.5). The first gives the variational principle

$$a^3\leqslant\frac{1}{3}\int_0^\infty\left[\phi_t'^2+\kappa^2\phi_t^2\right]r^4\,dr \tag{5.10}$$

while the second gives

$$a^3\leqslant a_t^3-\frac{1}{3}\int_0^\infty\phi_t(L\phi_t)r^2\,dr\,. \tag{5.11}$$

The latter principle has a form familiar from a similar expression for the scattering length in quantummechanics.[13] The former is the most convenient in practical calculations. Once a variational calculation has been set up and a best trial function $\phi_t(r)$ has been found by applying either (5.10) or (5.11), one can go back to (3.14) and compare the values for the friction coefficient as given by (3.7) and (3.14).

VI. PERTURBATION THEORY

It is straightforward to do ordinary perturbation theory with the strength of the potential $\kappa^2(r)$ as a small parameter. We shall carry this scheme only to first order. The zero order solution $\phi_0(r)=1$ corresponds to the unperturbed flow. From (3.4) it follows that the first order perturbation satisfies

$$r^2\phi_1''+4r\phi_1'-\kappa^2(r)r^2=0\,. \tag{6.1}$$

Solving this one finds

$$\phi_1(r)=-\frac{1}{3}\int_r^\infty r'\kappa^2(r')\,dr'-\frac{1}{3r^3}\int_0^r r'^4\kappa^2(r')\,dr', \tag{6.2}$$

where we have chosen the constants of integration to suit the boundary conditions at zero and infinity. Provided the potential $\kappa^2(r)$ falls off more rapidly than $1/r^5$ the asymptotic behavior is given by

$$\phi_1(r)=-\frac{1}{3r^3}\int_0^\infty r'^4\kappa^2(r')\,dr'+o(1/r^3)\text{ as }r\to\infty\,. \tag{6.3}$$

If one uses the value for A_1 implied by Eq. (6.3) in (3.7) one finds for f_r the free draining result (4.6), which we had found by using the unperturbed function $\phi_0=1$ in (3.14). The first order correction to the free draining limit can be found by using the first order function (6.2) in (3.14). The result can be cast in the form

$$f_r^{(0)}+f_r^{(1)}=\tfrac{2}{3}n\zeta\langle r^2\rangle-\frac{8\pi}{9}\frac{\zeta^2}{\eta_0}$$
$$\times\int_0^\infty\int_0^\infty r_>r_<^4\rho(r)\rho(r')\,dr\,dr' \tag{6.4}$$

where $r_<(r_>)$ is the smaller (larger) of r and r'. For the important case of the Gaussian distribution.

$$\rho(r)=n(3/2\pi\langle r^2\rangle)^{3/2}\exp[-3r^2/2\langle r^2\rangle]\,. \tag{6.5}$$

The integral in (6.4) can be evaluated explicitly. In terms of Kirkwood's dimensionless parameter

$$X=(1/6\pi^{3/2})(n\zeta/\eta_0\langle r^2\rangle^{1/2})=\tfrac{1}{9}(\tfrac{2}{3})^{1/2}\kappa^2(0)\langle r^2\rangle \tag{6.6}$$

one finds

$$f_r^{(0)} + f_r^{(1)} = \tfrac{2}{3} n\zeta \langle r^2 \rangle [1 - \tfrac{1}{4}\sqrt{3}\, X] . \tag{6.7}$$

Hence to this approximation one has a correction factor

$$G(X) = 1 - \tfrac{1}{4}\sqrt{3}\, X + O(X^2) \tag{6.8}$$

which is to be compared with a similar factor for the sphere (4.4)

$$G_s(X) = 1 - \tfrac{10}{7}\sqrt{\tfrac{3}{2}}\, X + O(X^2) . \tag{6.9}$$

This shows that for the Gaussian the corrections to the free draining result are smaller by a factor of about $\frac{1}{4}$. The friction coefficient of the corresponding sphere is smaller than that for the Gaussian. The approximation (6.8) to $G(X)$ leads to values for f_r that agree within 10% with the results obtained by Kirkwood, Zwanzig, and Plock[14] for $X \leqslant 0.5$.

Clearly the perturbation theory can be carried systematically to any desired order. For strong potentials, however, a different type of expansion is called for. In the region where the potential is strong a WKB approximation should work well. In the region of large r where the potential vanishes, or at least is weak, the present approximation scheme will be the most suitable. It is difficult to devise an analytic scheme which simultaneously works in all regions. Thus our strategy will be to do WKB in the region of small r, ordinary perturbation theory in the region of large r, and to fit the approximate solutions by continuity at a point R_0 where the potential has an intermediate value. Subsequently the best value of R_0 can be determined by applying the variational principle (5.10). Finally, the approximate value for the rotational drag f_r is found either from (3.7) and (5.10), or by substituting the best approximate function in (3.14).

The trial function $\phi_t(r)$ in the region $R_0 < r < \infty$ is

$$\phi_t(r) = 1 - \frac{A_t}{r^3} - \frac{1}{3}\int_r^\infty r' \kappa^2(r')\, dr' + \frac{1}{3r^3}\int_r^\infty r'^4 \kappa^2(r')\, dr' , \tag{6.10}$$

where A_t is a constant which will be determined from continuity of ϕ_t and ϕ_t' at $r = R_0$. In applying WKB in the region $0 \leqslant r < R_0$ we are guided by the known solution (4.2) for constant κ^2, when the two independent solutions of the differential equation are

$$\phi_\pm(r) = \frac{e^{\pm\kappa r}}{r^2}\left(1 \mp \frac{1}{\kappa r}\right) \quad (\text{constant } \kappa) . \tag{6.11}$$

Accordingly we put

$$\phi(r) = \frac{\psi'(r)}{r^2} - \frac{\psi(r)}{r^3} \tag{6.12}$$

and find for ψ the differential equation

$$r\psi''' - \psi'' - \kappa^2(r)(r\psi' - \psi) = 0 \tag{6.13}$$

We now apply the WKB perturbation scheme by writing

$$\epsilon^3 r\psi''' - \epsilon^2\psi'' - \kappa^2(r)(\epsilon r\psi' - \psi) = 0 ,$$

$$\psi(r, \epsilon) = \exp[\chi(r, \epsilon)/\epsilon] , \tag{6.14}$$

$$\chi(r, \epsilon) = \chi_0(r) + \epsilon\chi_1(r) + \epsilon^2\chi_2(r) + \cdots ,$$

where ϵ is a formal expansion parameter which finally is put equal to unity. Expanding in powers of ϵ one finds to zeroth order

$$\chi_0'^2 = \kappa^2(r), \quad \chi_0(r) = \pm\int \kappa(r')\, dr' , \tag{6.15}$$

and to first order

$$\chi_1' = -\frac{\chi_0''}{2\chi_0'}\,\frac{1 - 3r\chi_0'}{1 - r\chi_0'} , \tag{6.16}$$

so that

$$\chi_1(r) = -\int^r \frac{\kappa'(r')}{\kappa(r')}\,\frac{1 \mp 3r'\kappa(r')}{1 \mp r\kappa(r')}\, dr' . \tag{6.17}$$

We therefore have to this order the two independent solutions

$$\psi_\pm(r) = \exp[\pm K(r) - L(r)] , \tag{6.18}$$

where

$$K(r) = \int_0^r \left[\kappa(r') + \frac{\kappa'(r')r'}{1 - \kappa^2(r')r'^2}\right] dr' ,$$
$$L(r) = \int_0^r \frac{\kappa'(r')}{2\kappa(r')}\,\frac{1 - 3\kappa^2(r')r'^2}{1 - \kappa^2(r')r'^2}\, dr' . \tag{6.19}$$

The trial function $\phi_t(r)$ in $0 \leqslant r < R_0$ follows from (6.12) and must be chosen as the linear combination which is regular at $r = 0$. Hence on $(0, R_0)$

$$\phi_t(r) = \tfrac{1}{2} B_t \left\{\frac{[\psi_+'(r) - \psi_-'(r)]}{r^2} - \frac{[\psi_+(r) - \psi_-(r)]}{r^3}\right\} . \tag{6.20}$$

Finally the constants A_t and B_t are determined by requiring continuity of ϕ_t and ϕ_t' at $r = R_0$. This leaves R_0 as the only undetermined parameter.

The trial function $\phi_t(r, R_0)$ can now be substituted in (5.10) and the best value of R_0 can be determined. The rotatory friction coefficient follows from (3.7) with (5.10), or from (3.14). Note that for the uniform sphere one automatically finds the exact solution. Numerical work on the Gaussian distribution will be reported elsewhere.

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APPENDIX

In this appendix we demonstrate a fundamental property of the Oseen fields. Consider a velocity and pressure distribution $(\mathbf{V}, P)$ defined by

$$\mathbf{V}(\mathbf{r}) = \int \mathbf{T}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{X}(\mathbf{r}')\, d\mathbf{r}' ,$$
$$P(\mathbf{r}) = \int \mathbf{Q}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{X}(\mathbf{r}')\, d\mathbf{r}' , \tag{A1}$$

where $\mathbf{T}(\mathbf{R})$ and $\mathbf{Q}(\mathbf{R})$ are defined in (2.3), and where $\mathbf{X}(\mathbf{r})$ is a given continuous force density. We shall prove that then

$$\eta_0\nabla^2\mathbf{V} - \nabla P = -\mathbf{X}(\mathbf{r}), \quad \nabla\cdot\mathbf{V} = 0 . \tag{A2}$$

By differentiation one has

$$\partial T_{\alpha\beta}/\partial R_\gamma = (1/8\pi\eta_0 R^2)[-\delta_{\alpha\beta}e_\gamma + \delta_{\alpha\gamma}e_\beta + \delta_{\beta\gamma}e_\alpha - 3e_\alpha e_\beta e_\gamma] \tag{A3}$$

where $\mathbf{e} = \mathbf{R}/R$. When differentiating $\mathbf{V}$ in (A1) one must be careful with the interchange of differentiation and integration. The integrals in (A1) do not change in value when a small sphere of infinitesimal radius ϵ and $\mathbf{r}$ is excluded from the region of integration. Hence one finds

$$\frac{\partial V_\alpha}{\partial r_\gamma} = \frac{\partial}{\partial r_\gamma}\int_v^\Omega T_{\alpha\beta}X_\beta\,d\mathbf{r}' = \int_v^\Omega \frac{\partial T_{\alpha\beta}}{\partial r_\gamma}X_\beta\,d\mathbf{r}' - \int_s T_{\alpha\beta}X_\beta e_\gamma\,ds\ , \tag{A4}$$

where the second integral is over the surface of the small sphere. Taking the limit $\epsilon \to 0$ one finds that the surface integral vanishes. From the first integral and (A3) it follows that $\nabla\cdot\mathbf{V} = 0$. Taking a second derivative of V_α one obtains

$$\frac{\partial^2 V_\alpha}{\partial r_\gamma \partial r_\delta} = \int_v^\Omega \frac{\partial^2 T_{\alpha\beta}}{\partial r_\gamma \partial r_\delta}X_\beta d\mathbf{r}' - \int_s \frac{\partial T_{\alpha\beta}}{\partial r_\gamma}X_\beta e_\delta\,ds\ . \tag{A5}$$

Substituting (A3) one can perform the angular integrations over the surface of the small sphere using

$$\overline{e_\alpha e_\beta} = \tfrac{1}{3}\delta_{\alpha\beta},\ \overline{e_\alpha e_\beta e_\gamma e_\delta} = \tfrac{1}{15}(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma})\ , \tag{A6}$$

where the overhead bar indicates angular averaging. Hence one finds

$$\int_s \frac{\partial T_{\alpha\beta}}{\partial r_\gamma}e_\delta\,ds = \frac{1}{15\eta_0}[4\delta_{\alpha\beta}\delta_{\gamma\delta} - \delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma}]\ , \tag{A7}$$

so that

$$\frac{\partial^2 V_\alpha}{\partial r_\gamma \partial r_\gamma} = \int_v^\Omega \frac{\partial^2 T_{\alpha\beta}}{\partial r_\gamma \partial r_\gamma}X_\beta\,d\mathbf{r}' - \frac{2}{3\eta_0}X_\alpha(\mathbf{r})\ . \tag{A8}$$

Similarly

$$\frac{\partial P}{\partial r_\alpha} = \int_v^\Omega \frac{\partial Q}{\partial r_\alpha}X_\beta\,d\mathbf{r}' + \tfrac{1}{3}X_\alpha(\mathbf{r})\ . \tag{A9}$$

Combining these identities using (2.4) one finds that (A2) is satisfied. This analysis also shows that Eqs. (2.17–19) are consistent with (2.12).

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[9] Professor Walter Stockmayer has kindly drawn our attention to the work of A. Isihara [Adv. Polum. Sci. **5**, 531 (1968)] who introduces a different approximation to the mean field approximation discussed here. In our notation Isihara's approximation is $\langle n(\mathbf{r})\mathbf{f}(\mathbf{r}')\rangle = \langle n(\mathbf{r})n(\mathbf{r}')\rangle\mathbf{F}(\mathbf{r}')/\rho(\mathbf{r}')$ followed by the approximation $\langle n(\mathbf{r})n(\mathbf{r}')\rangle = \rho(\mathbf{r})g(\mathbf{r}-\mathbf{r}')$. Unlike our mean field approximation $\langle n(\mathbf{r})f(\mathbf{r}')\rangle = \rho(\mathbf{r})\mathbf{F}(\mathbf{r}')$, the resulting equation for the velocity field $\mathbf{V}(\mathbf{r})$ obtained by Isihara does not satisfy the Debye–Bueche equation, Eq. (2.20).

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