I. REMARKS ON THE ARCHIBALD TECHNIQUE FOR DETERMINING MOLECULAR WEIGHTS IN THE ULTRACENTRIFUGE

II. THE HYDRODYNAMIC ALIGNMENT OF ROD-LIKE MOLECULES IN CENTRIFUGAL FIELDS

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ABSTRACT

I

The theoretical validity of the linear extrapolation of concentration gradient usually used in Archibald measurements of molecular weights is discussed.

II

Intrinsic and concentration-dependent hydrodynamic alignment of rod-like molecules are considered in an attempt to explain the observed increased sedimentation coefficients with field and concentration. An entropy mechanism is also discussed.

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I. INTRODUCTION

Ultracentrifugal measurements afford a very useful and practical way of determining certain physical properties of macromolecules (1). The measurement of molecular weights, with which this work is concerned, falls among these. The theory of the method is based on a relationship connecting molecular weight with the ratio of sedimentation and diffusion coefficients. The ratio of sedimentation and diffusion coefficients can, in turn, be deduced from the distribution of particle concentration in the centrifuge cell (2). If the centrifuge is allowed to run long enough at constant speed to establish a thermodynamic equilibrium between sedimentation and diffusion, the distribution of particle concentration about any point in the cell is sufficient, along with other very easily obtained parameters, to calculate the molecular weight of a sample. In the absence of thermodynamic equilibrium between sedimentation and diffusion, the useful data are the particle distributions either at the inner or at the outer boundary of the cell; however, particle concentrations at other points within the cell are also of interest, since such data are necessary for accurate determinations of particle distributions at the boundaries (3).

Experimentally it is much more convenient to work in the absence of thermodynamic equilibrium, chiefly because it takes so long to achieve it (a matter of days is common). A difficulty with non-equilibrium systems, however, is that available methods to measure particle distributions do not function properly at the boundaries. This is due to the fact that they are based on optics and are often plagued with interference effects there (4). To ascertain the conditions at the boundary, the usual procedure is a linear extrapolation of the quantities of interest from those found in the regions where they can be measured to their values at the boundaries.

The problem investigated here was specifically the theoretical validity of this extrapolation. According to an analytical solution, the distribution of particles near the inner boundary in the absence of thermodynamic equilibrium does not behave in a simple way as a function of distance from the boundary. Results from a numerical solution, however, indicate that linear extrapolation is a good thing to do. From this it was concluded that the validity of the linear extrapolation is not easy to understand theoretically. A possible means of improving the extrapolation is suggested.

II. BASIC THEORY

The derivation of the equation connecting the ratio of sedimentation and diffusion coefficients with molecular weight is most conveniently accomplished for these purposes by considering the mathematical formulation of those processes occurring within the cell before and during equilibrium.

Schematically the cell can be represented as in Figure 1.

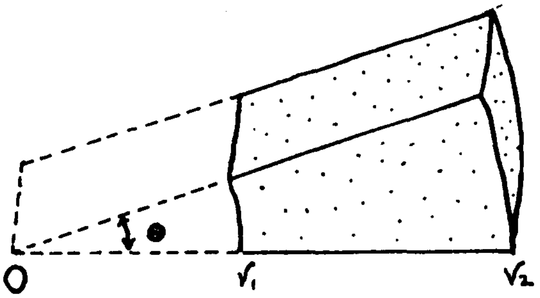

Figure 1

The coordinates chosen are the usual polar ones-- r, θ, z , where r and θ have clear significance, and z refers to the thickness of the cell. $\hat{e}_r$ is a unit vector pointing outward from the axis of rotation 0. The dots within the solid lines represent macromolecules. None of the phenomena which will be considered possess any dependence on θ and z.

When the centrifuge begins operation, the centrifugal force of magnitude $\omega^2 r$ per unit mass (where ω is the angular velocity of the rotation in radians per second, and $r_1 \leq r \leq r_2$) operates on the solute macromolecules. This will induce a net flow of these particles toward the outer boundary r_2 . The particle velocities so induced in these macromolecular systems is small enough to allow use of the hydrodynamic result that this velocity is proportional to the external force applied. The proportionality constant is called the sedimentation coefficient, denoted by s .

$$\text{velocity} = s\,\omega^2 r\,\hat{e}_r \tag{1}$$

s , of course, depends on the size, shape, and mass of the particles of interest. If the concentration of particles at r is C(r, t) , then the sedimenting number of particles or flow crossing unit area per unit time is

$$\text{sedimenting flow} = C(r,t)\; s\,\omega^2 r\,\hat{e}_r \tag{2}$$

Such a sedimentation flow will, of course, cause particles to be pulled away from the inner boundary at r_1 , and to be packed against the outer wall at r_2 . A concentration gradient is therefore set up in these two general areas, which, according to Fick's first law will induce a diffusion flow of the solute particles. This current is

$$\text{diffusion flow} = -D\,\frac{\partial C(r,t)}{\partial r}\,\hat{e}_r \tag{3}$$

where D is the diffusion coefficient.

The total flow is the sum of the sedimenting and diffusing flows.

$$\text{total flow} = \left(s\,\omega^2 r\, C(r,t) - D\,\frac{\partial C(r,t)}{\partial r}\right)\hat{e}_r \tag{4}$$

Since these currents of particles are in opposite directions, they will tend to counterbalance each other, and, if the centrifuge is run long enough, an equilibrium between the two currents will be established such that the total flow vanishes at each point within the cell. The concentration is nonuniform but time independent at equilibrium. We then have, since the flow is zero,

$$s\omega^2 r C(r) - D\frac{\partial C(r)}{\partial r} = 0 \tag{5}$$

This can be rearranged to give

$$\frac{S}{D} = \frac{1}{\omega^2 r}\;\frac{1}{C(r)}\;\frac{dC(r)}{dr} \tag{5'}$$

If the weak dependences of s and D on concentration are neglected, the solution to this differential equation is

$$C(r) = C_o\,\frac{s\omega^2}{2D}(r_2^2 - r_1^2)\left[\exp\left(\frac{s\omega^2}{2D}(r_2^2 - r_1^2)\right) - 1\right]\exp\left(\frac{s\omega^2}{2D}(r^2 - r_1^2)\right) \tag{6}$$

where C_o is the original uniform concentration throughout the cell. Equation 6 would then represent the concentration profile at equilibrium.

Another use may be made of equation 5', stating that the total flow is zero everywhere at equilibrium. It is possible to apply thermodynamics to the cell when 5' holds. For example, the total thermodynamic potential per mole of solute macromolecules which is the sum of the chemical and centrifugal potentials,

$$\begin{aligned}\mu_{TOT} &= \mu_{CHEM} + \mu_{CENTRIFUGAL} \\ &= \mu_o(T,P) + RT \ln \gamma C(r) - \frac{M}{2}\omega^2 r^2\end{aligned} \tag{7}$$

where γ is the activity coefficient and M is the molecular weight, must at equilibrium be constant throughout the cell. Differentiating:

$$\frac{\partial \mu}{\partial r} = 0 = \frac{\partial \mu_o(T,P)}{\partial r} + RT\left(\frac{\partial \ln C(r)}{\partial r} + \frac{\partial \ln \gamma}{\partial \ln C(r)}\,\frac{\partial \ln C(r)}{\partial r}\right) - M\omega^2 r$$

$$= \frac{\partial \mu_o(T,P)}{\partial P}\,\frac{\partial P}{\partial r} + RT\,\frac{\partial \ln C(r)}{\partial r}\left(1 + \frac{\partial \ln \gamma}{\partial \ln C(r)}\right) - M\omega^2 r$$

where p is the pressure. From a thermodynamic identity

$$\frac{\partial \mu_o(T,P)}{\partial P} = \bar{v} M$$

where $\bar{v}$ is the partial specific volume of solute particles.

The quantity $\frac{\partial p}{\partial r}$ can be calculated by considering the increase in force per unit area at r due to the external field. If the pressure at r is p(r), then the pressure at r + dr is

$$P(r) + \frac{\partial P(r)}{\partial r}\,dr = P(r) + \frac{\rho\omega^2 r\, d(\text{volume})}{\text{area}}$$

$$= P(r) + \rho\omega^2 r\, dr$$

where ρ is the solution density. Therefore,

$$\frac{dP}{dr} = \rho\omega^2 r \tag{8}$$

Substituting this we get

$$M\omega^2 r - M\bar{v}\rho\omega^2 r = \frac{RT}{C(r)}\frac{\partial C(r)}{\partial r}\left(1+\frac{\partial \ln \gamma}{\partial \ln C(r)}\right)$$

which can be rearranged to

$$M = \frac{RT}{\omega^2(1-\bar{v}\rho)}\frac{\partial C(r)}{\partial r}\frac{1}{rC(r)}\left(1+\frac{\partial \ln \gamma}{\partial \ln C(r)}\right) \tag{9}$$

If this is combined with equation 5', the result is

$$M = \frac{RTs}{D(1-\bar{v}\rho)}\left(1+\frac{\partial \ln \gamma}{\partial \ln C(r)}\right) \tag{10}$$

This is the thermodynamic relationship already referred to, which connects the molecular weight with the ratio of the sedimentation and diffusion coefficients.

In the case of infinite dilution, 10 becomes

$$M = \frac{RTs}{D(1-\bar{v}\rho)} \tag{11}$$

At infinite dilution, s and D are independent of concentration, while the activity coefficient becomes unity. Equation 11 was first derived by Svedberg (2), and along with equation 9 forms the theoretical base for the determination of molecular weights in the ultracentrifuge.

III. USE OF THE EXPERIMENTAL DATA

Experimentally the usual quantity obtained is the refractive index gradient (4). This is measured by taking photographs of the cell using Schlieren optics while the centrifuge is in operation. The actual mechanical details are rather involved (5), but for the present purposes are unimportant and will not be considered. The refractive index is assumed to be proportional to the concentration gradient. It will be assumed that this proportionality constant is available and henceforth only concentration gradients will be used in the discussion.

If the concentration gradient is known throughout the cell, the concentration can be found by the following formula (6):

$$C(r,t) = C_0 + \int_{r_1}^{r} \frac{\partial C(r,t)}{\partial r}\, dr + \int_{r_1}^{r_2} \left(\frac{r_2^2 - r^2}{r_2^2 - r_1^2}\right) \frac{\partial C(r,t)}{\partial r}\, dr \qquad (12)$$

To derive this, we note that the total amount of material in the cell is constant and independent of time.

$$\theta z \int_{r_1}^{r_2} C_0\, r\, dr = \theta z\, C_0 \left(\frac{r_2^2 - r_1^2}{2}\right) = \theta z \int_{r_1}^{r_2} C(r,t)\, r\, dr$$

or

$$C_0 (r_2^2 - r_1^2) = 2 \int_{r_1}^{r_2} C(r,t)\, r\, dr$$

Integrate by parts

$$C_o(r_2^2 - r_1^2) = \left[r_2^2\, C(r_2,t) - r_1^2\, C(r_1,t)\right] - \int_{r_1}^{r_2} r^2\, \frac{\partial C(r,t)}{\partial r}\, dr \tag{13}$$

Use the mathematical identity

$$C(r_2,t) = \int_{r_1}^{r_2} \frac{\partial C(r,t)}{\partial r}\, dr + C(r_1,t)$$

to obtain, when combined with equation 13,

$$C(r_1,t) = C_o + \int_{r_1}^{r_2} \left(\frac{r_2^2 - r^2}{r_2^2 - r_1^2}\right) \frac{\partial C(r,t)}{\partial r}\, dr \tag{14}$$

Combine equation 14 with the mathematical identity

$$C(r,t) = \int_{r_1}^{r} \frac{\partial C(r',t)}{\partial r'}\, dr' + C(r_1,t)$$

to obtain equation 12

$$C(r,t) = C_o + \int_{r_1}^{r} \frac{\partial C(r',t)}{\partial r'}\, dr' + \int_{r_1}^{r_2} \left(\frac{r_2^2 - r^2}{r_2^2 - r_1^2}\right) \frac{\partial C(r,t)}{\partial r}\, dr \tag{12}$$

The two quantities $\frac{\partial C(r,t)}{\partial r}$ and $C(r,t)$ are now available for the calculation of molecular weights, the former being measured and the latter being calculated from measured values of $\frac{\partial C(r,t)}{\partial r}$. If an equilibrium situation is present, the ratio s/D can be computed from any conjugate pair of $C(r,t)$ and $\left(\frac{\partial C(r,t)}{\partial r}\right)$ via equation 9. In the absence of thermodynamic equilibrium, which, as stated earlier, is much more convenient experimentally, the ratio s/D can be computed from the conjugate pairs $C(r_1,t)$ and $\left(\frac{\partial C(r,t)}{\partial r}\right)_{r=r_1}$, $C(r_2,t)$ and $\left(\frac{\partial C(r,t)}{\partial r}\right)_{r=r_2}$. This is due to the non-vanishing of the total flow

$$\text{total flow} = \left(s\omega^2 r\, C(r,t) - D\,\frac{\partial C(r,t)}{\partial r}\right)\hat{e}_r \tag{4}$$

under non-equilibrium conditions at all points in the cell except at the boundaries $r = r_1, r_2$. At these points the total flow must clearly vanish since there are physical boundaries present which material cannot cross. Archibald (3) first pointed out the usefulness of data extracted from the boundary. Archibald's method represents a valuable tool in the determination of molecular weights.

Accurate values of concentration and concentration gradient at the boundaries are clearly necessary for Archibald calculations. As has been stated previously, however, the optical devices available for these measurements are inefficient at a boundary (4). The measured concentration gradient is estimated at the boundary by extrapolation from the region nearby by means of a straight line. The inner boundary at r_1 is customarily used to avoid activity effects as much as possible. Typical pictures of concentration gradients obtained experimentally for short times of centrifugation have a linear look about them. The problem investigated here is specifically the validity of a linear extrapolation, to remove any nagging doubts.

IV. THE APPROACH TO EQUILIBRIUM

To establish the linearity or non-linearity of the concentration gradient curve, it is necessary to investigate the behavior of this quantity near the boundary under non-equilibrium conditions. The equation governing approach to equilibrium in these systems is a simple expression of conservation of mass.

$$\frac{\partial C(r,t)}{\partial t} = -\operatorname{div}\left(s\omega^2 r\, C(r,t) - D\,\frac{\partial C(r,t)}{\partial r}\right)\hat{e}_r \qquad (15)$$

with boundary conditions

$$s\omega^2 r\, C(r,t) = D\,\frac{\partial C(r,t)}{\partial r} \qquad r = r_1, r_2$$

$$C(r,t) = C_0 \qquad t < 0 \qquad (16)$$

In words, this says that the change in number of particles per fixed unit volume per unit time is equal to the number of particles flowing into (or out of) this volume per unit time. This equation was first derived by Lamm (7).

It is instructive to investigate physically what happens during a short Archibald run. At t = 0, the concentration is uniform throughout the cell and $\left(\frac{\partial C(r,t)}{\partial r}\right)_{r=r_1} = 0$. The concentration profile is like

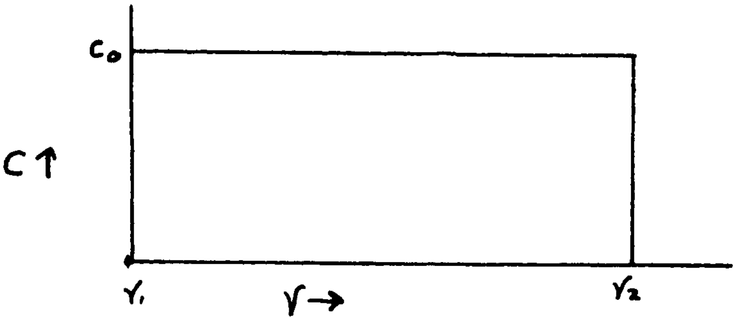

Figure 2

If, for $t > o$, diffusion is inoperative, the solute particles will move away from the inner boundary, r_1, and pack against the outer boundary, r_2, due to the action of the centrifugal field. The concentration would then be zero in a region beginning at r_1 and ending at some $r > r_1$. It would be some constant value corresponding to packed molecules in another region ending at the outer boundary r_2 and beginning at some $r < r_2$.

Between these two regions, there is initially no concentration gradient. That, in fact, no gradient will be set up for pure sedimentation can be seen as follows:

Consider a band of solute molecules of width dr at r at t 0

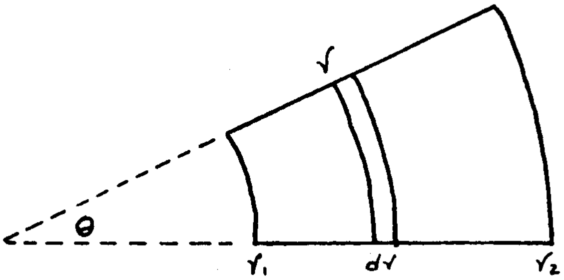

Figure 3

The volume of this band is $\theta z r\,dr$ at $t = 0$. From equation 1

$$\text{sedimentation velocity} = s\omega^2 r\,\hat{e}_r \tag{1}$$

it follows that after a time dt the boundary at r has moved to a point $r + s\omega^2 r\,dt$, and the boundary at $r + dr$ has moved to $(r + dr)(1 + s\omega^2 dt)$. Hence the new width of the band is

$$(r+dr)(1+s\omega^2 dt) - r(1+s\omega^2 dt) = dr(1+s\omega^2 dt)$$

The new volume of the band is

$$\theta z(1+s\omega^2 dt)^2\,dr \approx \theta z\,dr(1+2s\omega^2 dt)$$

The relative increase in volume during the time dt is

$$\frac{\theta z r\,dr(1+2s\omega^2 dt)}{\theta z r\,dr} = 1+2s\omega^2 dt$$

This is independent of r and demonstrates that in the case of pure sedimentation no concentration gradient is set up. Therefore, in the region between the zones of zero concentration near the inner boundary and packed molecules near the outer boundary, the concentration is constant, independent of r, and dependent only on time. The time dependence must be such that the concentration decreases, since the volume available to a band increases. The concentration profile shown in Figure 2 becomes

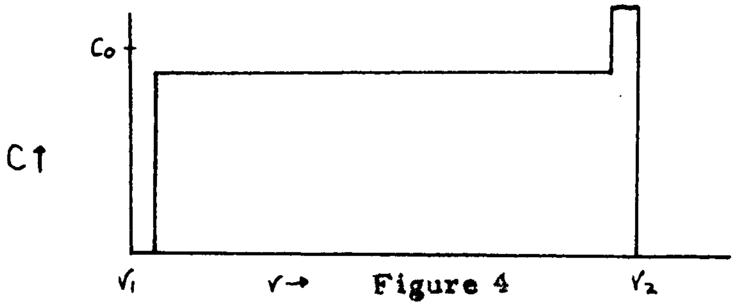

Figure 4

The flat portion between the regions of zero concentration and packed molecules is called the plateau region. Diffusion does occur, of course, at the boundaries of this central region, but some time is required before the plateau is destroyed. The concentration profile actually looks more like

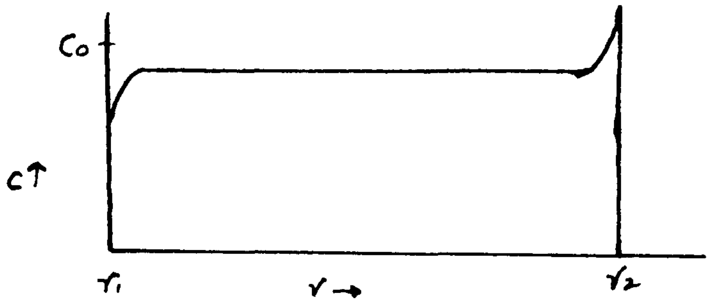

Figure 5

In the plateau region, therefore, there is no diffusion because there is no concentration gradient, and the Lamm equation becomes

$$\frac{\partial c(r,t)}{\partial t} + \operatorname{div}\left(s\omega^2 r\, C(r,t)\right)\hat{e}_r \tag{17}$$

or

$$\frac{\partial C(r,t)}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r} r\, s\omega^2 r\, C(t) = 0$$

$$\frac{\partial c(t)}{\partial t} = -2s\omega^2 c(t) \tag{18}$$

$$C = C_o \exp\left(-2s\omega^2 t\right)$$

It might be mentioned that the decrease of particles in the time interval 0-t within a region bounded by r_1 and some point in the plateau region, r_p say, has to be equal to the number of particles crossing the surface r_p

$$\Theta z \int_{r_1}^{r_p} \left[C_0 - C(r,t)\right] r\,dr = s\omega^2 r_p \int_0^t C(r_p,t)\,dt\,\Theta z r_p$$

or

$$\int_{r_1}^{r_p} \left[C_0 - C(r,t)\right] r\,dr = s\omega^2 r_p^2 \int_0^t e^{-2s\omega^2 t}\,dt$$

After a small amount of manipulation, this becomes

$$C(r,t) = C_0 - \frac{1}{r_1^2} \int_{r_1}^{r_p} r^2 \frac{\partial C(r,t)}{\partial r}\,dr \tag{19}$$

This formula can be used instead of equation 12 if a plateau is present. It was first derived by Klainer and Kegeles (8).

The importance of the existence of a plateau in a treatment of the Lamm equation is that it greatly simplifies the boundary conditions. The outer boundary can be disregarded for phenomena occurring near the inner boundary, if a plateau is present, and its conditions replaced by

$$C(\infty,t) = C_0 e^{-2s\omega^2 t} \quad \text{= constant in space}$$

The conditions are now

$$s\omega^2 r_1 \, C(r,t) = D \frac{\partial c(r,t)}{\partial r} \qquad r = r_1$$

$$C(\infty,t) = C_0 e^{-2s\omega^2 t} = \text{constant in space} \qquad (20)$$

$$C(r,t) = C_0 \qquad t < 0$$

V. THE WORK OF FUJITA AND MacCOSHAM

It was decided to attempt to investigate the linearity of the concentration gradient curve by performing a numerical integration of the Lamm equation subject to plateau boundary conditions, and taking a careful look at the constancy of the quantity $\frac{\partial^2 C(r,t)}{\partial r^2}$ near the boundary r_1. None of the available analytic solutions found were particularly useful. The exact analytic solution of Archibald (9) was too tedious to work with (10). Oka's solution is a formal one of no practical value (11). Faxen (12) used an approximation

$$\frac{2D}{s\omega^2 r_1^2} << 1$$

which does not fit the conditions of the present situation.

When the numerical work was well under way, the work of Fujita and MacCosham (13) was discovered in the literature. These authors have presented an approximate solution to the Lamm equation subject to plateau boundary conditions. The analytic form of the results is not unduly complicated. Subject to the severity of the approximation involved, it should be possible to deduce from their work the concentration gradient near the boundary and thus investigate its linearity. It was decided to go through with the numerical work to find out how good this approximation was.

Fujita and MacCosham began with the Lamm equation

$$\frac{\partial C(r,t)}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}\, r\left(s\omega^2 r\, C(r,t) - D\,\frac{\partial C(r,t)}{\partial r}\right) = 0$$

New variables were defined

$$\frac{c}{c_0} = e^{-\tau} u \qquad \frac{r}{r_1} = e^{z/2}$$

$$\tau = 2s\omega^2 t \qquad \epsilon = \frac{2D}{r_1^2\,\omega^2 s}$$

Substitution of these into the Lamm equation gave

$$\frac{\partial u}{\partial \tau} = \epsilon\, e^{-z}\,\frac{\partial^2 u}{\partial z^2} - \frac{\partial u}{\partial z}$$

The approximation made by Fujita and MacCosham was to neglect the variation of the factor e^{-z} from unity for mathematical convenience.

$$e^{-z} = \left(\frac{r_1}{r}\right)^2 \approx 1$$

As to order of magnitude, $r_1 \sim 5.6$ cm., $r \sim 5.6-$ cm. in the region of interest. So at most

$$e^{-z} = \left(\frac{5.6}{6.0}\right)^2 \approx 0.935$$

or about 7% variation.

After this approximation, the equation becomes

$$\frac{\partial u}{\partial \tau} = \epsilon \frac{\partial^2 u}{\partial z^2} - \frac{\partial u}{\partial z}$$

or in a more condensed notation

$$u_\tau = \epsilon u_{zz} - u_z$$

A new variable was defined

$$u = v \exp\left(\frac{z}{2\epsilon} - \frac{\tau}{4\epsilon}\right)$$

whereupon the equation became

$$v_\tau = \epsilon v_{zz}$$

subject to the boundary conditions

$$v = \exp\left(-\frac{z}{2\epsilon}\right) \qquad 0 < z < \infty \qquad \tau = 0$$

$$v = 2\epsilon v_z \qquad z = 0 \qquad \tau > 0$$

This equation is of the heat flow type, which has been intensely studied by Carslaw and Jaeger (14), from which the solution was determined to be

$$c/c_0 = \frac{e^{-\tau}}{2}\left\{ \operatorname{erfc}\left(\frac{\tau - z}{2\sqrt{\epsilon\tau}}\right) - \sqrt{\frac{\tau}{\epsilon}}\,\frac{2}{\sqrt{\pi}}\,\exp\left(\frac{(\tau - z)^2}{4\epsilon\tau}\right) + \left(1 + \frac{z+\tau}{\epsilon}\right)\operatorname{erfc}\left(\frac{\tau + z}{2\sqrt{\epsilon\tau}}\right) e^{z/\epsilon} \right\} \tag{21}$$

$$\frac{\partial c/c_0}{\partial r/r_1} = \frac{e^{-\tau - z/2}}{\epsilon}\left\{ \operatorname{erfc}\left(\frac{z+\tau}{2\sqrt{\epsilon\tau}}\right)\left(2 + \frac{z+\tau}{\epsilon}\right) e^{z/\epsilon} - \sqrt{\frac{\tau}{\epsilon}}\,\frac{2}{\sqrt{\pi}}\,\exp\left(-\frac{(\tau - z)^2}{4\epsilon\tau}\right) \right\} \tag{22}$$

$$\operatorname{erfc}(x) = 1 - \operatorname{erf}(x) = 1 - \frac{2}{\sqrt{\pi}}\int_0^x e^{-y^2}\,dy$$

VI. NUMERICAL INTEGRATION

The Lamm equation is

$$\frac{\partial c}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r} r\left(s\omega^2 r c - D\frac{\partial c}{\partial r}\right) = 0$$

with boundary conditions

$$C = C_o \qquad t < 0$$

$$s\omega^2 C = D\frac{\partial c}{\partial r} \qquad r = r_1$$

$$c(\infty, t) = C_o e^{-2s\omega^2 t}$$

= constant in space

Dimensionless variables are defined

$$c/c_o = \gamma \qquad \theta = \frac{tD}{r_1^2}$$

$$r/r_1 = \rho \qquad \lambda = \frac{s\omega^2 r_1^2}{D}$$

Then

$$\frac{\partial \gamma}{\partial \theta} + \frac{1}{\rho}\frac{\partial}{\partial \rho}\rho\left(\lambda\rho\gamma - \frac{\partial\gamma}{\partial\rho}\right) = 0$$

or

$$\frac{\partial\gamma}{\partial\theta} + 2\lambda\gamma + \lambda\rho\frac{\partial\gamma}{\partial\rho} - \frac{1}{\rho}\frac{\partial}{\partial\rho}\rho\frac{\partial\gamma}{\partial\rho} = 0 \tag{23}$$

subject to

$$\frac{\partial\gamma}{\partial\rho} = \lambda\rho\gamma \qquad \text{at } \rho = 1$$

$$\gamma = \text{constant} \quad \text{as } \rho \to \infty$$

since we are interested in a solution with plateau present.

This differential equation is now replaced by a finite difference equation, i.e., the derivatives are replaced by finite differences. The basic idea behind this (13) approach is to set up a grid, or net, in space-time, and treat γ, ρ, and θ as discrete rather than continuous variables.

Quantities $\Delta\rho$, $\Delta\theta$ are defined such that ρ assumes the values $1, 1+\Delta\rho, 1+2\Delta\rho, \ldots\ldots, 1+m\Delta\rho, \ldots\ldots$, and θ assumes values $0, \Delta\theta, 2\Delta\theta, 3\Delta\theta, \ldots\ldots, n\Delta\theta, \ldots\ldots$ Therefore, γ_m^n refers to $(1+m\Delta\rho, n\Delta\theta)$. Schematically this can be represented

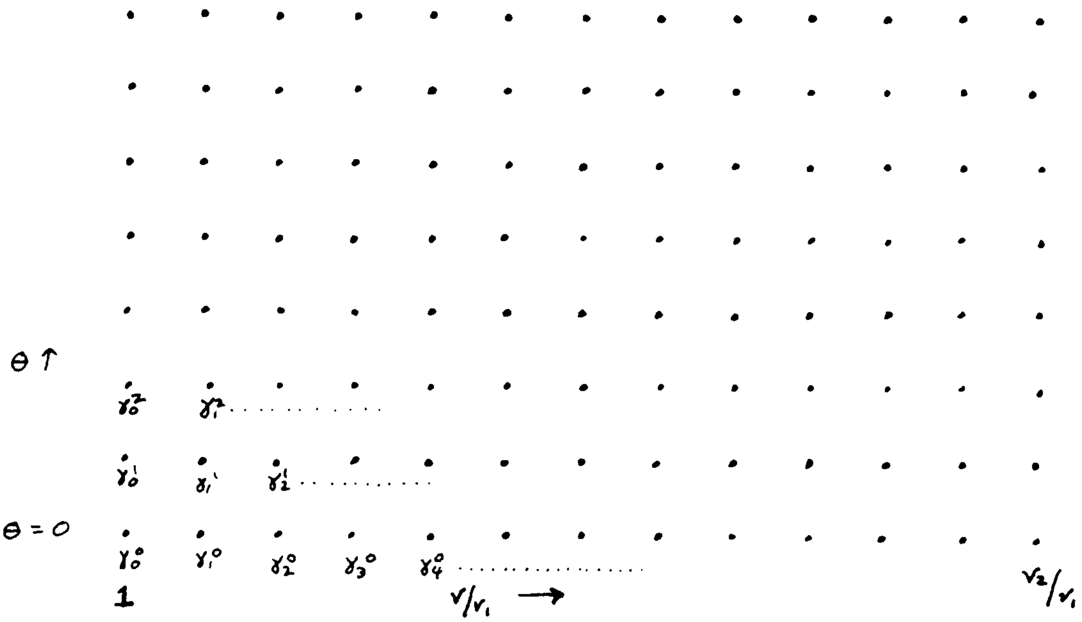

Figure 6

$\Delta\rho$ and $\Delta\theta$ should be as small as convenient to approximate as closely as possible the actual values of the derivatives. A necessary restriction on these quantities to prevent propagation of errors introduced by the use of finite, rather than infinitesimal, differences (15, 16), is that

$$\Delta\theta \leq \tfrac{1}{2}(\Delta\rho)^2$$

The derivatives become

$$\frac{\partial\gamma}{\partial\theta} \Rightarrow \frac{\gamma_m^{n+1} - \gamma_m^n}{\Delta\theta} \tag{24}$$

$$\frac{\partial\gamma}{\partial\rho} \Rightarrow \frac{\gamma_{m+1}^n - \gamma_{m-1}^n}{2\Delta\rho}$$

$$\frac{1}{\rho}\frac{\partial}{\partial\rho}\rho\frac{\partial\gamma}{\partial\rho} \Rightarrow \frac{1}{\rho_m\Delta\rho}\left(\rho_{m+\frac{1}{2}}\frac{\gamma_{m+1}^n - \gamma_m^n}{\Delta\rho} - \rho_{m-\frac{1}{2}}\frac{\gamma_m^n - \gamma_{m-1}^n}{\Delta\rho}\right)$$

Since

$$\frac{\rho_{m\pm\frac{1}{2}}}{\rho_m} = 1 \pm \frac{\Delta\rho}{2\rho_m} = 1 \pm \frac{\Delta\rho}{2(1+m\Delta\rho)}$$

the above becomes

$$\frac{1}{(\Delta\rho)^2}\left[\left(1+\frac{\Delta\rho}{2(1+m\Delta\rho)}\right)\gamma_{m+1}^n - 2\gamma_m^n + \left(1-\frac{\Delta\rho}{2(1+m\Delta\rho)}\right)\gamma_{m-1}^n\right] \tag{25}$$

Lamm's equation then takes the form

$$\frac{\gamma_m^{n+1}-\gamma_m^n}{\Delta\theta} = -2\lambda\gamma_m^n - \lambda(1+m\Delta\rho)\,\frac{\gamma_{m+1}^n-\gamma_{m-1}^n}{2\Delta\rho}$$

$$+\frac{1}{(\Delta\rho)^2}\left[\left(1+\frac{\Delta\rho}{2(1+m\Delta\rho)}\right)\gamma_{m+1}^n - 2\gamma_m^n + \left(1-\frac{\Delta\rho}{2(1+m\Delta\rho)}\right)\gamma_{m-1}^n\right]$$

The following parameters are defined

$$\xi = \frac{\Delta\theta}{2\Delta\rho}$$

$$\mathcal{K} = 1 - 2\frac{\Delta\theta}{(\Delta\rho)^2} - 2\lambda\,\Delta\theta$$

$$\beta = \frac{\Delta\theta}{(\Delta\rho)^2}$$

whereupon Lamm's equation becomes

$$\gamma_m^{n+1} = \gamma_m^n\,\mathcal{K} + \gamma_{m+1}^n\left\{\beta + \left(\frac{\xi}{1+m\Delta\rho} - \lambda\,\xi\,(1+m\Delta\rho)\right)\right\}$$

$$+\gamma_{m-1}^n\left\{\beta - \left(\frac{\xi}{1+m\Delta\rho} - \lambda\,\xi\,(1+m\Delta\rho)\right)\right\} \qquad (26)$$

This is a type of recursion relationship. It allows us to advance in time, or gives us the values of all γ_m^n at n + 1 if we know the γ_m's at n.

The above formula does not hold for the calculation of γ_o^n for which the boundary condition must be used. The condition is

$$\left(\frac{\partial\gamma}{\partial\rho}\right)_{\rho=1} = \lambda\,\gamma(\rho=1)$$

or

$$\gamma_o' = \lambda\gamma_o$$

To make use of this, we write γ_o as a power series in $\Delta\rho$ about γ_1

$$\gamma_o = \gamma_1 - \Delta\rho\,\frac{\partial\gamma_1}{\partial\rho}$$

Now

$$\gamma_0' = \gamma_1' - \Delta\rho\,\gamma_1'' = \lambda\gamma_0$$

$$\gamma_1' = \frac{\gamma_2 - \gamma_0}{2\Delta\rho}$$

$$\gamma_1'' = \frac{\gamma_2 - 2\gamma_1 + \gamma_0}{(\Delta\rho)^2}$$

When these equations are solved for γ_0, the result is

$$\gamma_0 = g_1\gamma_1 + g_2\gamma_2 \tag{27}$$

where

$$g_1 = \frac{4}{3 + 2\lambda\Delta\rho} \qquad g_2 = -\frac{1}{3 + 2\lambda\Delta\rho}$$

Lamm's equation is essentially now in the form of a routine recursion relationship of the type admirably suited for digital computers. A program was written for the Burroughs 220 at the Institute, and the solution of the equation obtained there.

The scheme of calculation is straightforward. The parameters in braces in equation 26 were calculated and stored in memory for $0 \le m \le 1000$. Then the memory cells were loaded with γ_m^o, or unity. The proper new γ's were computed according to equations 26 and 27. When γ_9^n and γ_{10}^n differed in the 5th decimal place, the integration was extended by 10 units. The same was true for γ_{19}^n and γ_{20}^n, γ_{29}^n and γ_{30}^n, and so forth. Physically this just means that the system was integrated out to the plateau and stopped, but continued when the plateau was pushed farther out by diffusion. After the integration had proceeded the equivalent of 5 minutes centrifuge time, the computer was allowed to print out the concentration and concentration gradient data contained in memory, and then allowed to proceed to do 5 more minutes worth.

The system picked for study was the hemoglobin system. The data used were obtained from Dr. William Hutchinson of these laboratories.

$s = 4.50 \times 10^{-13}$ sec

$M = 66,800$ gm/mole

$\bar{v} = 0.749$ cm/gm

density $= 0.998$ gm/cm

$r_1 = 5.7$ cm

$\omega = 9.340$ rev/min

$\varkappa = 0.3047623586$

$\Delta t = 1$ sec

$\Delta \theta = 2.01875450 \times 10^{-8}$

$\lambda = 21.32450842$

$\Delta \rho = 2.409852114 \times 10^{-4}$

$\xi = 4.18854438 \times 10^{-5}$

$\beta = 0.347683752$

$\lambda \xi = 8.931864990 \times 10^{-4}$

VII. COMPARISON OF COMPUTER AND FUJITA-MacCOSHAM RESULTS

The results given by the computer were compared with those predicted by the Fujita-MacCosham formulae. They agreed remarkably well, being within 0.1% near the inner boundary after reasonable run times.

The concentration gradient profile at 45 minutes from the numerical solution

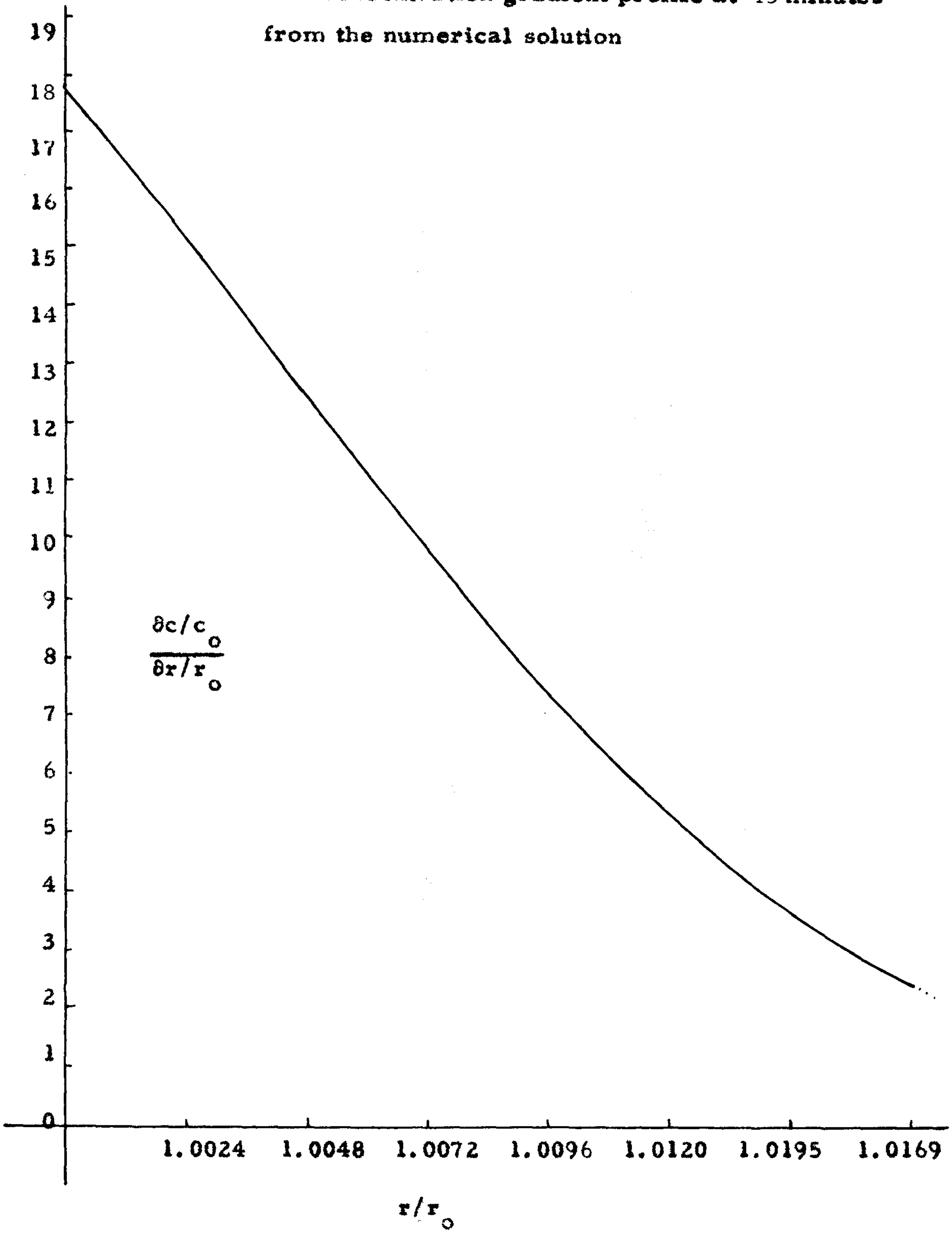

Figure 7

	γ		$\partial\gamma / \partial\rho$	
m	Fujita-MacCosham	Computer	Fujita-MacCosham	Computer
		30 min.		
0	.8617	.8621	18.36	18.38
5	.8826	.8832	16.64	16.66
10	.9016	.9023	14.88	14.89
15	.9186	.9191	13.10	13.12
20	.9332	.9339	11.40	11.38
50	.9839	.9844	3.47	3.51
100	.9980	.9981	.01	.00
∞	.9984	.9984	0	0
		45 min.		
0	.8325	.8331	17.75	17.76
5	.8532	.8536	16.46	16.47
10	.9054	.9059	12.38	12.40
15	.9197	.9200	11.06	11.06
20	.9319	.9326	9.74	9.76
50	.9679	.9684	5.35	5.32
100	.9956	.9956	.55	.52
∞	.9977	.9976	0	0

The excellence of agreement leads to the conclusion that the Fujita-MacCosham formulae can serve as an excellent guide to the theoretical line shape near the boundary of the concentration gradient curve. The validity of the customary linear extrapolation of $\partial C/\partial r$ from the region of good Schlieren definition back to the boundary can be investigated by expanding the Fujita-MacCosham formula in a

Taylor series about $\rho = 1$. The coefficients will, of course, be time dependent. If $\frac{\partial^2 C}{\partial r^2}$ and higher terms are small relative to $C(r)$ and $\frac{\partial C}{\partial r}$ for times of interest, then theoretical justification of the extrapolation will be established.

VIII. EXPANSION OF THE FUJITA-MacCOSHAM FORMULA AND CONCLUSIONS

Taylor's formula is

$$\gamma(\rho,\tau) = \gamma(\rho=1,\tau) + \gamma'(1,\tau)(\rho-1) + \frac{1}{2}\gamma''(1,\tau)(\rho-1)^2 + \frac{1}{6}\gamma'''(1,\tau)(\rho-1)^3 + \cdots$$

Since the Fujita-MacCosham formula is most conveniently expressed in terms of the variables z and τ, it is advantageous to perform some mathematical transformations before calculating the necessary derivatives with respect to ρ.

$$\rho = e^{z/2}$$

$$\frac{\partial}{\partial \rho} = 2e^{-z/2}\frac{\partial}{\partial z}$$

$$\frac{\partial^2}{\partial \rho^2} = 4e^{-z}\frac{\partial^2}{\partial z^2} - 2e^{-z}\frac{\partial}{\partial z}$$

$$\frac{\partial^3}{\partial \rho^3} = 8e^{-3z/2}\frac{\partial^3}{\partial z^3} - 12e^{-3z/2}\frac{\partial^2}{\partial z^2} + 4e^{-3z/2}\frac{\partial}{\partial z}$$

$$\frac{\partial^4}{\partial \rho^4} = 16e^{-2z}\frac{\partial^4}{\partial z^4} - 48e^{-2z}\frac{\partial^3}{\partial z^3} + 44e^{-2z}\frac{\partial^2}{\partial z^2} - 12e^{-2z}\frac{\partial}{\partial z}$$

and so forth.

In addition, the equation

$$u_\tau = \epsilon u_{zz} - u_z$$

where $\gamma = e^{-\tau}u$ is useful, as well as the boundary condition $u(1,\tau) = \epsilon u_z(1,\tau)$.

Since the derivatives with respect to ρ are expressible in terms of derivatives with respect to z, it is convenient to set up a table of z derivatives evaluated at $z = 0$ (or $\rho = 1$). Define $\lambda = \frac{2}{\epsilon}$.

Then at $\rho = 1$, or $z = 0$,

$$u_z = \frac{\lambda}{2} u$$

$$u_{zz} = \frac{\lambda}{2} u_\tau + \frac{\lambda^2}{4} u$$

$$u_{zzz} = \frac{\lambda^2}{2} u_\tau + \frac{\lambda^3}{8} u$$

$$u_{zzzz} = \frac{\lambda^2}{4} u_{\tau\tau} + \frac{3\lambda^3}{8} u_\tau + \frac{\lambda^4}{16} u$$

and so forth.

In addition,

$$u(z=0,\tau) = \frac{1}{2}\left\{\left(2+\frac{\tau}{\epsilon}\right) \operatorname{erfc}\sqrt{\frac{\tau}{4\epsilon}} - \frac{2}{\sqrt{\pi}}\sqrt{\frac{\tau}{\epsilon}}\, e^{-\tau/4\epsilon}\right\}$$

$$u_\tau(z=0,\tau) = \frac{1}{2\epsilon} \operatorname{erfc}\sqrt{\frac{\tau}{4\epsilon}} - \frac{1}{\sqrt{\epsilon\pi\tau}}\, e^{-\tau/4\epsilon}$$

$$u_{\tau\tau}(z=0,\tau) = \frac{1}{2\tau\sqrt{\pi\epsilon\tau}}\, e^{-\tau/4\epsilon}$$

and so forth.

These expressions can be combined to give at $\rho = 1$, or $z = 0$,

$$u_\rho = \lambda u$$

$$u_{\rho\rho} = 2\lambda u_\tau + \lambda(\lambda-1)u$$

$$u_{\rho\rho\rho} = \lambda(\lambda-1)(\lambda-2)\,u + 2\lambda(2\lambda-3)\,u_\tau$$

$$u_{\rho\rho\rho\rho} = \lambda(\lambda-1)(\lambda-2)(\lambda-3)\,u - 2\lambda(6\lambda-11)\,u_\tau + 4\lambda^2 u_{\tau\tau}$$

and so forth.

Using the data from the hemoglobin system, we have after a 45 minute run

$e^{-\tau} = 0.9977$ $\quad u = 0.8344$ $\quad u_{\tau\tau} = 8163.7896$

$\lambda = 23.3245$ $\quad u_\tau = -33.1029$

Hence

$$C/Co = e^{-\tau}u = 0.8325 + 17.7530\,(\rho-1) - 523.8765\,(\rho-1)^2$$
$$-8,115.9355\,(\rho-1)^3 + 617,303.3892\,(\rho-1)^4 + \cdots$$

After a run of 90 minutes, the parameters become

$$C/Co = 0.7689 + 16.3974\,(\rho-1) - 300.64\,(\rho-1)^2 - 5.102.22\,(\rho-1)^3$$
$$+ 225,877\,(\rho-1)^4 + \cdots$$

A cursory examination of these expressions will indicate that the terms of higher order in the Taylor expansion are not small, and $\frac{\partial C}{\partial r}$ curves are not linear. The higher order terms alternate in sign in a rather random fashion and apparently tend to cancel out.

It would seem that a much safer, although more laborious, procedure than the linear extrapolation to find $\frac{\partial C}{\partial r}$ at the boundary would be to put the measurable experimental data into the Fujita-MacCosham formula and provide some sort of best fit to determine the parameter ϵ. This would most likely require aid from computers. Only ϵ is needed because it is equal to $\frac{2D}{r_1^2 s\omega^2}$ and thus contains the ratio s/D plus other known parameters. A possible scheme is to do a linear extrapolation of the $\frac{\partial C}{\partial r}$ curve to get $\frac{s}{D}$, calculate ϵ, and then fiddle with this value of ϵ until good agreement with the Fujita-MacCosham formula is reached.

It should be mentioned here that the concentration dependence of s and D has not been taken into account. Also, the effects of polydispersity have not been investigated.

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16. Private discussion with Dr. Joel Franklin.

I. Introduction

Hearst and Vinograd have discovered that the sedimentation coefficients of deoxyribonucleic acid and tobacco mosaic virus increase as the angular velocity of the centrifuge increases (1). The phenomenon is highly concentration dependent, and appears to vanish at zero concentration. T-4 phage DNA displays a field independent sedimentation coefficient of about 550 S at a concentration of OD^{260} 0.122, but at OD^{260} 0.458, the sedimentation coefficient varies from about 280 S at 4,908 RPM to about 450 S at 20,410 RPM. *E. Coli* DNA at OD^{260} 0.36 has a field independent sedimentation coefficient of 250 S, but at OD^{260} 2.7 the sedimentation coefficient varies from about 130 S at 9,945 RPM to about 150 S at 56,100 RPM. TMV at 0.2 mg/ml shows a sedimentation coefficient of about 178 S at 4,908 RPM and 185 S at 20,410 RPM; at 0.6 mg/ml the coefficient is about 185 S at 4,908 RPM and 193 S at 20,410 RPM. Although the TMV data indicate that this effect does not extrapolate out at zero concentration, Hearst and Vinograd point out that more work needs to be done in the low concentration region to determine just what happens at zero concentration. It is not unreasonable to expect the sedimentation coefficients at different fields to coincide at zero concentration.

Hearst and Vinograd were unable to offer any definite theoretical explanation of the effect. They concluded that a likely origin of the anomaly is an alignment of the molecules. A long rigid rod-like particle oriented parallel to an applied field sediments twice as fast through the medium as a particle aligned perpendicular to the field, so since both particles possess rod-like characteristics, the magnitude of the effect lies within this range. The two most obvious mechanisms for alignment, as mentioned by Hearst and Vinograd, are concentration-dependent hydrodynamic alignment and an entropy alignment such as that operative in the formation of liquid crystals.

Hydrodynamic alignment is considered in detail here. The model used corresponds to a rigid inflexible rod, whose properties are much more characteristic of TMV than DNA. This work can thus be considered to be restricted somewhat in scope. The results of the calculations are applied solely to TMV. They predict a dependence on concentration for the sedimentation coefficient which is within 6% of experiment, and indicate that the expected field and concentration dependent hydrodynamic alignment is sufficiently small that it cannot be detected experimentally and also that the molecules tend to align perpendicular, not parallel, to the field. Therefore, according to these calculations, any hydrodynamic alignment present would decrease rather than increase the sedimentation coefficient with an increase in field.

A few preliminary comments concerning tactoid formation are presented. It is shown that the effects of an angular anisotropy due to the excluded volume effect are too small to be observed. This is true, of course, in regions of low concentration where no liquid crystals are formed.

Before concentration dependent phenomena are considered, the consequences of a sphere moving through an infinite medium and a brief sketch of rotatory brownian motion will be discussed in order to form a framework for later theory. Also, as a matter of completeness, certain types of intrinsic alignments and sedimentation coefficients will be presented, all but one of which were worked out in the course of this investigation.

II. Spheres under Stokes Flow in an Infinite Medium

The equations governing the flow of incompressible viscous fluids are the Navier-Stokes equations (2)

$$\rho\left(\frac{\partial \vec{v}}{\partial t} + \vec{v} \cdot \nabla \vec{v}\right) = -\nabla p + \eta \nabla^2 \vec{v}$$

$$\nabla \cdot \vec{v} = 0$$

where ρ is the density, p the pressure, and η the viscosity. If the flow is steady state, $\frac{\partial \vec{v}}{\partial t} = 0$. In case the velocities are low, the quadratic terms $\rho \vec{v} \cdot \nabla \vec{v}$ are neglected. To this approximation the hydrodynamic equations are linear

$$\eta \nabla^2 \vec{v} = \nabla p$$

$$\nabla \cdot \vec{v} = 0$$

For a sphere moving through the medium with velocity $U \hat{e}_z$, the exact solutions to these equations are (2)

$$v_x = \frac{3Ua}{4r}\ (1 - \frac{a^2}{r^2})\ \sin\theta\ \cos\theta\ \cos\varphi \tag{1a}$$

$$v_y = \frac{3Ua}{4r}\ (1 - \frac{a^2}{r^2})\ \sin\theta\ \cos\theta\ \sin\varphi \tag{1b}$$

$$v_z = \frac{3Ua}{4r}\ [(1 + \cos^2\theta) + \frac{a^2}{3r^2}(1 - 3\cos^2\theta)] \tag{1c}$$

$U\hat{e}_z$ is the velocity of the sphere with respect to fluid infinitely far away, a is the radius of the sphere, r is the distance from the center of the sphere to an external point of interest, and θ and φ are polar angles defined in the usual manner. At $r = a$, it can be easily verified that these expressions give $v_x = v_y = 0$; $v_z = U$ so that the requirement of no slip on the sphere surface is satisfied.

If the quantity a/r becomes considerably less than unity, the leading terms are

$$v_x = \frac{3Ua}{4r}\ \sin\theta\ \cos\theta\ \cos\varphi = \frac{3Ua}{4r}\ \frac{zx}{r^2} \tag{2a}$$

$$v_y = \frac{3Ua}{4r}\ \sin\theta\ \cos\theta\ \sin\varphi = \frac{3Ua}{4r}\ \frac{zy}{r^2} \tag{2b}$$

$$v_z = \frac{3Ua}{4r}\ (1 + \cos^2\theta) = \frac{3Ua}{4r}\ (1 + \frac{z^2}{r^2}) \tag{2c}$$

If the sphere had been moving in the $\hat{e}_x$, rather than $\hat{e}_z$, direction, the result for $a/r << 1$ would have been, by symmetry,

$$v_x = \frac{3Ua}{4r}\ (1 + \frac{x^2}{r^2}) \tag{3a}$$

$$v_y = \frac{3Ua}{4r}\ \frac{xy}{r^2} \tag{3b}$$

$$v_z = \frac{3Ua}{4r}\ \frac{xz}{r^2} \tag{3c}$$

Likewise, the results for a sphere moving in the $\hat{e}_y$ direction are

$$v_x = \frac{3Ua}{4r}\,\frac{xy}{r^2} \tag{4a}$$

$$v_y = \frac{3Ua}{4r}\left(1 + \frac{y^2}{r^2}\right) \tag{4b}$$

$$v_z = \frac{3Ua}{4r}\,\frac{yz}{r^2} \tag{4c}$$

According to Stokes' law the sphere exerts a force upon the fluid in the direction of its motion of magnitude $6\pi\eta a U$. The effect of neglecting the higher order terms is equivalent to treating spheres of vanishingly small radii, or point forces.

It is convenient to define a tensor $\underset{\sim}{T}\;(r, r')$ such that the fluid velocity at any point $\vec{r}$ due to the action of a point force at $\vec{r}\,'$ is obtained as indicated in equation 5,

$$\vec{V}(\vec{r}) = \underset{\sim}{T}(\vec{r}, \vec{r}\,') \cdot \vec{F}(\vec{r}\,') \tag{5}$$

From equations 2, 3, and 4, this tensor is seen to be

$$T(\vec{r}, \vec{r}\,') = \frac{1}{8\pi\eta\,|\vec{r}\,'-\vec{r}|}\left\{\begin{matrix} 1 + \sin^2\theta'\cos^2\varphi' & \sin^2\theta'\sin\varphi'\cos\varphi' & \sin\theta'\cos\theta'\cos\varphi' \\ \sin^2\theta'\cos\varphi'\sin\varphi' & 1 + \sin^2\theta'\sin^2\varphi' & \sin\theta'\cos\theta'\sin\varphi' \\ \sin\theta'\cos\theta'\cos\varphi' & \sin\theta'\cos\theta'\sin\varphi' & 1 + \cos^2\theta' \end{matrix}\right\} \tag{6}$$

The primes on the angles refer to the coordinates of the vector $\vec{r}\,'-\vec{r}$. It is sometimes convenient to write this in dyadic form

$$\underset{\sim}{T}(\vec{r}, \vec{r}\,') = \frac{1}{8\pi\eta\,|\vec{r}\,'-\vec{r}|}\left(\underset{\sim}{1} + \hat{e}_{\vec{r}\,'-\vec{r}}\,\hat{e}_{\vec{r}\,'-\vec{r}}\right) \tag{7}$$

III. Rotatory Brownian Motion Theory

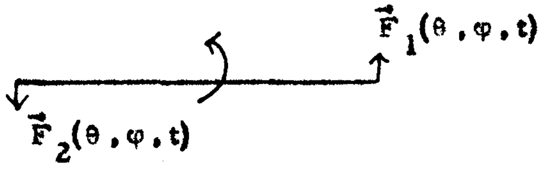
In the first part of this thesis, an expression called the Lamm equation, denoting conservation of matter, was deduced. In words, this states that the decrease in number of particles per unit volume per unit time equals the divergence of current of particles across the boundaries of unit volume.

$$\frac{\partial c(r,t)}{\partial t} = -\operatorname{div}\,(\overrightarrow{\text{flow}})$$

The same sort of relationship can be deduced for angular orientations of rigid rod-like molecules. Call $f(\theta, \varphi, t)$ the angular distribution function, such that the fraction of rods having their long axes aligned in the solid angle $\sin\theta \, d\theta \, d\varphi$ at time t is $f(\theta, \varphi, t) \sin\theta \, d\theta \, d\varphi$. There then is the quite analogous equation

$$\frac{\partial f(\theta, \varphi, t)}{\partial t} = -\operatorname{div}(\overrightarrow{\text{angular flow}})$$

If there is an external force on the particle which gives rise to a net torque, $\vec{\tau}(\theta, \varphi, t)$, there will tend to be a rotational angular flow.



The angular velocity which this torque induces is

$$\vec{\omega} = \vec{\tau}(\theta, \varphi, t) \cdot \underset{\sim}{R}^{-1} \tag{8}$$

where $\underset{\sim}{R}$ is the rotational friction tensor, which for rods is clearly diagonal in a coordinate system using the long axis of the rod as an axis (this means that the rod tends to rotate only in the direction of the applied force). This flow will cause points to move with velocity $\vec{\omega} \times \hat{e}_r$, so that the flow due to external forces is

$$f(\theta, \varphi, t)\, (\vec{\tau}(\theta, \varphi, t) \cdot \underset{\sim}{R}^{-1}) \times \hat{e}_r$$

If $f(\theta, \varphi, t)$ is nonuniform, Brownian motion will tend to destroy the nonuniformity (4) by setting up a counterflow of velocity

$$- \underset{\sim}{D}_R \cdot \nabla_\Omega f(\theta, \varphi, t)$$

The symbol ∇_Ω means gradient with respect to angular coordinates only. $\underset{\sim}{D}_R$ is the rotational diffusion tensor, which is also diagonal for rods in the same type of coordinate system.

The total angular flow is then

$$f(\theta, \varphi, t)\, (\vec{\tau}(\theta, \varphi, t) \cdot \underset{\sim}{R}^{-1}) \times \hat{e}_r - \underset{\sim}{D}_R \cdot \nabla_\Omega f(\theta, \varphi, t)$$

and

$$\frac{\partial f(\theta, \varphi, t)}{\partial t} = - \operatorname{div} (\overrightarrow{\text{total angular flow}})$$

In steady states of interest here, $f(\theta, \varphi, t)$ is time independent and the total flow vanishes (4). Therefore,

$$(\vec{\tau}(\theta, \varphi) \cdot \underset{\sim}{R}^{-1}) \times \hat{e}_r = \underset{\sim}{D}_R \cdot \nabla_\Omega \ln f(\theta, \varphi) \qquad (9)$$

From a generalization of a result due to Einstein (5)

$$\underset{\sim}{D}_R = kT\, \underset{\sim}{R}^{-1}$$

so that

$$\vec{\tau}(\theta, \varphi) \times \hat{e}_r = kT\, \nabla_\Omega \ln f(\theta, \varphi) \qquad (9')$$

IV. Intrinsic Distribution Functions and Sedimentation Coefficients

Using the ideas just developed on brownian motion, four types of angular distributions in a time-independent external field for a single rod will be developed. The last three are new. The four cases will be:

A. Stokes flow in an infinite medium

B. Oseen flow in an infinite medium

C. Stokes flow in the presence of a wall

D. Stokes flow in a radial centrifugal field.

IVa. Stokes Flow in an Infinite Medium

According to the method of Kirkwood and Riseman (6), a rod-like molecule is represented as far as hydrodynamic interactions are concerned by a system of dimensionless hydrodynamic elements, being 2n + 1 in number, with 0 in the center, lying all on the same straight line a distance b apart. This model is so constructed that its length and the actual physical length of the molecule are the same. Each hydrodynamic element is assumed to possess the same characteristic friction constant ζ.

The force which element i exerts upon the fluid is

$$\vec{F}_i = \zeta \, \vec{w}_i \tag{10}$$

where $\vec{w}_i$ is the velocity of the element with respect to the fluid velocity which would exist at the location of element i if i were not present. It is convenient to write

$$\vec{w}_i = \vec{v}_i - \vec{u}_i \tag{11}$$

where $\vec{v}_i$ is the velocity of the i^{th} element with respect to the lab, and $\vec{u}_i$ is the velocity which the fluid would possess with respect to the lab if element i were not present. If $\vec{u}_i$ arises solely from velocities induced by the other elements of the chain

$$\vec{u}_i = \sum_{i \neq j} \underset{\sim}{T}_{ij} \cdot \vec{F}_j \tag{12}$$

Then

$$\vec{w}_i = \vec{v}_i - \sum_{i \neq j} \underset{\sim}{T_{ij}} \cdot \vec{F}_j$$

and

$$\vec{F}_i = \zeta \vec{w}_i = \zeta \vec{v}_i - \zeta \sum_{i \neq j} \underset{\sim}{T}_{ij} \cdot \vec{F}_j \tag{13}$$

For an isolated particle such as this in a space and time constant external field, the only source of a torque is a hydrodynamic one induced internally. However, since $\underset{\sim}{T}_{ij}$ does not have an antisymmetric part, it follows there is no such torque. This means that the angular distribution function is uniform and that there is no tendency toward rotation irrespective of the orientation of the molecule. Therefore,

$$\vec{v}_i = \vec{v}_j = \vec{v}$$

and

$$\vec{F}_i = \zeta \vec{v} - \zeta \sum_{i \neq j} \underset{\sim}{T}_{ij} \cdot \vec{F}_j \tag{14}$$

It is now advantageous to proceed according to Saito (7). Instead of viewing the action from some external, fixed coordinate system, a position on the molecule itself is assumed, defining the z' axis along the long axis of the rod, and the others mutually perpendicular to it and to each other.

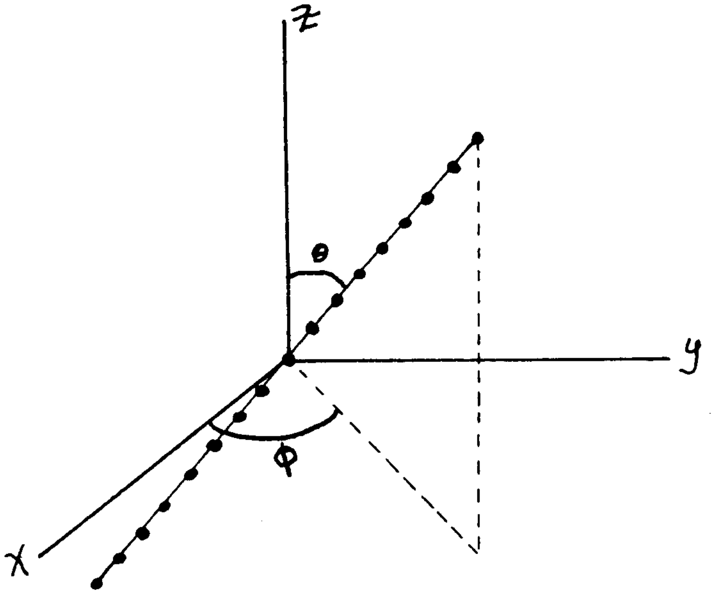


Figure 1

The matrix of this transformation between laboratory and rod-fixed coordinates is

$$\underset{\sim}{\alpha} = \left\{\begin{matrix} \cos\theta\ \cos\varphi & -\sin\varphi & \sin\theta\ \cos\varphi \\ \cos\theta\ \sin\varphi & \cos\varphi & \sin\theta\ \sin\varphi \\ -\sin\theta & 0 & \cos\theta \end{matrix}\right\} \qquad (15)$$

Then

$$\underset{\sim}{\alpha} \cdot \vec{F}_i = \zeta\, \underset{\sim}{\alpha} \cdot \vec{U} - \zeta \sum_{i \neq j} \underset{\sim}{\alpha} \cdot \underset{\sim}{T_{ij}} \cdot \vec{F}_j$$

$$= \zeta\, \underset{\sim}{\alpha} \cdot \vec{U} - \zeta \sum_{i \neq j} \underset{\sim}{\alpha} \cdot \underset{\sim}{T_{ij}} \cdot \underset{\sim}{\alpha}^{-1} \cdot \underset{\sim}{\alpha} \cdot \vec{F}_j$$

or

$$\vec{F}_i{}' = \zeta\, \vec{U}{}' - \lambda \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \cdot \sum_{i \neq j} \frac{\vec{F}_j{}'}{|i-j|} \qquad (16)$$

where

$$\lambda = \frac{\zeta}{8\pi \eta b}$$

Equations 16, along with the further condition

$$\frac{\mathcal{F} M}{N} \begin{pmatrix} 0 \\ 0 \\ -1 \end{pmatrix} = \sum{}' \ \vec{F}_i \tag{17}$$

suffice to determine the individual $\vec{F}_i$. $\mathcal{F}$ is the force magnitude per unit mass corrected for buoyancy, M is the molecular weight, and N is Avogadro's number.

The sum in equation 16 is now approximated by an integral. Here $s = i/n$, $t = j/n$.

$$\vec{F}'(s) = \zeta \vec{v}' - \lambda \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \cdot \int_{-1}^{1} \frac{\vec{F}'(t)}{|t-s|} \, dt$$

with the condition on the kernel

$$\begin{cases} \dfrac{1}{|t-s|} \leq n \\ \text{zero otherwise} \end{cases}$$

For convenience, two new functions are defined

$$\vec{F}'(t)\cdot\hat{e}_{x'} = \zeta\,\psi^{(1)}(t)\,\vec{v}'\cdot\hat{e}_{x'} \tag{18a}$$

$$\vec{F}'(t)\cdot\hat{e}_{y'} = \zeta\,\psi^{(1)}(t)\,\vec{v}'\cdot\hat{e}_{y'} \tag{18b}$$

$$\vec{F}'(t)\cdot\hat{e}_{z'} = \zeta\,\psi^{(2)}(t)\,\vec{v}'\cdot\hat{e}_{z'} \tag{18c}$$

The integral equation becomes

$$\begin{Bmatrix} \psi^{(1)}(s) \\ \psi^{(1)}(s) \\ \psi^{(2)}(s) \end{Bmatrix} = \begin{Bmatrix} 1 \\ 1 \\ 1 \end{Bmatrix} - \lambda \int_{-1}^{1} \begin{Bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{Bmatrix} \begin{Bmatrix} \psi^{(1)}(t) \\ \psi^{(1)}(t) \\ \psi^{(2)}(t) \end{Bmatrix} \frac{dt}{|s-t|} \tag{19}$$

$$\frac{1}{|s-t|} \leq n$$

The vector components here do not mix, as opposed to equation 14. The solutions for $\psi^{(1)}(s)$ and $\psi^{(2)}(s)$ were given by Kirkwood and Riseman (6)

$$\psi^{(1)}(s) = \frac{1}{1+2\lambda\,(\ln 2n-1)}\left\{1+\frac{2\lambda}{\pi}\sum_{k=1}^{\infty}\frac{(-1)^k}{k}\;\frac{\mathrm{Si}\,2\pi k\,\cos\pi k s}{1-2\lambda\,\mathrm{Ci}\left(\frac{\pi k}{n}\right)}\right\} \tag{20a}$$

$$\psi^{(2)}(s) = \frac{1}{1+4\lambda\,(\ln 2n-1)}\left\{1+\frac{4\lambda}{\pi}\sum_{k=1}^{\infty}\frac{(-1)^k}{k}\;\frac{\mathrm{Si}\,2\pi k\,\cos\pi k s}{1-4\lambda\,\mathrm{Ci}\left(\frac{\pi k}{n}\right)}\right\} \tag{20b}$$

where

$$Si\,(x) = \int_{0}^{x} \frac{\sin y}{y}\,dy$$

$$Ci\,(x) = \int_{x}^{\infty} \frac{\cos y}{y}\,dy$$

From the definitions of the ϕ's, it follows that

$$\vec{F}(s) = \underset{\sim}{\alpha}^{-1} \cdot \vec{\mathcal{F}}'(s)$$

$$= \zeta\,\underset{\sim}{\alpha}^{-1} \cdot \begin{Bmatrix} \psi^{(1)}(s) & 0 & 0 \\ 0 & \psi^{(1)}(s) & 0 \\ 0 & 0 & \psi^{(2)}(s) \end{Bmatrix} \cdot \underset{\sim}{\alpha} \cdot \underset{\sim}{\alpha}^{-1} \cdot \vec{V}' \qquad (21)$$

The force on the particle is taken in the minus z direction, so that from equation 17

$$\frac{\mathcal{F}M}{N}\begin{Bmatrix}0\\0\\1\end{Bmatrix} = n\,\zeta\,\underset{\sim}{\alpha}^{-1} \cdot \int_{-1}^{1} \begin{Bmatrix} \phi^{(1)}(s) & 0 & 0 \\ 0 & \phi^{(1)}(s) & 0 \\ 0 & 0 & \phi^{(2)}(s) \end{Bmatrix} ds \cdot \underset{\sim}{\alpha} \cdot \vec{V}$$

$$= n\zeta\,\underset{\sim}{\alpha}^{-1} \cdot \begin{Bmatrix} \Omega^{(1)}(1) & 0 & 0 \\ 0 & \Omega^{(1)}(1) & 0 \\ 0 & 0 & \Omega^{(2)}(1) \end{Bmatrix} \cdot \underset{\sim}{\alpha} \cdot \vec{V}$$

where

$$\int_{-x}^{x} \phi(s)\,ds = \Omega(x)$$

Multiplying both sides on the right by

$$\underset{\sim}{\alpha} \cdot \begin{Bmatrix} \dfrac{1}{\Omega^{(1)}(1)} & 0 & 0 \\ 0 & \dfrac{1}{\Omega^{(1)}(1)} & 0 \\ 0 & 0 & \dfrac{1}{\Omega^{(2)}(1)} \end{Bmatrix} \cdot \underset{\sim}{\alpha}^{-1}$$

it follows that

$$V = \frac{\mathcal{F} M}{n \zeta N} \alpha \cdot \begin{Bmatrix} [\Omega^{(1)}(1)]^{-1} & 0 & 0 \\ 0 & [\Omega^{(1)}(1)]^{-1} & 0 \\ 0 & 0 & [\Omega^{(2)}(1)]^{-1} \end{Bmatrix} \cdot \alpha^{-1} \cdot \begin{Bmatrix} 0 \\ 0 \\ -1 \end{Bmatrix}$$

$$= \frac{\mathcal{F} M}{n \zeta N} \left[\frac{\mathbb{1}}{\Omega^{(1)}(1)} - \hat{e}_r \hat{e}_r \left(\frac{1}{\Omega^{(2)}(1)} - \frac{1}{\Omega^{(1)}(1)} \right) \right] \cdot \begin{Bmatrix} 0 \\ 0 \\ -1 \end{Bmatrix} \tag{22}$$

The quantity

$$\underset{\sim}{\mathfrak{m}} = \frac{1}{n \zeta \Omega^{(1)}(1)} \left[\mathbb{1} - \hat{e}_r \hat{e}_r \left(1 - \frac{\Omega^{(1)}(1)}{\Omega^{(2)}(1)} \right) \right] \tag{23}$$

is the mobility tensor. From the relationship

$$\lim_{n \to \infty} \frac{\Omega^{(1)}(1)}{\Omega^{(2)}(1)} = \lim_{n \to \infty} \frac{1 + 4\lambda\,(\ln 2n - 1)}{1 + 2\lambda\,(\ln 2n - 1)} = 2$$

follows

$$\lim_{n \to \infty} \underset{\sim}{M} = \frac{1}{n \zeta \Omega^{(1)}(1)} \left(\underset{\sim}{\mathbb{1}} + \hat{e}_r \hat{e}_r \right)$$

When the particle is aligned parallel to its translational motion, the zz component of this tensor is twice as large as that for a particle aligned perpendicular to its motion. This is in agreement with results obtained by previous methods (8).

The force which an individual element exerts on the fluid in terms of laboratory coordinates is obtained by substituting equation 22 into equation 21. The result is

$$\vec{F}(s) = \frac{\mathcal{F} M}{N} \left[\frac{\psi^{(1)}(s)}{\Omega^{(1)}(1)} \underset{\sim}{\mathbb{1}} - \hat{e}_r \hat{e}_r \left(\frac{\psi^{(1)}(s)}{\Omega^{(1)}(1)} - \frac{\psi^{(2)}(s)}{\Omega^{(2)}(1)} \right) \right] \begin{Bmatrix} 0 \\ 0 \\ -1 \end{Bmatrix} \qquad (24)$$

It is instructive to note that this function is even in s

$$\vec{F}(s) = \vec{F}(-s)$$

This is quite to be expected, since there is no hydrodynamic or external torque on the particle.

IVb. Rods under Oseen Flow in Infinite Medium

The Navier-Stokes equations are

$$\rho \left(\frac{\partial \vec{v}}{\partial t} + \vec{v} \cdot \nabla \vec{v} \right) = -\nabla p + \eta \nabla^2 \vec{v}$$

$$\nabla \cdot \vec{v} = 0$$

For steady-state phenomena of interest here, $\frac{\partial \vec{v}}{\partial t} = 0$. In Section II, the terms $\vec{v} \cdot \nabla \vec{v}$ were completely neglected. This linearized the equations, for which solutions had long since been worked out for a sphere. From the sphere analysis it was possible to deduce the Oseen tensor.

It is possible, however, to proceed somewhat differently. It is now convenient to consider the sphere at rest with respect to laboratory coordinates, and allow fluid infinitely far away to be moving with velocity $U\hat{e}_z$ (9). Then, instead of neglecting completely the inertial terms $\vec{v} \cdot \nabla \vec{v}$, these are approximated by $U \frac{\partial}{\partial z} \vec{v}$. Thus, for steady-state flow, the Navier-Stokes equations become

$$\begin{aligned} \rho U \frac{\partial}{\partial z} \vec{v} &= - \nabla p + \eta \nabla^2 \vec{v} \\ \nabla \cdot \vec{v} &= 0 \end{aligned} \qquad (25)$$

These equations are called the linearized Oseen equations. Oseen gave the solutions for spheres (3). A more or less detailed analysis can be found in Lamb's <u>Hydrodynamics</u> (9).

Define $\sigma = \frac{U\rho}{2\eta}$. The approximate solutions for a sphere, given in Lamb, are

$$u_x = \frac{3Ua}{4} \sin\theta \cos\phi \left[\left(\frac{1}{\sigma r^2} + \frac{1}{r} \right) e^{-\sigma r (1 - \cos\theta)} - \frac{1}{\sigma r^2} - \frac{a^2 \cos\theta}{r^3} \right] \quad (26a)$$

$$u_y = \frac{3Ua}{4} \sin\theta \sin\phi \left[\left(\frac{1}{\sigma r^2} + \frac{1}{r} \right) e^{-\sigma r (1 - \cos\theta)} - \frac{1}{\sigma r^2} - \frac{a^2 \cos\theta}{r^3} \right] \quad (26b)$$

$$u_z = \frac{3Ua}{4}\left[\left(\frac{1}{r} + \frac{\cos\theta}{r} + \frac{\cos\theta}{\sigma r^2}\right)e^{-\sigma r(1-\cos\theta)} - \frac{\cos\theta}{\sigma r^2} + \frac{a^2}{3r^3}\left(1 - 3\cos^2\theta\right)\right] \tag{26c}$$

It is readily verified that as $\sigma \to 0$, these solutions coincide with Stokes solutions. Upon neglecting terms in a^2/r^2 and expanding the exponentials to first order in σ, the result is

$$u_x = \frac{3Ua}{4}\sin\theta\cos\phi\left[\frac{\cos\theta}{r} - \frac{\sigma}{2} + \frac{\sigma}{2}\cos^2\theta\right] \tag{27a}$$

$$u_y = \frac{3Ua}{4}\sin\theta\sin\phi\left[\frac{\cos\theta}{r} - \frac{\sigma}{2} + \frac{\sigma}{2}\cos^2\theta\right] \tag{27b}$$

$$u_z = \frac{3Ua}{4}\left[\frac{1}{r} + \frac{\cos^2\theta}{r} - \sigma + \frac{\sigma}{2}\cos\theta + \frac{\sigma}{2}\cos^3\theta\right] \tag{27c}$$

The Oseen tensor constructed from this is

$$T = \frac{\underset{\sim}{\mathbb{1}} + \hat{e}_r\,\hat{e}_r}{8\pi\eta r} - \frac{1}{8\pi\eta}\,\frac{\sigma}{2}\begin{pmatrix} 3 & 0 & 0 \\ 0 & 3 & 0 \\ 0 & 0 & 2 \end{pmatrix} + \frac{1}{8\pi\eta}\,\frac{3\sigma}{2}\cos\theta\,\underset{\sim}{\mathbb{1}}$$

$$= \frac{1}{8\pi\eta}\,\frac{\sigma}{2}\cos\theta\;\hat{e}_r\,\hat{e}_r - \frac{1}{8\pi\eta}\,\frac{\sigma}{2}\left(\hat{e}_z\,\hat{e}_r + \hat{e}_r\,\hat{e}_z\right) \tag{28}$$

It is easily seen that this tensor is to order σ^0 the same as the pure Stokes Oseen tensor.

To determine the motion of a molecule in an infinite medium to this approximation, it is necessary to write an equation analogous to equation 13

$$\vec{F}_i = \zeta \vec{v}_i - \zeta \sum_{i \neq j} \underset{\sim}{T}_{ij} \cdot \vec{F}_j \qquad (13)$$

The quantity $\vec{v}_i$ can be written

$$\vec{v}_i = \vec{v} + i b \vec{\omega} \times e_r \qquad (29)$$

where $\vec{v}$ is the velocity of the center of mass and $\vec{\omega}$ is the angular velocity of rotation. The latter term, which was not present in the pure Stokes flow, considered in the last section, arises because there is an antisymmetric part to $\underset{\sim}{T}_{ij}$ here which gives rise to an internally induced hydrodynamic torque in an isolated molecule for certain orientations. From the symmetry of the situation, it follows that $\vec{\omega}$ can possess only an $\hat{e}_\varphi$ component. According to equation 8

$$\vec{\omega} = \vec{\tau}(\theta) \cdot \underset{\sim}{R}^{-1} \qquad (8)$$

The main interest here, however, lies not in how a single molecule behaves instantaneously but in how a particle behaves on the average. Assuming ergodicity this is equivalent to considering how an ensemble of hydrodynamically noninteracting particles behave . In this case the motions on brownian motion apply, and

$$(\vec{\tau}(\theta) \cdot \underset{\sim}{R}^{-1}) \times \hat{e}_r = \underset{\sim}{D}_R \cdot \nabla \ln f(\theta) \qquad (9)$$

and equation 29 becomes

$$\vec{v}_i = \vec{v} + i b \underset{\sim}{D}_R \cdot \nabla \ln f(\theta) = \vec{v} + i b D^{\theta\theta} \frac{\partial \ln f(\theta)}{\partial \theta} \qquad (30)$$

It is important to realise that a diffusion back flow has been added here to satisfy the requirements of brownian motion. This flow exactly cancels the flow induced by the hydrodynamic torque. Hence on the average a molecule does not rotate in any orientation.

Combining equations 30 and 13 gives

$$\vec{F}_i = \zeta \vec{v} - \zeta \sum_{i \neq j} \underset{\sim}{T}_{ij} \cdot \vec{F}_j + \zeta i b D^{\theta\theta} \frac{\partial \ln f(\theta)}{\partial \theta} \qquad (31)$$

These equations 31, along with the conditions

$$\frac{\mathcal{F} M}{N} \begin{pmatrix} 0 \\ 0 \\ -1 \end{pmatrix} = \sum_{i=-n}^{n} \vec{F}_i \qquad (17)$$

and

$$(\hat{e}_r \times \sum_{i=-n}^{n} i b \vec{F}_i) \times \hat{e}_r = kT \nabla \ln f(\theta) \qquad (32)$$

suffice to determine the $\vec{F}_i$'s and $f(\theta)$. Equation 32 is merely a statement of equation 9'.

It is convenient to separate out the symmetric and antisymmetric parts of equation 31.

$$\vec{F}_i + \vec{F}_{-i} = 2\zeta \vec{v} - \zeta \sum_{i \neq j} [\underset{\sim}{T}_{ij} \cdot \vec{F}_j + \underset{\sim}{T}_{-i-j} \cdot \vec{F}_{-j}] \qquad (33a)$$

$$\vec{F}_i - \vec{F}_{-i} = 2\, i \zeta\, b D^{\theta\theta} \frac{\partial \ln f(\theta)}{\partial \theta}\, e_\theta - \zeta \sum_{i \neq j} [\underset{\sim}{T}_{ij} \cdot \vec{F}_j - \underset{\sim}{T}_{-i-j} \cdot \vec{F}_{-j}] \quad (33b)$$

The Oseen Oseen tensors are here

$$\underset{\sim}{T}_{ij} \quad \frac{\mathbb{1} + \hat{e}_r \hat{e}_r}{8\pi\eta b |i-j|} - \frac{1}{8\pi\eta} \frac{\sigma}{2} \begin{pmatrix} 3 & 0 & 0 \\ 0 & 3 & 0 \\ 0 & 0 & 2 \end{pmatrix} + \frac{1}{8\pi\eta} \frac{3\sigma}{2} \cos\theta\, \mathbb{1}\, \mathrm{sgn}(i-j)$$

$$+ \frac{1}{8\pi\eta} \frac{\sigma}{2} \cos\theta\, \hat{e}_r \hat{e}_r\, \mathrm{sgn}(i-j) - \frac{1}{8\pi\eta} \frac{\sigma}{2} (\hat{e}_z \hat{e}_r + \hat{e}_r \hat{e}_z)\, \mathrm{sgn}(i-j) \quad (34a)$$

$$\underset{\sim}{T}_{-i-j} = \frac{\mathbb{1} + \hat{e}_r \hat{e}_r}{8\pi\eta b |i-j|} - \frac{1}{8\pi\eta} \frac{\sigma}{2} \begin{pmatrix} 3 & 0 & 0 \\ 0 & 3 & 0 \\ 0 & 0 & 2 \end{pmatrix} - \frac{1}{8\pi\eta} \frac{3\sigma}{2} \cos\theta\, \mathbb{1}\, \mathrm{sgn}(i-j) \quad (34b)$$

$$- \frac{1}{8\pi\eta} \frac{\sigma}{2} \cos\theta\, \hat{e}_r \hat{e}_r\, \mathrm{sgn}(i-j) + \frac{1}{8\pi\eta} \frac{\sigma}{2} (\hat{e}_z \hat{e}_r + \hat{e}_r \hat{e}_z)\, \mathrm{sgn}(i-j)$$

where sgn x = +1 if x > 0, and sgn x = -1 if x < 0. The signum function comes in because the actual angles of interest in these tensors are those of the vectors $\vec{i} - \vec{j}$, and $\vec{j} - \vec{i}$, respectively. The angles θ and φ which appear in the formulae are those which the molecule makes with external axes. When $\vec{i} - \vec{j}$ or $\vec{j} - \vec{i}$ change direction, the direction cosines of the angles of interest change sign, but θ and φ remain the same. To take this into account requires the factor sgn(i - j) for terms which change sign on inversion of the molecular long axis.

Combining equations 34a and 34b gives

$$\underset{\sim}{T}_{-i-j} = T_{ij} - \frac{1}{8\pi\eta} 3\sigma \cos\theta\, \underset{\sim}{\mathbb{1}}\, \mathrm{sgn}(i-j) - \frac{1}{8\pi\eta} \sigma \cos\theta\, \hat{e}_r \hat{e}_r\, \mathrm{sgn}(i-j)$$

$$+ \frac{1}{8\pi\eta} \sigma (\hat{e}_z \hat{e}_r + \hat{e}_r \hat{e}_z)\, \mathrm{sgn}(i-j) \quad (35)$$

The distribution function $f(\theta)$ will now be computed. Equation 33b becomes, upon combination with equation 35,

$$\vec{F}_i - \vec{F}_{-i} = i\,2\zeta\, b\, D^{\theta\theta} \frac{\partial \ln f(\theta)}{\partial \theta}\, \hat{e}_\theta - \zeta \sum_{i \neq j} \underset{\sim}{T_{ij}} \cdot (\vec{F}_j - \vec{F}_{-j})$$

$$+ \frac{\sigma\zeta}{8\pi\eta} \left\{ \hat{e}_z \hat{e}_r + \hat{e}_r \hat{e}_z - 3\cos\theta\, \mathbb{1} - \cos\theta\, \hat{e}_r \hat{e}_r \right\} \cdot \sum_{i \neq j} \vec{F}_{-j}\, \mathrm{sgn}(i-j) \quad (36)$$

Define $(\vec{F}_i - \vec{F}_{-i}) \cdot e_\theta \equiv \Theta_i$. Equation 36 then becomes to order σ

$$\Theta_i = i\,2\zeta b D^{\theta\theta} \frac{\partial \ln f(\theta)}{\partial \theta} - \lambda \sum_{i \neq j} \frac{\Theta_j}{|i-j|}$$

$$- \frac{\sigma\zeta}{8\pi\eta} \left\{ \sin\theta\, \hat{e}_r + 3\cos\theta\, \hat{e}_\theta \right\} \cdot \sum_{i \neq j} F_{-j}\, \mathrm{sgn}(i-j) \quad (37)$$

The quantity $\sigma \sum_{i \neq j} \vec{F}_{-j}\, \mathrm{sgn}(i-j)$ can be evaluated properly to order σ by substituting the functions worked out in section IVA, equation 24.

$$\sum \vec{F}_{-j}\, \mathrm{sgn}(i-j) \approx n \int_{-1}^{x} \vec{F}(s)\, ds - n \int_{x}^{1} \vec{F}(s)\, ds = n \int_{-x}^{x} \vec{F}(s)\, ds$$

$$= \frac{\mathcal{F} M}{N} \left\{ \frac{\Omega^{(1)}(x)}{\Omega^{(1)}(1)}\, \underset{\sim}{\mathbb{1}} - \hat{e}_r \hat{e}_r \left(\frac{\Omega^{(1)}(x)}{\Omega^{(1)}(1)} - \frac{\Omega^{(2)}(x)}{\Omega^{(2)}(1)} \right) \right\} \cdot \begin{pmatrix} 0 \\ 0 \\ -1 \end{pmatrix} \quad (38)$$

Allowing Θ_i to vary continuously as $\Theta(x)$ rather than discretely, substituting 38 into 37, and approximating the sum by an integral leads to

$$\Theta(x) \doteq x\, 2n \zeta\, b\, D^{\theta\theta} \frac{\partial \ln f(\theta)}{\partial \theta} - \lambda \int_{-1}^{1} \frac{\Theta(y)}{|x-y|}\, dy$$

$$+ \frac{\mathcal{F} M \sigma\zeta}{8\pi\eta N} \left(\frac{\Omega^{(2)}(x)}{\Omega^{(2)}(1)} - 3\, \frac{\Omega^{(1)}(x)}{\Omega^{(1)}(1)} \right) \sin\theta \cos\theta \quad (39)$$

This equation is of the form

$$\phi(x) = f(x) - \lambda \int_{-1}^{1} \frac{\phi(y)}{|x-y|}\, dy \qquad \frac{1}{|x-y|} \leq n \tag{40}$$

for which a general solution was given by Kirkwood and Riseman (6).

$$\phi(x) = \frac{f_0}{1+2\lambda(\ln 2n-1)} + \sum_{\substack{k=-\infty \\ \neq 0}}^{\infty} \frac{\left(f_k - \frac{\mu_k}{\mu_0} f_0\right) e^{i\pi k x}}{1-2\lambda\, Ci\left(\frac{\pi |k|}{n}\right)} \tag{41}$$

Where

$$f_k = \frac{1}{2}\int_{-1}^{1} f(x)\, e^{-i\pi k x}\, dx \tag{42a}$$

$$\mu_k = \frac{(-1)^{k+1}\, \lambda\, Si\, 2\pi k}{\pi k} \tag{42b}$$

Explicitly

$$f(x) = x\, 2n b\, \zeta\, D^{\theta\theta} \frac{\partial \ln f}{\partial \theta} + \frac{F M \sigma}{8\pi\eta N}\left(\frac{\Omega^{(2)}(x)}{\Omega^{(2)}(1)} - 3\frac{\Omega^{(1)}(x)}{\Omega^{(1)}(1)}\right) \sin\theta\cos\theta \tag{43}$$

Since f(x) is an odd function of x here, f_0 is zero. Thus the solution formally reduces to

$$\phi(x) = \sum_{\substack{k=-\infty \\ \neq 0}}^{\infty} \frac{f_k\, e^{i\pi k x}}{1-2\lambda\, Ci\left(\frac{\pi |k|}{n}\right)} \tag{44}$$

Now

$$\Omega^{(2)}(x) = \frac{2}{1+4\lambda(\ln 2n-1)}\left(x+\frac{4\lambda}{\pi^2}\sum_{k=1}^{\infty}\frac{(-1)^k}{k^2}\,\frac{\mathrm{Si}\,2\pi k\,\sin\pi k x}{1-4\lambda\,\mathrm{Ci}\left(\frac{\pi|k|}{n}\right)}\right) \quad (45a)$$

$$\Omega^{(1)}(x) = \frac{2}{1+2\lambda(\ln 2n-1)}\left(x+\frac{2\lambda}{\pi^2}\sum_{k=1}^{\infty}\frac{(-1)^k}{k^2}\,\frac{\mathrm{Si}\,2\pi k\,\sin\pi k x}{1-2\lambda\,\mathrm{Ci}\left(\frac{\pi|k|}{n}\right)}\right) \quad (45b)$$

so that

$$f_k = \frac{-i(-1)^k}{\pi k}\,2nb\,\zeta\,D^{\theta\theta}\,\frac{\partial\ln f(\theta)}{\partial\theta} +$$

$$+\frac{\mathcal{F}M\sigma\zeta}{8\pi\eta N}\left\{\left(-\frac{i(-1)^k}{\pi k}-\frac{2i\lambda}{\pi^2}\,\frac{(-1)^k}{k^2}\,\frac{\mathrm{Si}\,2\pi k}{1-4\lambda\,\mathrm{Ci}\left(\frac{\pi k}{n}\right)}\right)\right. \quad (46)$$

$$\left.-3\left(-\frac{i(-1)^k}{\pi k}-\frac{i\lambda}{\pi^2}\,\frac{(-1)^k}{k^2}\,\frac{\mathrm{Si}\,2\pi k}{1-2\lambda\,\mathrm{Ci}\left(\frac{\pi k}{n}\right)}\right)\right\}\sin\theta\cos\theta$$

The second terms in the f_k coming from the k' sums in the $\Omega(x)$'s will be neglected, since they are considerably smaller than the first terms. This follows, since for small k, $\mathrm{Ci}(\pi k/n)$ goes like $\ln(\gamma\pi k/n)$ (6), where γ is Euler's constant, and thus is about -2.5 for n about 50; for small k then $(1 - 2\lambda\,\mathrm{Ci}(\pi k/n))$ is larger than one. If k is large, $\mathrm{Ci}(\pi k/n)$ goes like $(\sin\pi k/n)/(\pi k/n)$, but then the extra factor of $1/\pi k$ in the second terms reduces their size significantly. $Si(2\pi k)$ is about 1.5 for any value of k allowed. In addition, $\lambda < 1$. With this simplification, equation 46 becomes

$$f_k = -\frac{i(-1)^k}{\pi k}\left(2nb\zeta D^{\theta\theta}\frac{\partial \ln f(\theta)}{\partial\theta} - \frac{2\mathcal{F}M\sigma\zeta}{8\pi\eta N}\sin\theta\cos\theta\right) \tag{47}$$

and

$$\Theta(x) = 4\left(nb\zeta D^{\theta\theta}\frac{\partial \ln f(\theta)}{\partial\theta} - \frac{\mathcal{F}M\sigma\zeta}{8\pi\eta N}\sin\theta\cos\theta\right)\sum_{k=1}\frac{(-1)^k}{\pi k}\,\frac{\sin\pi k x}{1-2\lambda Ci\,\frac{\pi k}{n}} \tag{48}$$

This gives the $\hat{e}_\theta$ component of $\vec{F}_i - \vec{F}_{-i}$ to order σ. There is also an $\hat{e}_r$ component of $\vec{F}_i - \vec{F}_{-i}$, but it gives no contribution to the torque.

The quantity

$$\sum_{i=-n}^{n} i\,b\,\vec{F}_i = \sum_{i=0}^{n} i\,b\,(\vec{F}_i - \vec{F}_{-i}) \tag{49}$$

must now be computed in order to use equation 32 to determine $f(\theta)$. Only the $\hat{e}_\theta$ part just calculated is of interest here. This gives

$$n^2 b\int_0^1 x\,\Theta(x)\,dx =$$

$$4n^2b\left(nb\zeta D^{\theta\theta}\frac{\partial \ln f(\theta)}{\partial\theta} - \frac{\mathcal{F}M\sigma\zeta}{8\pi\eta N}\sin\theta\cos\theta\right)\sum_{k=1}^{\infty}\frac{1}{\pi^2k^2}\,\frac{1}{1-2\lambda Ci\left(\frac{\pi k}{n}\right)} \tag{50}$$

or, using the function defined by Kirkwood and Riseman (6),

$$\frac{6}{\pi^2}\sum_{k=1}^{\infty}\frac{1}{k^2}\,\frac{1}{1-2\lambda Ci\left(\frac{\pi k}{n}\right)} = F\left(\frac{\lambda}{n}\right) \tag{51}$$

equation 50 becomes

$$n^2 b \int_0^1 x\, \Theta(x)\, dx\, \hat{e}_\theta = \frac{2}{3} F\left(\frac{\lambda}{n}\right) n^2 b \left(n b \zeta D^{\theta\theta} \frac{\partial \ln f(\theta)}{\partial \theta} - \frac{\mathcal{F} M \sigma \zeta}{8 \pi \eta N} \sin\theta \cos\theta \right) \hat{e}_\theta \tag{52}$$

and 32 gives

$$\frac{2}{3} F\left(\frac{\lambda}{n}\right) n^2 b \left(n b \zeta D^{\theta\theta} \frac{\partial \ln f(\theta)}{\partial \theta} - \frac{\mathcal{F} M \sigma \zeta}{8 \pi \eta N} \sin\theta \cos\theta \right) = kT \frac{\partial \ln f(\theta)}{\partial \theta} \tag{53}$$

Solving equation 53 for $\frac{\partial \ln f(\theta)}{\partial \theta}$ gives

$$\frac{\partial \ln f(\theta)}{\partial \theta} = \frac{\mathcal{F} M \sigma \zeta F\left(\frac{\lambda}{n}\right) n^2 b}{12 \pi \eta N \left(\frac{2}{3} F\left(\frac{\lambda}{n}\right) n^3 b^2 \zeta D^{\theta\theta} - kT \right)} \sin\theta \cos\theta \tag{54}$$

Assuming the value of $D^{\theta\theta}$ which was given by Kirkwood and Riseman (6)

$$D^{\theta\theta} = \frac{9}{4} \frac{kT}{b^2 \zeta n^3 F\left(\frac{\lambda}{n}\right)} \tag{55}$$

leads to

$$\frac{\partial \ln f(\theta)}{\partial \theta} = \frac{\mathcal{F} M \sigma \zeta F\left(\frac{\lambda}{n}\right) n^2 b}{6 \pi \eta N kT} \sin\theta \cos\theta \tag{56}$$

which gives upon integration

$$f(\theta) = \mathcal{K} \exp\left(- \frac{\mathcal{F} M \sigma \zeta F\left(\frac{\lambda}{n}\right) n^2 b}{12 \eta N kT} \cos^2\theta \right) \tag{57}$$

where K is a normalizing factor.

Now

$$\sigma = \frac{U\rho}{2\eta} = \frac{\mathcal{F} s \rho}{2\eta} \tag{58}$$

where s is the sedimentation coefficient. Also

$$nb = \frac{\mathcal{L}}{2} \tag{59}$$

where $\mathcal{L}$ is the length of the molecule. Combining equations 58 and 59 with 57 gives

$$f(\theta) = \mathcal{K} \exp\left(-\frac{\mathcal{F}^2 M s \rho n \,\zeta \mathcal{L} F(\frac{\lambda}{n})}{48\pi \eta^2 \, N k T} \cos^2\theta\right) \tag{60}$$

In the centrifuge

$$\mathcal{F} = \omega^2 r \left(1 - \bar{v}\rho\right) \tag{61}$$

where r is the distance from the axis of rotation to the point of interest and 60 becomes

$$f(\theta) = \mathcal{K} \exp\left(-\frac{\omega^4 r^2 (1-\bar{v}\rho)^2 M s \rho n \,\zeta \mathcal{L} F(\frac{\lambda}{n})}{48\pi \eta^2 \, N k T} \cos^2\theta\right) \tag{62}$$

This function peaks at $\theta = \pi/2$, so there is a preferential orientation perpendicular to the field. For TMV, the parameters are (10)

$$\begin{array}{llll} \omega & = 30{,}000 \text{ rpm} & \rho & = 1 \text{ gm/cm}^3 \\ \omega^2 r & = 6 \times 10^7 \text{ cm/sec}^2 & \bar{v} & = 0.74 \text{ cm}^3/\text{gm} \\ M & = 4 \times 10^7 \text{ gm/mole} & \mathcal{L} & = 4 \times 10^{-5} \text{ cm} \\ \eta & = 10^{-2} \text{ gm/cm sec} & kT & = 3 \times 10^{-14} \text{erg} \\ s & = 1.85 \times 10^{-11} \text{ sec} & N & = 6 \times 10^{23} \end{array} \tag{63}$$

Let d be the diameter of the rod. Assuming $n = \mathcal{L}/d$, and $\zeta = 6\pi\eta d/2$, and taking note that $0 < F(\lambda/n) < 1$, the argument of the exponential is less than 2×10^{-6}. Using this number, the distribution function is approximately

$$f(\theta) = \frac{1}{2}\left(1 - 2\times 10^{-6}\left(\cos^2\theta - \frac{1}{3}\right)\right) \tag{64}$$

From this no observable orientation is expected to occur as a result of this mechanism.

To find the velocity of sedimentation, equation 33a must be considered.

$$\vec{F}_i + \vec{F}_{-i} = 2\zeta\vec{v} - \zeta\sum_{i\neq j}\left[\underset{\sim}{T}_{ij}\cdot\vec{F}_j + \underset{\sim}{T}_{-i-j}\cdot\vec{F}_{-j}\right] \tag{33a}$$

This is conveniently rewritten

$$\vec{F}_i + \vec{F}_{-i} = 2\zeta\vec{v} - \zeta\sum_{i\neq j}\underset{\sim}{T}_{ij}\cdot(\vec{F}_j + \vec{F}_{-j}) + \zeta\sum_{i\neq j}\left[\underset{\sim}{T}_{ij} - \underset{\sim}{T}_{-i-j}\right]\cdot\vec{F}_{-j} \tag{65}$$

The last term on the right side has already been evaluated to order σ and found to be odd in i. Since the function $\vec{F}_i + \vec{F}_{-i}$ is necessarily even in i, the odd part of $\zeta \sum_{i \neq j} \underset{\sim}{T}_{ij} \cdot (\vec{F}_j + \vec{F}_{-j})$ must exactly cancel $\zeta \sum_{i \neq j} (\underset{\sim}{T}_{ij} - \underset{\sim}{T}_{-i-j}) \cdot \vec{F}_{-j}$. Hence the interesting part of $\underset{\sim}{T}_{ij}$ is the even part

$$\underset{\sim}{T}_{ij}\,(\text{even}) = \frac{\mathbb{1} + \hat{e}_r \hat{e}_r}{8\pi\eta b|i-j|} - \frac{1}{8\pi\eta} \frac{\sigma}{2} \begin{pmatrix} 3 & 0 & 0 \\ 0 & 3 & 0 \\ 0 & 0 & 2 \end{pmatrix} \tag{66}$$

After removing the cancelling parts, equation 65 becomes

$$\begin{aligned} \vec{F}_i + \vec{F}_{-i} &= 2\zeta \vec{v} - \lambda \sum_{i \neq j} \frac{\mathbb{1} + \hat{e}_r \hat{e}_r}{|i-j|} \cdot (\vec{F}_j + \vec{F}_{-j}) \\ &\quad + \frac{\sigma b \zeta}{8\pi\eta} \frac{1}{2} \begin{pmatrix} 3 & 0 & 0 \\ 0 & 3 & 0 \\ 0 & 0 & 2 \end{pmatrix} \cdot \sum_j (F_j + F_{-j}) \\ &= \zeta \left(2\vec{v} - \frac{\mathcal{F} M \sigma}{4\pi\eta N} \hat{e}_z\right) - \lambda \sum_{i \neq j} \frac{\mathbb{1} + \hat{e}_r \hat{e}_r}{|i-j|} \cdot (\vec{F}_j + \vec{F}_{-j}) \end{aligned} \tag{67}$$

This, however, has precisely the same form as equation 14, with $\vec{v} - \frac{\mathcal{F} M\sigma}{4\pi\eta N} \hat{e}_z$ playing the role of $\vec{V}$. Consequently, from 22

$$\vec{v} - \frac{\mathcal{F} M \sigma}{8\pi\eta N} \hat{e}_z = \frac{\mathcal{F} M}{n\zeta N} \left(\frac{\mathbb{1}}{\Omega^{(1)}(1)} + \hat{e}_r \hat{e}_r \left(\frac{1}{\Omega^{(2)}(1)} - \frac{1}{\Omega^{(1)}(1)} \right) \right) \cdot \begin{pmatrix} 0 \\ 0 \\ -1 \end{pmatrix} \tag{68}$$

or

$$\vec{v} = \frac{\mathcal{F} M}{\eta \zeta N} \left[\left\{ \frac{\mathbb{1}}{\Omega^{(1)}(1)} + \hat{e}_r \hat{e}_r \left(\frac{1}{\Omega^{(2)}(1)} - \frac{1}{\Omega^{(1)}(1)} \right) \right\} \cdot \begin{pmatrix} 0 \\ 0 \\ -1 \end{pmatrix} + \frac{n \sigma \zeta}{8\pi\eta} \hat{e}_z \right] \tag{69}$$

The average sedimentation velocity is

$$\langle \vec{v} \rangle = \int_0^{\pi} f(\theta)\, \vec{v}\, \sin\theta\, d\theta \tag{70}$$

If a very long molecule is assumed such that $\Omega^{(2)}(1) = 2\,\Omega^{(1)}(1)$, the result of this integration is

$$\langle \vec{v} \rangle = -\frac{1}{\Omega^{(1)}(1)} \frac{\mathcal{F} M}{n\zeta N} \left(\frac{4}{3} - \frac{\Omega^{(1)}(1)\, \sigma\, n\, \zeta}{8\pi\eta} - 2 \times 10^{-7} \right) \tag{71}$$

From equation 23 it is clear that the quantity $n\zeta\,\Omega^{(1)}(1)$ is to order σ^{0} just $\frac{3M(1-\bar{v}\rho)}{4N\,S}$) since the average of the tensorial terms in the brackets is 4/3 $\hat{e}_z\hat{e}_z$ and the mobility tensor is directly related to the sedimentation coefficient by the formula

$$S = \langle M_{zz} \rangle_{AV} \frac{M}{N} (1 - \bar{V}\rho) \tag{72}$$

The average velocity then becomes

$$\langle \vec{v} \rangle = -\frac{1}{\Omega^{(1)}(1)} \frac{\mathcal{F} M}{n\zeta N} \left(\frac{4}{3} - 3\times 10^{-7} \right) \tag{73}$$

If there were no effect from the Oseen correction, the average velocity would be

$$\langle \vec{v} \rangle = -\frac{1}{\Omega^{(1)}(1)} \frac{\mathcal{F} M}{n\zeta N} \left(\frac{4}{3} \right) \tag{74}$$

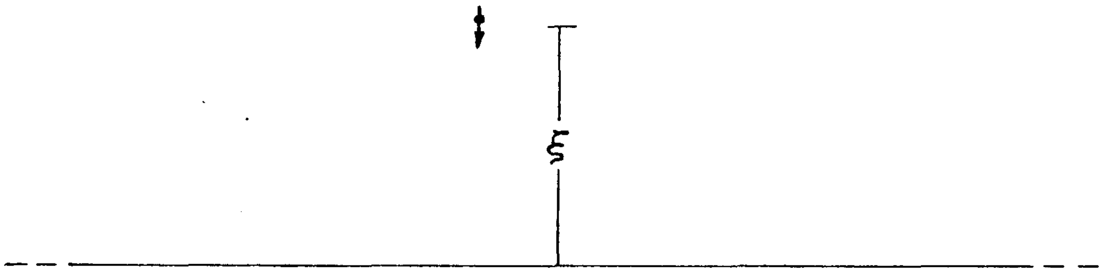
It is then obvious that the order of magnitude of this effect is quite unobservable experimentally, and is of only academic interest, since the sedimentation coefficient decreases by only about 10^{-5} percent.

IVC. Stokes Flow in a Medium Bounded by a Wall

The components of fluid velocity for a point force operating on a fluid in an infinite medium were stated in Section II. These components satisfied the equations

$$\eta \nabla^2 \vec{v} = -\nabla p$$
$$\nabla \cdot \vec{v} = 0$$

If now an infinite plane wall is inserted in the medium, the flow is of course altered since the fluid velocity must vanish at the wall.



This modified flow was computed by Lorentz (11) by noting that if the quantities $V_x^{(1)}$, $V_y^{(1)}$, $V_z^{(1)}$, and $p^{(1)}$ satisfy the hydrodynamic equations, then so do the quantities

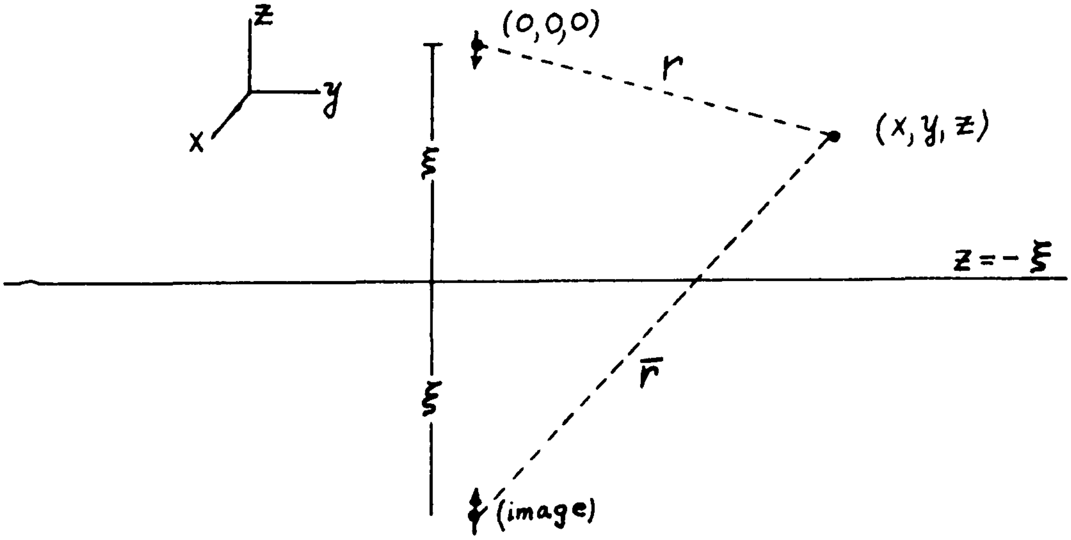
$$v_x^{(2)} = -v_x^{(1)} - 2(z+\xi)\frac{\partial v_z^{(1)}}{\partial x} + (z+\xi)^2 \nabla^2 v_x^{(1)} \tag{75a}$$

$$v_y^{(2)} = -v_y^{(1)} - 2(z+\xi)\frac{\partial v_z^{(1)}}{\partial y} + (z+\xi)^2 \nabla^2 v_y^{(1)} \tag{75b}$$

$$v_z^{(2)} = v_z^{(1)} - 2(z+\xi)\frac{\partial v_z^{(1)}}{\partial z} + (z+\xi)^2 \nabla^2 v_z^{(1)} \tag{75c}$$

$$p^{(2)} = p^{(1)} + 2(z+\xi)\frac{\partial p^{(1)}}{\partial z} - 4\eta\frac{\partial v_z^{(1)}}{\partial z} \tag{75d}$$

These formulae 75 are general for the coordinates x, y, or z, so that in place of v_z, either v_x or v_y could be substituted. The usefulness of the formulae is shown as follows:



Consider the point force above the plane to be situated at the origin of a right-handed cartesian coordinate system. The z direction points upward perpendicular to the plane, which is situated at z = -ξ and extends infinitely in the x and y directions. If the plane were absent, the solutions for velocity components would be just those for pure Stokes flow

$$v_x = \frac{F}{8\pi\eta}\ \frac{xz}{r^3} \tag{2a}$$

$$v_y = \frac{F}{8\pi\eta}\ \frac{yz}{r^3} \tag{2b}$$

$$v_z = \frac{F}{8\pi\eta}\left(\frac{1}{r} + \frac{z^2}{r^3}\right) \tag{2c}$$

Upon addition of the plane, the velocity components must vanish at $z = -\xi$. The component v_z can clearly be made to vanish by adding an image point force on the other side of the plane, in the same manner as electrostatic potentials for point charges in front of infinite conducting planes are constructed. The v_x and v_y components, however, are seen to add rather than cancel, but if the components are transformed according to equations 37, the boundary conditions at $z = -\xi$ will be satisfied upon the addition of the thus transformed point force velocities.

The total flow for this situation is

$$v_x = \frac{F}{8\pi\eta}\left(\frac{xz}{r^3} - \frac{xz}{\bar{r}^3} - \frac{6x\xi(z+\xi)(z+2\xi)}{\bar{r}^5}\right) \tag{76a}$$

$$v_y = \frac{F}{8\pi\eta}\left(\frac{yz}{r^3} - \frac{yz}{\bar{r}^3} - \frac{6y\xi(z+\xi)(z+2\xi)}{\bar{r}^5}\right) \tag{76b}$$

$$v_z = \frac{F}{8\pi\eta}\left(\left[\frac{1}{r} + \frac{z^2}{r^3}\right] - \left[\frac{1}{\bar{r}} + \frac{(z+2\xi)^2}{\bar{r}^3}\right] + 2\xi(z+\xi)\left[\frac{1}{\bar{r}^3} - \frac{3(z+2\xi)^2}{\bar{r}^5}\right]\right) \tag{76c}$$

where $r = \left(x^2 + y^2 + z^2\right)^{\frac{1}{2}}$ $\quad \bar{r} = \left(x^2 + y^2 + (z+2\xi)^2\right)^{\frac{1}{2}}$

When $z = -\xi$, $v_x = v_y = v_z = 0$. The Oseen tensor is

$$T_{xx} = \frac{1}{8\pi\eta}\left\{\frac{1}{r} + \frac{x^2}{r^3} - \frac{1}{\bar{r}} - \frac{x^2}{\bar{r}^3} - 2\xi(z+\xi)\left(\frac{1}{\bar{r}^3} - \frac{3x^2}{\bar{r}^5}\right)\right\}$$

$$T_{xy} = \frac{1}{8\pi\eta}\left\{\frac{xy}{r^3} - \frac{xy}{\bar{r}^3} + \frac{6xy\xi(z+\xi)}{\bar{r}^5}\right\}$$

$$T_{xz} = \frac{1}{8\pi\eta}\left\{\frac{xz}{r^3} - \frac{xz}{\bar{r}^3} - \frac{6x\xi(z+2\xi)(z+\xi)}{\bar{r}^5}\right\}$$

$$T_{yz} = T_{xy}$$

$$T_{yy} = \frac{1}{8\pi\eta}\left\{\frac{1}{r} + \frac{y^2}{r^3} - \frac{1}{\bar{r}} - \frac{y^2}{\bar{r}^3} - 2\xi(z+\xi)\left(\frac{1}{\bar{r}^3} - \frac{3y^2}{\bar{r}^5}\right)\right\} \tag{77}$$

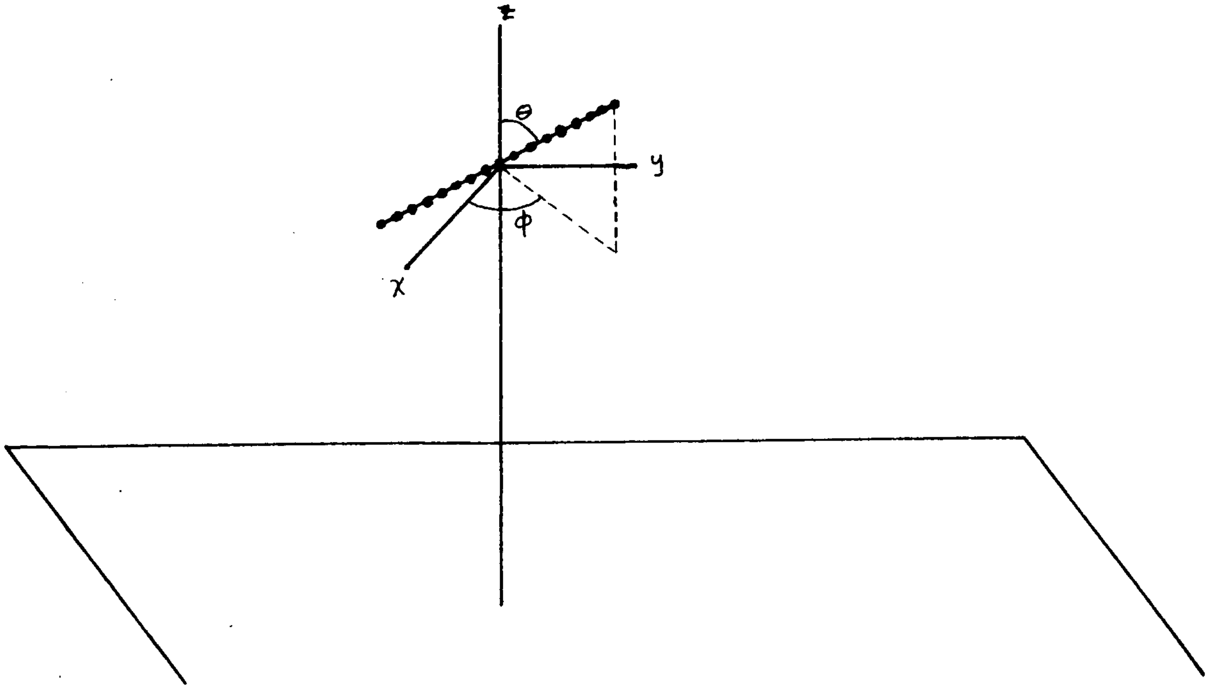
$$T_{yz} = \frac{1}{8\pi\eta}\left\{\frac{yz}{r^3} - \frac{yz}{\bar{r}^3} - \frac{6y\xi(z+2\xi)(z+\xi)}{\bar{r}^5}\right\}$$

$$T_{zx} = \frac{1}{8\pi\eta}\left\{\frac{xz}{r^3} - \frac{xz}{\bar{r}^3} + \frac{6x\xi(z+2\xi)(z+\xi)}{\bar{r}^5}\right\}$$

$$T_{zy} = \frac{1}{8\pi\eta}\left\{\frac{yz}{r^3} - \frac{yz}{\bar{r}^3} + \frac{6y\xi(z+2\xi)(z+\xi)}{\bar{r}^5}\right\}$$

$$T_{zz} = \frac{1}{8\pi\eta}\left\{\frac{1}{r} + \frac{z^2}{r^3} - \frac{1}{\bar{r}} - \frac{(z+2\xi)^2}{\bar{r}^3} + 2\xi(z+\xi)\left(\frac{1}{\bar{r}^3} - \frac{3(z+2\xi)^2}{\bar{r}^5}\right)\right\}$$

Now consider a long rod in front of the plane.



To compute the distribution function in this case, equation 31 is again employed

$$\vec{F}_i = \zeta\vec{v} - \zeta\sum \underset{\sim}{T}_{ij}\cdot\vec{F}_i + \zeta i b D^{\theta\theta}\frac{\partial \ln f(\theta)}{\partial\theta}\hat{e}_\theta \qquad (31)$$

which leads to equation 33b

$$\vec{F}_i - \vec{F}_{-i} = 2ibD^{\theta\theta}\frac{\partial \ln f(\theta)}{\partial\theta}\hat{e}_\theta - \zeta\sum\left[\underset{\sim}{T}_{ij}\cdot\vec{F}_j - \underset{\sim}{T}_{-i-j}\cdot\vec{F}_{-j}\right] \qquad (33b)$$

It is convenient to expand the Oseen tensor to first order in $b/\xi = \alpha$. Each force element as shown in the figure is treated as a separate entity.

Immediate relationships are

$$\begin{aligned}
x_{ij} &= (i-j)\, b \sin\theta\cos\phi \\
y_{ij} &= (i-j)\, b \sin\theta\sin\phi \\
z_{ij} &= (i-j)\, b \cos\theta \qquad\qquad (78) \\
\xi_j &= \xi(1+\alpha j\cos\theta) \\
\bar{r}_{ij} &= 2\xi\left[1+\alpha(i+j)\cos\theta+\frac{\alpha^2}{4}(i^2+j^2+2ij\cos 2\theta)\right]^{1/2} \approx 2\xi\left(1+\frac{\alpha}{2}(i+j)\cos\theta\right)
\end{aligned}$$

With these relationships, it is possible to develop the Oseen tensor to first order in α.

$$
\begin{aligned}
T_{xx}^{ij} &= \frac{1}{8\pi\eta}\left(\frac{1}{r} + \frac{x^2}{r^3} - \frac{3}{4\xi} + \frac{3\alpha}{8\xi}(i+j)\cos\theta\right) \\
T_{xy}^{ij} &= \frac{1}{8\pi\eta}\left(\frac{xy}{r^3}\right) = T_{yx}^{ij} \\
T_{xz}^{ij} &= \frac{1}{8\pi\eta}\left(\frac{xz}{r^3} - \frac{3\alpha}{8\xi}(i-j)\sin\theta\cos\phi\right) \\
T_{yy}^{ij} &= \frac{1}{8\pi\eta}\left(\frac{1}{r} + \frac{y^2}{r^3} - \frac{3}{4\xi} + \frac{3\alpha}{8\xi}(i+j)\cos\theta\right) \\
T_{yz}^{ij} &= \frac{1}{8\pi\eta}\left(\frac{yz}{r^3} - \frac{3\alpha}{8\xi}(i-j)\sin\theta\sin\phi\right) \\
T_{zx}^{ij} &= \frac{1}{8\pi\eta}\left(\frac{zx}{r^3} + \frac{3\alpha}{8\xi}(i-j)\sin\theta\cos\phi\right) \\
T_{zy}^{ij} &= \frac{1}{8\pi\eta}\left(\frac{zy}{r^3} + \frac{3\alpha}{8\xi}(i-j)\sin\theta\sin\phi\right) \\
T_{zz}^{ij} &= \frac{1}{8\pi\eta}\left(\frac{1}{r} + \frac{z^2}{r^3} - \frac{3}{2\xi} + \frac{3\alpha}{4\xi}(i+j)\cos\theta\right)
\end{aligned}
\qquad (79)
$$

These lead to the relations

$$
\begin{aligned}
T_{xx}^{-i-j} &= T_{xx}^{ij} - \frac{1}{8\pi\eta}\,\frac{3\alpha}{4\xi}\,(i+j)\cos\theta \\
T_{xy}^{-i-j} &= T_{xy}^{ij} \\
T_{xz}^{-i-j} &= T_{xz}^{ij} + \frac{1}{8\pi\eta}\,\frac{3\alpha}{4\xi}\,(i-j)\sin\theta\cos\phi \\
T_{yy}^{-i-j} &= T_{yy}^{ij} - \frac{1}{8\pi\eta}\,\frac{3\alpha}{4\xi}\,(i+j)\cos\theta \\
T_{yz}^{-i-j} &= T_{yz}^{ij} + \frac{1}{8\pi\eta}\,\frac{3\alpha}{4\xi}\,(i-j)\sin\theta\sin\phi \\
T_{zx}^{-i-j} &= T_{zx}^{ij} - \frac{1}{8\pi\eta}\,\frac{3\alpha}{4\xi}\,(i-j)\sin\theta\cos\phi \\
T_{zy}^{-i-j} &= T_{zy}^{ij} - \frac{1}{8\pi\eta}\,\frac{3\alpha}{4\xi}\,(i-j)\sin\theta\sin\phi \\
T_{zz}^{-i-j} &= T_{zz}^{ij} - \frac{1}{8\pi\eta}\,\frac{3\alpha}{2\xi}\,(i+j)\cos\theta
\end{aligned}
\tag{80}
$$

or

$$
\underset{\sim}{T}^{-i-j} = \underset{\sim}{T}^{ij} - \frac{3\alpha}{32\pi\eta\xi}\left\{\begin{matrix} (i+j)\cos\theta & 0 & -(i-j)\sin\theta\cos\phi \\ 0 & (i+j)\cos\theta & -(i-j)\sin\theta\sin\phi \\ (i-j)\sin\theta\cos\phi & (i-j)\sin\theta\sin\phi & 2(i+j)\cos\theta \end{matrix}\right\} \tag{81}
$$

Equation 33b now becomes

$$
\begin{aligned}
\vec{F}_i - \vec{F}_{-i} = {} & i\,2bD^{\theta\theta}\,\frac{\partial \ln f(\theta)}{\partial\theta}\,\hat{e}_\theta - \zeta\sum_{i\neq j}\underset{\sim}{T}_{ij}\cdot(\vec{F}_j - \vec{F}_{-j}) \\
& + \frac{3\alpha\zeta}{32\pi\eta\xi}\sum_j\left\{\begin{matrix} (i+j)\cos\theta & 0 & -(i-j)\sin\theta\cos\phi \\ 0 & (i+j)\cos\theta & -(i-j)\sin\theta\sin\phi \\ (i-j)\sin\theta\cos\phi & (i-j)\sin\theta\sin\phi & 2(i+j)\cos\theta \end{matrix}\right\}
\end{aligned}
\tag{82}
$$

This equation is treated in the same way as the expressions in section IVB.

$$\left(\vec{F}_i - \vec{F}_{-i}\right) \cdot \hat{e}_\theta = \Theta(x)$$

$$\underset{\sim}{T}_{ij} = \frac{1}{8\pi\eta nb} \frac{1}{|x-y|} \left(\underset{\sim}{\mathbb{1}} + \hat{e}_r \hat{e}_r\right) \qquad \begin{array}{l} x = i/n \\ y = j/n \end{array}$$

$\vec{F}_{-j}$ are functions worked out in IVA, and given in equation 24. Thus

$$\Theta(x) = x\left(2nb\zeta D^{\theta\theta} \frac{\partial \ln f(\theta)}{\partial\theta} - \frac{9\alpha \mathcal{F} M \zeta}{32\pi\eta\xi N} \sin\theta\cos\theta\right)$$

$$-\lambda \int_{-1}^{1} \frac{\Theta(y)}{|x-y|}\, dy \qquad \frac{1}{|x-y|} \geq n \tag{83}$$

The solution to this equation has essentially been worked in section IVB. It is only necessary to adapt equation 48 to the present purposes. The proper result is clearly

$$\Theta(x) = 4\left(n\zeta b D^{\theta\theta} \frac{\partial \ln f(\theta)}{\partial\theta} - \frac{9\alpha\mathcal{F}M\zeta}{64\pi\eta\xi N} \sin\theta\cos\theta\right) \sum_{k=1}^{\infty} \frac{(-1)^k \sin\pi k x}{\pi k\left(1 - 2\lambda \operatorname{Ci}\left(\frac{\pi k}{n}\right)\right)} \tag{84}$$

Procedures exactly analogous to those previous give

$$\frac{2}{3} F\left(\tfrac{\lambda}{n}\right) n^2 b \left(nb\zeta D^{\theta\theta} \frac{\partial \ln f(\theta)}{\partial\theta} - \frac{9\alpha\mathcal{F}M\zeta}{64\pi\eta N\xi} \sin\theta\cos\theta\right) = kT \frac{\partial \ln f(\theta)}{\partial\theta} \tag{85}$$

and

$$f(\theta) = \mathcal{K} \exp\left(-\frac{3\mathcal{F}M\zeta F\left(\frac{\lambda}{n}\right)\mathcal{L}^2}{64\pi\eta N kT \xi^2} \cos^2\theta\right)$$

$$f(\theta) = \mathcal{K} \exp\left(- \frac{3 \mathcal{F} M \zeta F(\frac{\lambda}{n}) \mathcal{L}^2}{64 \pi \eta N k T \xi^2} \cos^2\theta \right) \tag{86}$$

Using TMV data, assuming $\xi = 1$ cm and $d = 7.5 \times 10^{-7}$ cm, this exponential argument is less than 3×10^{-7}. The distribution function is approximately

$$f(\theta) = \frac{1}{2} \left(1 - 3 \times 10^{-7} \left(\cos^2\theta - \frac{1}{3} \right) \right) \tag{87}$$

No observable orientation is expected.

To determine the sedimentation velocity, the analog of equation 33a gives, after cancelling odd parts and keeping terms to order $1/\xi$

$$\vec{F}_i + \vec{F}_{-i} = 2\zeta \vec{v} - \lambda \sum_{i \neq j} \frac{(\mathbb{1} + \hat{e}_r \hat{e}_r) \cdot (\vec{F}_j + \vec{F}_{-j})}{|i-j|} - \frac{3 \zeta \mathcal{F} M}{4 \pi \eta N \xi} \hat{e}_z \tag{88}$$

Using the functions of equation 24 to evaluate the last term on the right, the result is

$$\vec{v} = \frac{\mathcal{F} M}{n N \zeta} \left[\left\{ \frac{\mathbb{1}}{\Omega^{(1)}(1)} + \hat{e}_r \hat{e}_r \left(\frac{1}{\Omega^{(1)}(1)} - \frac{1}{\Omega^{(2)}(1)} \right) \right\} \cdot \begin{pmatrix} 0 \\ 0 \\ -1 \end{pmatrix} + \frac{3 n \zeta}{32 \pi \eta \xi} \hat{e}_z \right] \tag{89}$$

Again assuming a very long molecule such that $\Omega^{(2)}(1) = 2\Omega^{(1)}(1)$, the average sedimentation velocity is

$$\begin{aligned} \langle \vec{v} \rangle = \int_0^{\pi} f(\theta) \vec{v} \sin\theta \, d\theta &\approx - \frac{\mathcal{F} M}{n N \zeta \Omega^{(1)}(1)} \left(\frac{4}{3} - \frac{3 n \zeta \Omega^{(1)}(1)}{32 \pi \eta \xi} - 3 \times 10^{-8} \right) \\ &\approx - \frac{\mathcal{F} M}{n N \zeta \Omega^{(1)}(1)} \left(\frac{4}{3} - 10^{-5} \right) \end{aligned} \tag{90}$$

This change in sedimentation velocity is also unobservable experimentally, and establishes that wall effects are negligible for these molecules if they are far enough from a wall that their length relative to the distance to the wall is very small. It may be of some academic interest, however, to note that there is a very slight tendency toward orientation parallel to the wall toward which the particles are sedimenting, and the net effect on the average sedimentation velocity is to decrease it by about 10^{-3} percent.

IVD. Particle in a Radial Field

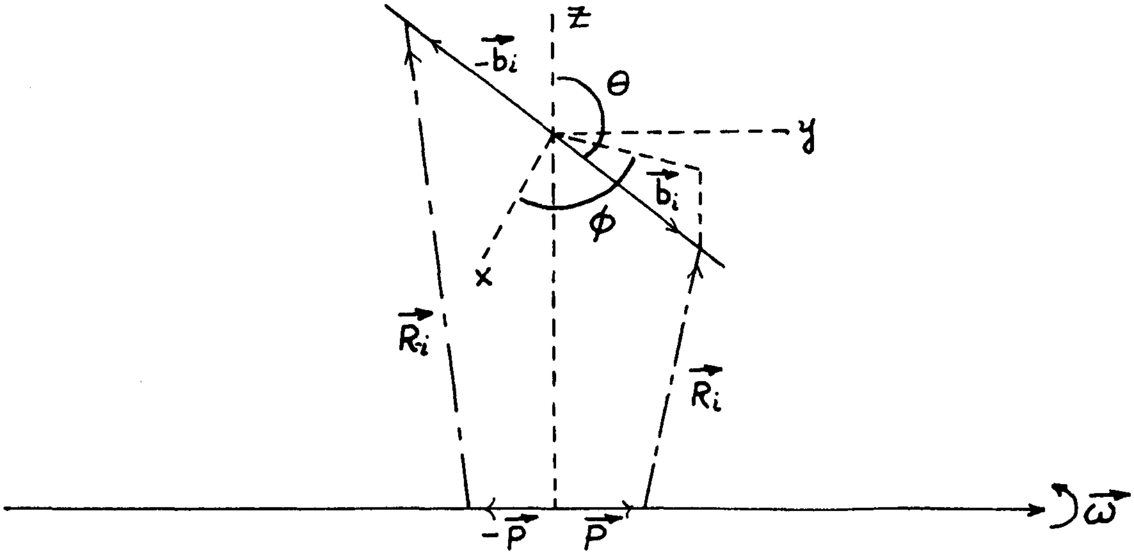
A radial field is produced in a rotating system such as the ultracentrifuge. The more distant a point is from the axis of rotation, the greater the centrifugal force. In the case of a rigid rod-like particle, it may be suspected that a torque may be induced by the external field, since some parts of the particle for certain orientations are farther from the axis of rotation than others. It can be shown that there may indeed exist a torque due to the centrifugal field for particles which do not lie in a plane perpendicular to the axis of rotation.

The external torque due to the centrifugal field will be computed as a function of particle orientation with respect to the axis of rotation. Once this is obtained, equation 9'

$$\vec{\tau}(\theta,\phi) \times \hat{e}_r = kT\,\nabla_\Omega \ln f(\theta,\phi) \qquad (9')$$

will be used to determine the distribution function.

Define an axis of rotation in the $\hat{e}_y$ direction, and place a rod-like molecule some distance away. Define the z axis to pass through the middle of the molecule.



The centrifugal force acting on element i is

$$\omega^2 \vec{R}_i \, m(1-\bar{v}\rho)$$

where m = mass of each individual element. The force on -i is

$$\omega^2 \vec{R}_{-i} \, m(1-\bar{v}\rho)$$

The torque on the particle is clearly

$$\vec{\tau} = mb\omega^2 \sum_{i=-n}^{n} i \, \hat{e}_r \times \vec{R}_i \, (1-\bar{v}\rho) \tag{91}$$

This can be simplified somewhat. From the figure it is clear that

$$2bi\,\hat{e}_r + \vec{R}_{-i} - 2\vec{p} - \vec{R}_i = 0 \tag{92}$$

and

$$\vec{p} = bi\,(\hat{e}_r \cdot \hat{e}_y)\,\hat{e}_y = b_i \sin\theta \sin\phi \; \hat{e}_y \tag{93}$$

Thus

$$\vec{R}_i - \vec{R}_{-i} = 2bi\,\hat{e}_r - 2\vec{\rho} = 2bi\left(\hat{e}_r - \sin\theta\,\sin\phi\,\hat{e}_y\right) \qquad (94)$$

The torque can now be written

$$\vec{\tau}(\theta\,\phi) = \omega^2 bm \sum_{i=0}^{n} i\,\hat{e}_r \times (\vec{R}_i - \vec{R}_{-i})\,(1 - \bar{V}\rho) = -I\omega^2 \sin\theta\sin\phi\,(\hat{e}_r \times \hat{e}_y)(1 - \bar{V}\rho)$$

where $I = 2\,m\,b\sum_{i=0}^{n} i^2(1 - \bar{v}\rho)$ = moment of inertia of the rod corrected for buoyancy.

Now $\qquad \hat{e}_y = \sin\theta\,\sin\phi\,\hat{e}_r + \cos\theta\sin\phi\,\hat{e}_\theta + \cos\phi\,\hat{e}_\phi$

and $\qquad \hat{e}_r \times \hat{e}_\theta = \hat{e}_\phi \qquad \hat{e}_r \times \hat{e}_\phi = -\hat{e}_\theta \qquad \hat{e}_r \times \hat{e}_r = 0$

so

$$\vec{\tau}(\theta,\phi) = -I\omega^2 \sin\theta\,\sin\phi\left(\cos\theta\sin\phi\,\hat{e}_\phi - \cos\phi\,\hat{e}_\theta\right) \qquad (95)$$

and $\qquad \vec{\tau}(\theta,\phi) \times \hat{e}_r = -I\omega^2 \sin\theta\sin\phi\left(\cos\theta\sin\phi\,\hat{e}_\theta + \cos\phi\,\hat{e}_\phi\right)$

Then equation 8 leads to

$$\frac{\partial \ln f(\theta,\phi)}{\partial\theta}\,\hat{e}_\theta + \frac{\partial \ln f(\theta,\phi)}{\partial\phi}\,\hat{e}_\phi = -I\omega^2\left(\sin\theta\cos\theta\sin^2\phi\,\hat{e}_\theta + \sin\theta\sin\phi\cos\phi\,\hat{e}_\phi\right)$$

The θ part gives

$$\ln f(\theta) = \frac{1}{2}\,\frac{I\omega^2}{kT}\,(\cos^2\theta\,\sin^2\varphi + A(\varphi)) + \ln K$$

The φ part gives

$$\ln f(\varphi) = \frac{1}{2}\,\frac{I\omega^2}{kT}\,(\sin^2\theta\,\cos^2\varphi + B(\theta)) + \ln K$$

Equating these leads immediately to

$A(\varphi) = \cos^2\varphi \qquad B(\theta) = \cos^2\theta$

Therefore

$$f(\theta,\phi) = \mathcal{K} \exp\left[-\frac{I\omega^2}{2KT}\sin^2\theta\sin^2\phi\right] \tag{96}$$

Hence there is a slight tendency to align parallel to the field. To first order in $\frac{I\omega^2}{kT}$, this becomes

$$f(\theta,\phi) = \mathcal{K}\left(1 - \frac{I\omega^2}{2KT}\sin^2\theta\sin^2\phi\right)$$

If $\sin^2\varphi$ is replaced by its average value ½, the result is

$$f(\theta) = \mathcal{K}\left(1 - \frac{I\omega^2}{4KT}\sin^2\theta\right)$$

The normalization condition gives to order $I\omega^2/kT$

$$f(\theta) = \frac{1}{2}\left\{1 + \frac{I\omega^2}{12KT}\left(3\cos^2\theta - 1\right)\right\} \tag{97}$$

Saito and Hasegawa began work on this problem after they found out that the present investigation had already gotten under way. They report a similar distribution function for the same conditions (12).

$$f(\theta) = \frac{1}{2}\left\{1 + \frac{I\omega^2}{6KT}\left(3\cos^2\theta - 1\right)\right\}$$

They have given no details of calculation. The origin of the discrepancy of the factor ½ is unknown at present.

It might be mentioned that the term in $\frac{I\omega^2}{kT}$ in equation 96 is exactly half of what is obtained if one assumes the field to be cartesian rather than radial.

The moment of inertia corrected for buoyancy for a rigid rod is $\frac{mL^2(1 - \bar{v}\rho)}{12}$. Hence for TMV it is 1.6×10^{-27}, and the correction to the distribution function is

$$f(\theta) = \frac{1}{2}\left(1 + 4.5 \times 10^{-8}(3\cos^2\theta - 1)\right) \tag{98}$$

This is too small to see experimentally.

V . Concentration Dependent Phenomena

The motion of a particle through a viscous medium disturbs the fluid at points removed from it. In certain cases it is possible to calculate approximately the magnitude of this disturbance, as was done, for example, by Stokes for the case of spheres. This will lead to a concentration dependence as follows:

Consider a particle at the origin of a coordinate system. Allow an external force $\vec{F}$ to act on the particle such that it moves with respect to the medium with a velocity

$$\vec{V} = \underset{\sim}{M} \cdot \vec{F}$$

where $\underset{\sim}{M}$ is the mobility tensor, or the reciprocal of the friction tensor. This quantity has tensorial character because the velocity of motion in the case of asymmetric particles is not necessarily in the direction of applied external force (See section IVA).

If the medium itself is moving with respect to an external observer, the motion of the particles will appear to change, or alternatively the mobility tensor will appear to be different. The medium, however, is indeed in motion if there are other particles present which are perturbing the fluid velocity. The degree of this perturbation will depend on how many particles are acting on the fluid and on their positions, or, in short, on the concentration of particles.

In the case of asymmetric particles, the orientation of a particle has a great deal to do with the velocity with which it moves through the medium. Very long rods, oriented parallel to the applied field, move twice as fast as those aligned perpendicular to the field, as was shown in Section IVA. Therefore, if there exists a preferential alignment of particles, the net average sedimentation coefficient will change over that for a system of randomly oriented particles. A nonuniform alignment with respect to the field will occur if the perturbed velocity at the site of a long rod includes a shear, for then a hydrodynamic torque will be exerted on the particle, the magnitude of which will be a function of the orientation of the rod. As explained in Section III, brownian motion will counterbalance this in such a way as to induce a nonuniform angular distribution function. The degree of shear, if it exists, will be a function of the concentration of particles and the magnitude of the external force acting on them; in turn, the angular distribution function will depend on the same parameters.

In this connection it is of interest to investigate the effect, at a single point, of the velocity perturbations due to a distribution of spheres in a medium, all of the same size and moving in the z direction with equal speeds. This perturbation is given by

$$\vec{v}(\vec{r}) = \sum_i \underset{\sim}{T}(\vec{r}, \vec{r}_i{}') \cdot \vec{F}_i(\vec{r}_i{}')$$

where $\underset{\sim}{T}(\vec{r}, \vec{r}_i{}')$ is an appropriate Oseen tensor, and the sum is over all spheres, or point forces. In the case of an infinite medium, representing the spheres by point forces gives

$$\vec{v}(\vec{r}) = \frac{F}{8\pi\eta} \sum_i \frac{\mathbb{1} + \hat{e}_{\vec{r}-\vec{r}_i{}'}\,\hat{e}_{\vec{r}-\vec{r}_i{}'}}{|\vec{r}-\vec{r}_i{}'|} \cdot \hat{e}_z \tag{99}$$

If the distribution of spheres is uniform throughout all space, and the sum replaced by an integral

$$\vec{v}(\vec{r}) = \frac{F}{8\pi\eta} \int_{Vol} \frac{\mathbb{1} + \hat{e}_{\vec{r}-\vec{r}'}\,\hat{e}_{\vec{r}-\vec{r}'}}{|\vec{r}-\vec{r}'|} \cdot \hat{e}_z \quad d\,(Vol) \Rightarrow \infty\,\hat{e}_z \tag{100}$$

This infinite result is not obtained physically. The model above which gives the infinite result must therefore be faulty. The mathematical origin of the infinity is the assumed additivity of effects from different force sources, and since these are all positive in the z direction and die off like 1/r, the integral diverges like r^2.

The reason this divergence does not occur physically is the inevitable presence of a "return flow" or "back flow." These terminologies mean that on the fluid velocity given by infinite medium Stokes solutions must be superposed additional velocities of opposite signs in order that the total fluid velocity vanishes on the likewise inevitable walls of the containing vessel, or on some other convenient surface. Of course, the walls of the vessel are not the only inevitable objects; there are also many other spheres surrounding any given one, and it is not unreasonable to expect these surrounding spheres to shield relatively distant regions of the medium from the effects of a given sphere, due to their finite rigid volume. Thus, sufficiently far away from any given sphere one would anticipate the medium to be completely and totally unaware of the actions of this given sphere. The velocities induced by it are "reflected" off its neighbors, and this gives rise to a "back flow." This latter effect may be approximated by inserting a hypothetical sphere of some convenient radius L around any sphere of interest, with the fluid velocity arising from the perturbing influence of the sphere made to vanish on the concentric hypothetical sphere and assigned the value zero outside the hypothetical sphere. It will be shown that either mechanism for back flow gives essentially equivalent results.

Therefore, there are two effects which tend to counterbalance each other in the perturbed fluid velocities. One is the tendency of a sphere to drag the fluid along with it, pushing forward the spheres ahead and pulling along those spheres behind. This effect is the infinite medium Stokes part and leads to the divergence discussed. The other effect is the reflected flow, either from the wall or neighboring particles, which cancels the divergence. Experimentally, there is a slight excess of back flow, which fact is attested by a decrease of sedimentation coefficients for spheres with concentration. The results of several studies done on glass beads hover about

$$V = \frac{F}{8\pi\eta} (1 - 5\varphi) \qquad (101)$$

where φ is the volume fraction of spheres (14).

For spheres sedimenting in a vessel, Burgers has made a theoretical study of the expected sedimentation velocity. The analysis is rather lengthy, so only the results will be given here. The predicted velocity is

$$V = \frac{F}{8\pi\eta} (1 - \frac{55}{8} \varphi) \qquad (102)$$

An amount $15/8\ \varphi$ of the correction factor comes from higher interactions between spheres, such as induced rotations and double velocity reflections. Omitting this leads to

$$V = \frac{F}{8\pi\eta} (1 - 5\varphi) \qquad (103)$$

This term 5φ in addition contains consideration of the finite size of the spheres and the average perturbation velocity on the surface of a test sphere in its absence, rather than the perturbation at the center. If, using Burgers approach, the average perturbation at the center of a test sphere due to the action of all other spheres, approximated by point forces, is calculated assuming a uniform distribution of the point forces about the test sphere but taking account of the excluded volume, the result is

$$V = \frac{F}{6\pi \eta a} \quad (1 - 6\varphi) \tag{104}$$

This value differs from experiment by only about 20% for small φ.

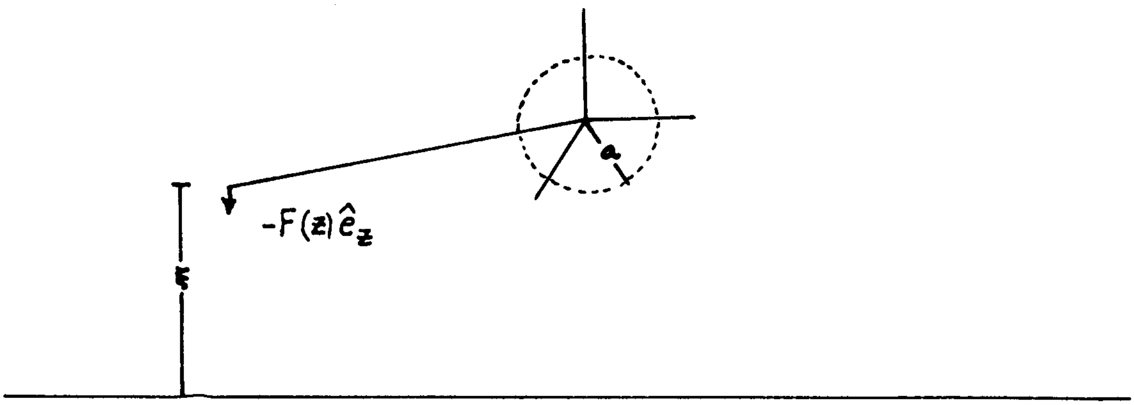
The primary interest in this work is in rigid rods, not spheres. The general scheme for calculation is to treat all particles having hydrodynamic interactions as point forces, but to take account of excluded volumes. The space and orientation averaging processes for rods are considerably more difficult than for spheres, and the approximations used to do this do not warrant any more accurate treatment.

VA. Spheres and the Wall

It will now be demonstrated how the value

$$V = \frac{F}{6\pi \eta a} \quad (1 - 6\varphi) \tag{104}$$

arises for a sphere moving perpendicularly to a plane wall of infinite extent. Equations 77 give the Oseen tensor for this case.



Consider a point force $-F(z)\,\hat{e}_z$ acting at r as shown in the diagram. For generality it is considered to be a function of z. The velocity at (0, 0, 0) due to this point force is

$$\vec{V}(0,0,0) = -T(0,r)\cdot F(z)\,\hat{e}_z \tag{105}$$

The location of the force is now averaged over all possible positions external to the volume excluded by the test sphere at the origin, and the average velocity perturbation at (0, 0, 0) thus computed. The distribution of forces is assumed uniform, and ranges in geometrical extent from

$$\rho = \sqrt{x^2+y^2} = 2a \longrightarrow \infty \qquad z = -\xi \rightarrow h$$

where a is the radius of a sphere, and h is arbitrary.

Clearly, the $\hat{e}_x$ and $\hat{e}_y$ components vanish on the average. The average velocity at (0, 0, 0) is then

$$\begin{aligned}\vec{v} &= -c\int_0^{2\pi} d\vartheta \int_{2a}^{\infty} \rho\, d\rho \int_{-\xi}^{h} dz \;\; T_{zz} \;\; F_z\, \hat{e}_z \\ &= -c\int_0^{2\pi} d\vartheta \int_0^{\infty} \rho\, d\rho \int_{-\xi}^{h} dz\; T_{zz}\;\; F(z)\,\hat{e}_z + c\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta\, d\theta \int_0^{2a} r^2 dr\; T_{zz}\, F(z)\,\hat{e}_z\end{aligned} \tag{106}$$

From equation 77

$$T_{zz} = \frac{1}{8\pi\eta}\left\{\frac{1}{r} + \frac{z^2}{r^3} - \frac{1}{\bar{r}} - \frac{(z+2\xi)^2}{\bar{r}^3} - 2\xi(z+\xi)\left(\frac{1}{\bar{r}^3} - \frac{3(z+2\xi)^2}{\bar{r}^5}\right)\right\}$$

$$= -\frac{1}{8\pi\eta}\,\frac{1}{\rho}\,\frac{\partial}{\partial\rho}\,\rho\frac{\partial}{\partial\rho}\left(-r+\bar{r}-\frac{2\xi(z+\xi)}{\bar{r}}\right) \tag{107}$$

It is convenient to convert the first integral in equation 106 into a surface integral.

$$c\int_0^{2\pi} d\vartheta \int_0^{\infty} \rho d\rho \int_{-\xi}^{h} dz\, T_{zz} F(z) =$$

$$\frac{c}{8\pi\eta}\int_0^{2\pi} d\vartheta \int_{-\xi}^{h} dz\, F(z)\left[\rho\frac{\partial}{\partial\rho}\left(-r+\bar{r}-\frac{2\xi(z+\xi)}{\bar{r}}\right)\right]_{\rho=\infty} = 0 \tag{108}$$

The second integral in equation 106 is, neglecting terms of order a/ξ.

$$\vec{v}(0) =$$

$$c\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta \int_0^{2a} r^2 dr\, T_{zz}\,\frac{\omega^2 M(1-\bar{v}\rho)}{N}\,(z_0 + r\cos\theta) \tag{109}$$

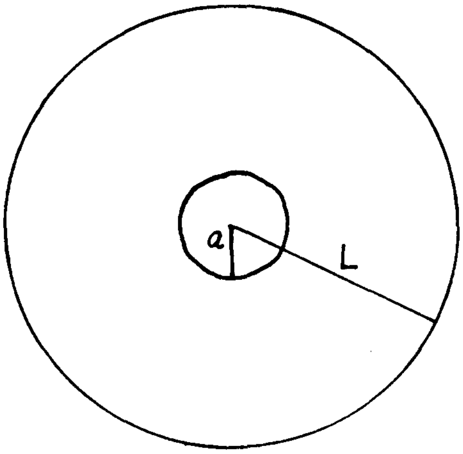
$$= \frac{4a^2 cF}{3\eta}$$

where $F = \frac{\omega^2 M}{N}(z_0 + r\cos\theta)(1-\bar{v}\rho)$ is the force due to a centrifugal field on the perturbing particle. Note that the radial field has been approximated by a cartesian one, but this should sufficiently approximate a centrifuge cell so as to lead to correct results. $\vec{v}(0)$ is a net fluid velocity opposite in direction to the motion of the test particle, and will thus tend to slow it down. The net velocity is then

$$\vec{V} = -\frac{F\hat{e}_z}{6\pi\eta a} + \frac{4a^2cF}{3\eta} = -\frac{F}{6\pi\eta a}(1-6\phi) \tag{110}$$

VC. Spheres and the Concentric Hypothetical Sphere

Cunningham (15) worked out the solutions to this problem many years ago, using the boundary conditions $0 = v_x = v_y = v_z$ at $r = L$, $v_x = v_y = 0$ at $r = a$, and $v_z = -v$ at $r = a$.



Define

$$\epsilon = a/L \tag{111a}$$

$$\beta = \frac{a^2(1-\epsilon^3)}{3(1-\epsilon^5)} \tag{111b}$$

$$\gamma = \frac{5(1-\epsilon^2)}{3L^3(1-\epsilon^5)} \tag{111c}$$

$$\delta = -\frac{9-5\epsilon^2-4\epsilon^5}{3L(1-\epsilon^5)} \tag{111d}$$

Then, if an external force acts on the small inner sphere in the minus z direction, the hydrodynamic velocities are (15)

$$v_x = -\sin\theta\cos\theta\cos\phi\left(-\frac{3\gamma}{5}r^2+\frac{1}{r}-\frac{3\beta}{r^3}\right)\frac{F}{8\pi\eta} \qquad (112a)$$

$$v_y = -\sin\theta\cos\theta\cos\phi\left(-\frac{3\gamma}{5}r^2+\frac{1}{r}-\frac{3\beta}{r^3}\right)\frac{F}{8\pi\eta} \qquad (112b)$$

$$v_z = \left(\gamma r^2+\frac{4}{3r}+\delta+(1-3\cos^2\theta)\left(\frac{\gamma r^2}{5}-\frac{1}{3r}+\frac{\beta}{r^3}\right)\right)\frac{F}{8\pi\eta} \qquad (112c)$$

If terms of order $\frac{a^2}{r^3}$ are neglected, the Oseen tensor is then

$$\begin{aligned}
T_{xx} &= \frac{1}{8\pi\eta}\left(\gamma r^2+\frac{4}{3r}+\delta+(1-3\sin^2\theta\cos^2\phi)\left(\frac{\gamma r^2}{5}-\frac{1}{3r}\right)\right)\\
T_{xy} &= \frac{1}{8\pi\eta}\sin^2\theta\sin\phi\cos\phi\left(-\frac{3}{5}\gamma r^2+\frac{1}{r}\right)\\
T_{xz} &= \frac{1}{8\pi\eta}\sin\theta\cos\theta\cos\phi\left(-\frac{3\gamma}{5}r^2+\frac{1}{r}\right)\\
T_{yx} &= T_{xy}\\
T_{yy} &= \frac{1}{8\pi\eta}\left(\gamma r^2+\frac{4}{3r}+\delta+(1-3\sin^2\theta\sin^2\phi)\left(\frac{\gamma r^2}{5}-\frac{1}{3r}\right)\right) \qquad (113)\\
T_{yz} &= \frac{1}{8\pi\eta}\sin\theta\cos\theta\sin\phi\left(-\frac{3\gamma}{5}r^2+\frac{1}{r}\right)\\
T_{zx} &= T_{xz}\\
T_{zy} &= T_{yz}\\
T_{zz} &= \frac{1}{8\pi\eta}\left(\gamma r^2+\frac{4}{3r}+\delta+(1-3\cos^2\theta)\left(\frac{\gamma r^2}{5}-\frac{1}{3r}\right)\right)
\end{aligned}$$

The analog of equation 109 is

$$\vec{v}(0) = -\frac{c\omega^2 M}{N}\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_{2a}^{L} T_{zz}\,(z_0 + r\cos\theta)\, r^2 dr\, \hat{e}_z$$

$$= -\frac{c\omega^2 M}{N}\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^{L} T_{zz}\,(z_0 + r\cos\theta)\, r^2 dr\, \hat{e}_z \; + \tag{114}$$

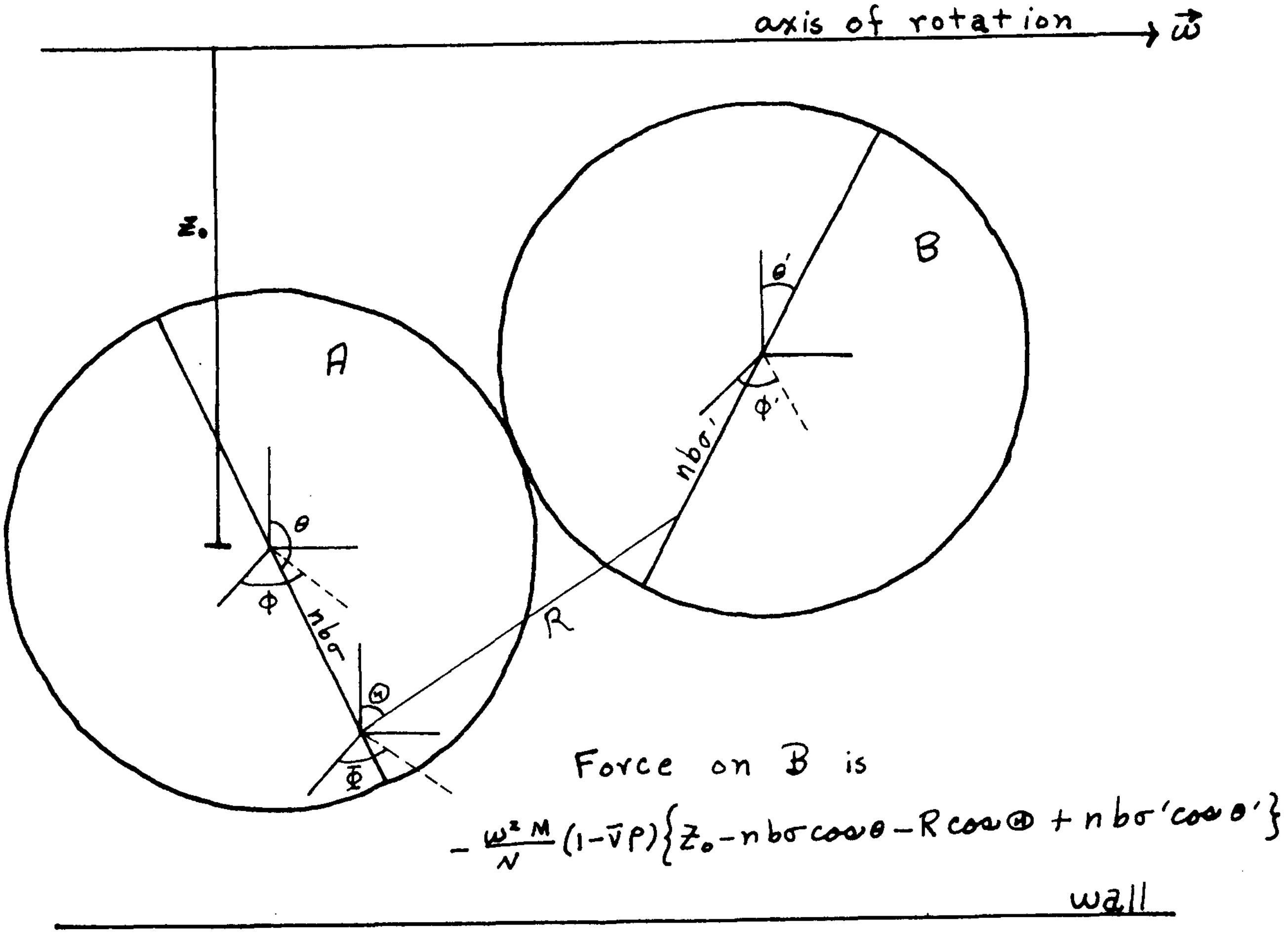
$$\frac{c\omega^2 M}{N}\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^{2a} T_{zz}\,(z_0 + r\cos\theta)\, r^2 dr\, \hat{e}_z = -\frac{a^2 cF}{9\eta} + \frac{4a^2 cF}{3\eta}$$

This is the same result as was obtained for the effect of a wall with the exception of the additional term $-\frac{a^2 cF}{9\eta}$. The velocity is

$$\vec{V} = -\frac{F}{6\pi\eta a} - \frac{a^2 cF}{9\eta} + \frac{4a^2 cF}{3\eta} = -\frac{F}{6\pi\eta a}\left(1 - \frac{11}{2}\,\phi\right)$$

VC. The Hydrodynamic Interactions of Rigid Rods

Consider the following figure:



Force on B is

$$-\frac{\omega^2 M}{N}(1-\bar{v}\rho)\left\{z_0 - nb\sigma\cos\theta - R\cos\Theta + nb\sigma'\cos\theta'\right\}$$

The velocity perturbations about the rod shown in box A due to the hydrodynamic elements of the rod in box B will be calculated. This will involve an average over regions outside the volume excluded by the particle in box A. To enable the mathematics to be carried out, the region excluded will be assumed to be a sphere of diameter 2nb, where 2nb is the length of the rod. The results so obtained will be multiplied by the factor 3d/8nb, where d is the diameter of the rod, in order to attempt to scale down the value to correspond more closely to that of the actual excluded volume, which is more like a disc of radius 2nb and thickness d. The quantity 3d/8nb is the ratio of disc volume to sphere volume. Just how drastic this approximation is will be tested by comparing the result to experimentally determined values for TMV.

Call σ' the fractional distance from the center of rod B to a point off center. The force exerted by $nb\sigma'$ on the fluid is denoted $\vec{F}(\sigma')$. $\underset{\sim}{T}(\sigma, \sigma')$ clearly depends on θ, φ, θ', φ', Θ, Φ, σ, σ', and R.

To get the effect at σ due to the entire particle in B, integrate over σ'

$$\eta \int_{-1}^{1} \underset{\sim}{T}(\sigma,\sigma') \cdot \vec{F}(\sigma')\, d\sigma'$$

To get the hydrodynamic perturbation at σ due to the particle B averaged over its possible orientations, integrate over θ' and φ', weighted with the proper angular distribution function $f(\theta')$.

$$\int_{\Omega'} d\Omega'\, f(\theta') \left[n \int_{-1}^{1} \underset{\sim}{T}(\sigma,\sigma') \cdot \vec{F}(\sigma')\, d\sigma' \right]$$

To get the average hydrodynamic perturbation at σ due to all the other particles like B, average the position of the center of mass of B over all allowable positions (assuming the radial distribution function to be uniform for simplicity) and multiply by the total number of particles.

$$c \int d\,(vol) \int_{\Omega'} d\Omega'\, f(\theta')\; \eta \int_{-1}^{1} \underset{\sim}{T}(\sigma,\sigma') \cdot \vec{F}(\sigma')\, d\sigma'$$

It can be shown that a condition analogous to equation 109 is also true here

$$\vec{V}(\sigma) = c\int d(vol)\int_{\Omega'} d\Omega'\, f(\theta')\, n\int_{-1}^{1} \underset{\sim}{T}(\sigma,\sigma')\cdot\vec{F}(\sigma')\,d\sigma'$$

$$= -c\int_{\substack{\text{excluded}\\ \text{volume}}} d(vol)\int_{\Omega'} d\Omega'\, f(\theta')\, n\int_{-1}^{1} \underset{\sim}{T}(\sigma,\sigma')\cdot\vec{F}(\sigma')\,d\sigma' \qquad (115)$$

This integral is evaluated in Appendix A.

It is interesting to consider the results when the Oseen tensor for the hypothetical sphere-surrounded hydrodynamic elements is used instead of the Oseen tensor for a rigid wall. The additional term over the excluded volume term, which was $-a^2cF/9\eta$ for spheres (see equation 114) is $-\dfrac{a^2c\,(z_0 - nb\sigma\cos\theta)\,\omega^2M(1-\bar{v}\rho)}{9\eta N}$ for this case, where a is the radius of a hydrodynamic element. This is worked out in Appendix B.

This term is neglected since the excluded volume term is much larger.

The quantity of interest then is the excluded volume integral in equation 115. The external force operating on particle B is

$$-\frac{\omega^2M(1-\bar{v}\rho)}{N}\left(z_0 - nb\sigma\cos\theta - R\cos\Theta + nb\sigma'\cos\theta'\right) \qquad (116)$$

The quantities $\vec{F}(\sigma')$ are approximated by the functions of equation 24. According to Appendix A, the value of this integral is

$$\vec{V}(\sigma) = \frac{c\omega^2 M \mathcal{L} d}{4\eta N}\left(Z_0 - \frac{3\mathcal{L}\sigma\cos\theta}{20}\right)\left(1-\bar{v}\rho\right)\hat{e}_z \tag{117}$$

From this the average perturbation over the entire molecule is

$$\frac{n}{2n+1}\int_{1}^{1}\vec{V}(\sigma)\,d\sigma = \frac{c\omega^2 M \mathcal{L} d Z_0 (1-\bar{v}\rho)}{4\eta N}\hat{e}_z \tag{118}$$

so that the velocity of the molecule on the average, in the absence of any preferred orientation, is

$$\vec{V} = -\frac{M\omega^2 Z_0 (1-\bar{v}\rho)}{\Xi N} + \frac{c\omega^2 M \mathcal{L} d Z_0 (1-\bar{v}\rho)}{3\eta N} \tag{119}$$

where Ξ is the average friction constant of the entire molecule. It is possible to compare this with experiment. For example, the sedimentation coefficient for TMV at very low concentration varies with concentration like $s_o(1 - 4C/7)$ where C is given in weight percent TMV (16). The ratio of this correction term to 118 is

$$\frac{4 s_0 \omega^2 Z_0}{\eta} C \, \frac{100 M c}{N C} \, \frac{4\eta N}{c\omega^2 M \mathcal{L} d Z_0 (1-\bar{v}\rho)} = 0.94 \tag{120}$$

This agreement with experiment is extremely gratifying, and indicates that the approximation of scaling down the excluded volume possibly possesses some validity.

The torque on the particle A is given by

$$\vec{\tau} = \frac{1}{2}\,\hat{e}_r \times n^2 b\zeta \int_{-1}^{1} \sigma\, \vec{v}(\sigma)\, d\sigma$$

$$= \sin\theta \cos\theta \; \frac{c\omega^2 M \mathcal{L}^3 d n \zeta (1-\bar{v}\rho)}{160\,\eta N}\, \hat{e}_\varphi \qquad (121)$$

The factor of $\frac{1}{2}$ comes from the fact that the field considered is cartesian rather than radial. See the comment at the end of Section IVd. Equation 9' now gives

$$kT\, \frac{\partial \ln f}{\partial \theta}\, \hat{e}_\theta = \vec{\tau} \times \hat{e}_r = \frac{c\omega^2 M \mathcal{L}^3 d n \zeta (1-\bar{v}\rho)}{160\,\eta N}\, \sin\theta \cos\theta\, \hat{e}_\theta \qquad (122)$$

or

$$f(\theta) = \mathcal{K} \exp\left(- \frac{c\omega^2 M \mathcal{L}^3 d n \zeta (1-\bar{v}\rho)}{320\,\eta N k T} \cos^2\theta \right) \qquad (123)$$

Assuming $n = \frac{\mathcal{L}}{d}$, $\zeta = 6\pi\eta d/2$, the argument of this exponential is of order 5×10^{-8} for TMV. This quite strongly indicates there is no hydrodynamic alignment which is measurable. The sign of the argument shows a slight preference to align perpendicular to the field. Such an alignment would in any case cause the sedimentation coefficient to decrease, rather than increase, with an increase in field. It is thus doubtful, on the basis of this model, that the mechanism for speed dependence as observed by Hearst and Vinograd has anything to do with hydrodynamic alignment, at least for TMV.

VI. Preliminary Comments on Liquid Crystals

It is well known that TMV solutions in water will separate into two phases if the concentration becomes high enough. This phenomenon occurs at about 2% volume fraction of TMV (17). No such phase separation is known for DNA, but these comments may throw some light on the situation anyway.

In the case of TMV at 2% concentration, the two phases are characterised by different concentrations and different degrees of alignment for the rod-like molecules. In the more concentrated phase the particles are seen to be oriented in a specific direction preferentially such that a fair degree of order is exhibited (hence the name liquid crystal), while the more dilute phase displays long-range angular isotropy. Onsager was able to explain this on a statistical mechanical basis, assuming pure repulsive forces of the hard core type (18).

Now it is clear that if a situation should occur wherein a large number of molecules should line up with each other and parallel to the applied field via a liquid crystal mechanism, the change in mobility factors with direction of motion would cause an observed increase in sedimentation coefficient. However, in the systems studied by Hearst and Vinograd, concentrations of TMV on the order of half a milligram per milliliter, or about 0.5% were used. This is considerably below the concentration level required for the separation of phases; hence it could be argued that no significant order of the liquid-crystal type will be said about this prospect shortly.

Even in the absence of liquid crystal formation there is a possibility of induced order worth considering, notably the excluded volume effect (19). In dilute solutions, particles possessing asymmetry have a slight tendency to assume configurations such that the maximum allowable volume per particle is achieved. This is due to the increase of translational entropy with increase of available geometrical volume. In the case of long rigid rods such as TMV, the relative orientation of two rods which gives the maximum allowed volume for each is clearly a parallel one. Therefore, since (as was shown in Section IVD) there is a slight tendency for each individual rod to align parallel to the field, given by the distribution function

$$f(\theta,\phi) = \mathcal{K} \exp\left(-\frac{I\omega^2}{2KT} \sin^2\theta \sin^2\phi\right) \tag{96}$$

the excluded volume effect will enhance this alignment.

To get the angular distribution function including the excluded volume effect, it is convenient to consider the definition of a one-body angular distribution function (20)

$$f_1(\theta,\phi) = \frac{1}{Q_N V^N} \int \cdots \int d'(1)\, d(2) \cdots d(N) \exp\left[-\frac{U}{KT}\right] \tag{123}$$

where N is the total number of particles in the system, V is the volume, d'(1) is the volume element associated with the center of mass of particle 1, but not its angular coordinates, d(i) is the volume and orientation element associated with particle i, U is the total potential energy, and Q_N is the configurational integral

$$Q_N = \int \cdots \int d(1) \ldots d(N) \, \exp\left[-\frac{U}{kT}\right] \tag{124}$$

The potential energy is

$$U = \sum_{i<j} u_{ij} + \sum_{s} u_s' \tag{125}$$

where u_{ij} is the interaction energy between particles i and j, and u_s' is the potential energy due to an external field. From equation 96

$$u_s' = \frac{I\omega^2}{2} \sin^2\theta_s \sin^2\phi_s \tag{126}$$

In addition, the approximation of hard core interactions for the u_{ij} are assumed, such that

$u_{ij} = 0$ if particles i and j do not intersect (127a)

$u_{ij} = -\infty$ if particles i and j intersect (127b)

Following Mayer and Mayer (21), define f_{ij}

$$e^{-u_{ij}/kT} = 1 + f_{ij} \tag{128}$$

so that equation 123 becomes

$$f_1(\theta,\phi) = \frac{1}{Q_N V^N}\int\cdots\int d'(1)\; d(2)\cdots d(N)\, e^{-\sum u'_s/kT}\Big(1+\sum_{i<j} f_{ij}+\cdots\Big) \tag{129}$$

By employing the techniques of Mayer's cluster integrals, it can be shown that this becomes (22, 23)

$$f_1(\theta,\phi) = \mathcal{K}\sum_{\ell\geq 0} B'_\ell\, c^\ell \tag{130}$$

where

$$B'_\ell = \frac{1}{\ell!}\int\cdots\int d'(1)\, d(2)\cdots d(\ell+1)\,\underset{irreducible}{\Big[\sum\prod f_{ij}\Big]}\Big[\prod_{i=1}^{\ell+1} e^{-u'_i/kT}\Big] \tag{131}$$

and K is a normalizing constant. Then, to first order in the particle concentration,

$$f_1(\theta,\phi) = \mathcal{K}\Big[V e^{-u_1/kT} + c\, e^{-u_1/kT}\iint e^{-u_2/kT} f_{12}\, d'(1)\, d(2)\Big] \tag{132}$$

The integral on the right can be evaluated by keeping the angular variables fixed and integrating first with respect to the spatial variables of particle 2, since u'_2 depends only on angular variables. According to the hard core potentials,

$f_{12} = 0$ if particles 1 and 2 do not intersect (133a)

$f_{12} = -1$ if particles 1 and 2 intersect (133b)

This integral with respect to the coordinates of particle thus represents the negative of the volume denied by particle 2 to particle 1, if their orientations are kept constant. This value, according to Onsager (18), is

$$\left(2\ell^2 d + \frac{\pi d^3}{2}\right)\sin\gamma + \left[\frac{\pi(1+|\cos\gamma|)}{2} + 2E(\sin\gamma)\,\ell d^2\right] \tag{134}$$

where ℓ is the length of a rod, d the diameter, γ the angle made by the long axes of rods 1 and 2, and

$$E(\sin\gamma) = \int_0^{\frac{\pi}{2}}\left(1-\sin^2\gamma\,\sin^2\phi\right)^{\frac{1}{2}} d\phi$$

The integration over the spatial coordinates of particle 1 just gives a factor of the total volume. Since $\ell \gg d$, only the maximum term in equation 134 will be kept, which is $2\ell^2 d\sin\gamma$. Hence, equation 132 becomes

$$f_1(\theta,\phi) = \mathcal{K} V e^{-u_1/kT}\left[1 + 2c\ell^2 d\int_{\Omega_2} e^{u_2/kT}\sin\gamma\, d\Omega_2\right] \tag{135}$$

From equation 96,

$$\begin{aligned} u_1 &= \frac{I\omega^2}{2}\sin^2\theta_1\sin^2\phi_1 \\ u_2 &= \frac{I\omega^2}{2}\sin^2\theta_2\sin^2\phi_2 \end{aligned} \tag{136}$$

Using the approximation

$$e^{-u/kT} \simeq 1 - \frac{u}{kT} = 1 - \frac{I\omega^2}{2kT}\sin^2\theta\sin^2\phi \tag{137}$$

the integral is

$$\int_{\Omega_2} \left(1 - \frac{I\omega^2}{2kT} \sin^2\theta_2 \sin^2\phi_2\right) \sin\gamma \, d\Omega_2 \tag{138}$$

The first term is elementary, but the second is not a trivial integration. In Appendix C it is shown to be

$$\int_{\Omega_2} \sin^2\theta_2 \sin^2\phi_2 \sin\gamma \, d\Omega_2 = \frac{\pi^2}{8}\left(3 - \sin^2\theta_1 \sin^2\phi_1\right) \tag{139}$$

Equation 132 is then

$$f_1(\theta,\phi) = \mathcal{K} V \Bigg(1 - \frac{I\omega^2}{2kT} \sin^2\theta_1 \sin^2\phi_1 + 2\ell^2 d\,\pi^2 - \frac{I\omega^2}{kT}\,\frac{3\pi^2\ell^2 dc}{8} - \frac{7\pi^2\ell^2 dc\, I\omega^2}{8kT} \sin^2\theta_1 \sin^2\phi_1\Bigg) \tag{140}$$

In the future φ_1 will hold no interest, so $\sin^2\varphi$ is replaced by its average value ½. Thus,

$$f_1(\theta) = \mathcal{K} V \Bigg(1 - \frac{I\omega^2}{4kT} + 2\ell^2 dc\pi^2 - \frac{13\pi^2\omega^2 I\ell^2 dc}{16\,kT} + \cos^2\theta_1 \left(\frac{I\omega^2}{4kT}\right)\left(1 + \frac{7\pi^2\ell^2 dc}{4}\right)\Bigg) \tag{141}$$

Normalization gives

$$f_1(\theta) = \frac{1}{2}\left\{ 1 + \frac{\frac{I\omega^2}{4KT}\left(1 + \frac{7\pi^2 \ell^2 dc}{4}\right)}{1 - \frac{I\omega^2}{4kT} + 2\ell^2 dc\,\pi^2 - \frac{13\pi^2 I\omega^2 \ell^2 dc}{16KT}} \left(\cos^2\theta - \frac{1}{3}\right) \right\} \tag{142}$$

When numbers are substituted into this expression, it is immediately seen that the validity of keeping only the first order terms in the concentration is in jeopardy. The reason lies in the fact that at a concentration of ¼ % by weight, the product of concentration and excluded volume per pair exceeds unity for TMV.

$$2\ell^2 dc\pi^2 = 1.8 \tag{143}$$

Keeping this in mind, the previous data for TMV give, at ¼ % by weight concentration

$$f_1(\theta) = \frac{1}{2}\left(1 + 4.2 \times 10^{-8}(3\cos^2\theta - 1)\right) \tag{144}$$

This correction, as it stands, is unobservable experimentally. The fact that it is slightly smaller than the intrinsic correction given by equation 98

$$f_1(\theta) = \frac{1}{2}\left(1 + 4.5 \times 10^{-8}(3\cos^2\theta - 1)\right) \tag{98}$$

undoubtedly reflects the invalidity of using the first order correction to the concentration, as indicated in equation 143. Before the much more difficult task of using higher order terms in the concentration is considered, however, it is prudent to reflect if such a procedure is justified. The answer is clearly no, since concentration correction terms to the alignment of order 1 will be necessary before this mechanism will give anything which is experimentally observable. Note that the alignment term will always contain the factor $\frac{I\omega^2}{kT}$, which is of order 10^{-7} , and this then requires the concentration factor itself to be of order 10^7 for the result to be observable. It is inconceivable that a more accurate treatment will give a correction of this size. Therefore, since at this point the interest is in explaining an experimental phenomenon and not in academic curiosities, this alignment mechanism will be dropped as a possibility.

VII. Summary and Discussion

The main purpose of this investigation, notably to find a mechanism which will cause a field alignment of rod-like molecules of sufficient magnitude to perceptibly increase the observed sedimentation coefficient, has been unsuccessful. Hydrodynamic alignment has been investigated in some detail, and on the basis of the results obtained, it can probably be ruled out as the origin of the phenomenon. One aspect of entropy alignment, the excluded volume effect in dilute solutions, was also shown to be insufficient in magnitude to serve as the basic mechanism.

Another aspect of an entropy effect which was not considered here is the formation of small aggregates of aligned molecules. If an aggregate is formed, it should behave like a much larger molecule and thus feel the aligning effects of the field more. In addition, the larger size of an aggregate induces faster sedimentation, so if the formation of aggregates is field-dependent such that the number and size of these clusters increases with applied field, then the sedimentation coefficient will increase with applied field also.

A mechanism for higher stability in a cluster with increasing field is available. It has been shown that the potential energy of a rigid rod due to an applied radial field is

$$\frac{I\omega^2}{2} \sin^2\theta \sin^2\phi = \frac{I\omega^2}{2} \cos^2\vartheta \tag{145}$$

where ϑ is the angle made by the rod's long axis and the axis of rotation. This tends to align the rods perpendicular to the axis of rotation. The randomizing effect of brownian motion is thus less intense, which fact leads to a higher stability for the cluster.

There is another interesting aspect to this in its own right. According to Onsager's theory of liquid crystals (18), the angular distribution function is given by the solution to the equation

$$\ln 4\pi f(\hat{a}) = \lambda - 1 - c \int_{\Omega'} \beta(\hat{a}, \hat{a}') f(\hat{a}')\, d\Omega' \tag{146}$$

where λ is a Lagrangian multiplier arising from a normalization condition, and $\beta(\hat{a},\hat{a}')$ is a factor having to do with the excluded volume. The critical concentration occurs when a value of c is reached at which an angularly anisotropic function f(a) leads to a system of lower free energy than one which is isotropic at the same concentration. The inclusion of the potential energy of the radial field leads to an additional term in this equation

$$\ln 4\pi f(\hat{a}) = \lambda - 1 + \frac{I\omega^2}{2kT}\cos^2\vartheta - c\int_{\Omega'} \beta(\hat{a},\hat{a}')\, f(\hat{a}')\, d\Omega' \tag{147}$$

The effect of this on the critical value of c might be of interest and perhaps should be investigated. It is clear on physical grounds that the critical value of c will be decreased, but just how much effect the radial field will have has not as yet been studied.

APPENDIX A

The integral of interest is

$$\vec{\mathcal{V}}(\sigma) = -c\int_{\substack{\text{excluded}\\ \text{volume}}}\int_{\Omega'} d\Omega'\, f(\theta')\, n\int_{-1}^{1} \underset{\sim}{T}(\sigma,\sigma')\cdot\vec{F}(\sigma')\,d\sigma'$$

First, it is noted that the maximum distance apart which the centers of molecule A and molecule B enjoy within the excluded volume is 2nb. It is therefore convenient to write the limits of the variable R from 0 to a value commensurate with given orientations of A, B, and their relative positions. For this it is necessary to have R as such a function.

For convenience define

$$\cos\beta = \frac{\overrightarrow{nb\sigma}\cdot\vec{R}}{nb\sigma R} = \sin\theta\sin\Theta\cos(\Phi-\phi)+\cos\Theta\cos\theta$$

$$\cos\gamma = \frac{\overrightarrow{nb\sigma'}\cdot\vec{R}}{nb\sigma' R} = \sin\theta'\sin\Theta\cos(\Phi-\phi')+\cos\Theta\cos\theta'$$

$$\cos\delta = \frac{\overrightarrow{nb\sigma}\cdot\overrightarrow{nb\sigma'}}{n^2b^2\sigma\sigma'} = \sin\theta\sin\theta'\cos(\phi-\phi')+\cos\theta\cos\theta'$$

Then

$$2nb = \left|\overrightarrow{nb\sigma}+\vec{R}-\overrightarrow{nb\sigma}'\right|$$

or

$$4n^2b^2 = n^2b^2\sigma^2+R^2+n^2b^2\sigma'^2+2nb\sigma R\cos\beta-2nb\sigma' R\cos\gamma-2n^2b^2\sigma\sigma'\cos\delta$$

This is a quadratic equation in R

$$R^2 + R(2nb\sigma\cos\beta - 2nb\sigma'\cos\gamma) + n^2b^2\sigma^2 + n^2b^2\sigma'^2 - 4n^2b^2 - 2n^2b^2\sigma\sigma'\cos\delta = 0$$

$$R = nb\left[\sigma'\cos\gamma - \sigma\cos\beta + \sqrt{4 - \sigma^2 - \sigma'^2 + \sigma^2\cos^2\beta + \sigma'^2\cos^2\gamma - 2\sigma\sigma'\cos\beta\cos\gamma + 2\sigma\sigma'\cos\delta}\,\right]$$

As given here, R depends on θ, φ; θ', φ'; Θ, Φ; σ, σ'.

The integral of interest then becomes

$$-C\int_0^{2\pi} d\Phi \int_0^{\pi} \sin\Theta\, d\Theta \int_{-1}^{1} d\sigma' \int_0^{2\pi} d\phi' \int_0^{\pi} \sin\theta'\, d\theta' \int_0^{R} R'^2\, dR'\; \underset{\sim}{T}(\sigma,\sigma') \cdot \vec{F}(\sigma')\, f(\theta')$$

A very good approximation to $\vec{F}(\sigma')$ should be the function given in equation 24 of the text:

$$\vec{F}(\sigma') = \frac{\mathcal{F}M}{\eta N}\left\{\frac{\psi^{(1)}(\sigma')}{\Omega^{(1)}(1)}\underset{\sim}{\mathbb{I}} - \hat{e}_{r'}\hat{e}_{r'}\left(\frac{\psi^{(1)}(\sigma')}{\Omega^{(1)}(1)} - \frac{\psi^{(2)}(\sigma')}{\Omega^{(2)}(1)}\right)\right\}\begin{pmatrix}0\\0\\-1\end{pmatrix}$$

Here

$$\mathcal{F} = \omega^2(1-\bar{v}\rho)\left(z_0 - nb\sigma\cos\theta - R'\cos\Theta + nb\sigma'\cos\theta'\right)$$

and

$$\underset{\sim}{T}(\sigma,\sigma') = \frac{1}{8\pi\eta R'}\left(\underline{\mathbb{I}} + \vec{e}_{R'}\vec{e}_{R'}\right)$$

The integral is then explicitly

$$\frac{CM\omega^2(1-\bar{v}\rho)}{8\pi\eta N}\int_0^{2\pi} d\Phi \int_0^{\pi} \sin\Theta\, d\Theta \int_{-1}^{1} d\sigma' \int_0^{2\pi} d\phi' \int_0^{\pi} \sin\theta'\, d\theta' \int_0^{R} R'\, dR'\, \left(z_0 - nb\sigma\cos\theta\right.$$

$$\left. - R'\cos\Theta + nb\sigma'\cos\theta'\right) f(\theta')\left\{\frac{\psi^{(1)}(\sigma')}{\Omega^{(1)}(1)}\left(\mathbb{I} + \hat{e}_R\hat{e}_R\right) - \right.$$

$$\left. - \left(\hat{e}_{r'}\hat{e}_{r'} + \hat{e}_R\hat{e}_{r'}\cos\gamma\right)\left(\frac{\psi^{(1)}(\sigma')}{\Omega^{(1)}(1)} - \frac{\psi^{(2)}(\sigma')}{\Omega^{(2)}(1)}\right)\right\}\begin{pmatrix}0\\0\\1\end{pmatrix}$$

Before proceeding further, it is convenient to expand R as a Taylor series in σ'. Define $4 - \sigma^2 + \sigma^2 \cos^2\beta = X$. Then

$$R = nb\Big[\left(-\sigma\cos\beta + \sqrt{X}\right) + \sigma'\left(\frac{\sigma(\cos\delta - \cos\beta\cos\gamma)}{\sqrt{X}}\right) +$$

$$+\sigma'^2\left(\frac{(4-\sigma^2+\sigma^2\cos^2\beta(-1+\cos^2\gamma) - \sigma\left(\cos\beta\cos\gamma - \cos\delta\right)^2}{2\sqrt{X}}\right) + \cdots\Big]$$

$$= nb\left(A + \sigma' B + \sigma'^2 C\right)$$

Further, to order σ^2

$R^2 = n^2b^2[A^2 + 2AB\sigma' + (B^2 + 2AC)\sigma'^2]$

$R^3 = n^3b^3[A^3 + 3AB\sigma' + 3(A^2C + AB^2\ \sigma'^2]$

Actual evaluation of the integral is now begun. It is convenient to integrate with respect to R' first, and to expand the integrand less the ϕ functions in powers of σ'. To order σ', the integrand is, less certain terms which obviously vanish,

$$f(\theta')\left\{(z_0 - nb\sigma\cos\theta)\frac{n^2b^2A^2}{2} - \cos\Theta\,\frac{n^3b^3A^3}{3}\right\}\frac{\psi^{(1)}(\sigma')}{\Omega^{(1)}(1)}\left(\hat{e}_z + \hat{e}_{R'}\cos\Theta\right)$$

It is seen that the variables σ', θ', and φ' can be integrated out immediately, and that to this order the form of $f(\theta')$ is immaterial. Thus, the integral is

$$\frac{c M \omega^2 (1-\bar{v}\rho)}{8\pi\eta N} \int_0^{2\pi} d\Phi \int_0^{\pi} \sin\Theta \, d\Theta \left\{ \frac{n^2 b^2 A^2}{2} (z_0 - nb\sigma\cos\theta) - \right.$$

$$\left. - \cos\Theta \, \frac{n^3 b^3 A^3}{3} \right\} (\hat{e}_z + \hat{e}_R \cos\Theta)$$

To order σ^2

$$\int_0^{2\pi} d\Phi \int_0^{\pi} \sin\theta \, d\Theta \, A^2 (\hat{e}_z + \hat{e}_R \cos\Theta)$$

$$= \int_0^{2\pi} d\Phi \int_0^{\pi} \sin\Theta \, d\Theta \, (2\sigma^2\cos^2\beta + 4 - \sigma^2 - 4\sigma\cos\beta) \begin{pmatrix} \sin\Theta\cos\Theta\cos\Phi \\ \sin\Theta\cos\Theta\sin\Phi \\ 1+\cos^2\Theta \end{pmatrix}$$

$$= (4-\sigma^2) \begin{pmatrix} 0 \\ 0 \\ \frac{16\pi}{3} \end{pmatrix} + 2\sigma^2\pi \begin{pmatrix} \frac{8}{15}\sin\theta\cos\theta\cos\phi \\ \frac{8}{15}\sin\theta\cos\theta\sin\phi \\ \frac{8}{5} + \frac{8}{15}\cos^2\theta \end{pmatrix}$$

$$= \frac{64\pi}{3}\hat{e}_z - \frac{32}{15}\pi\sigma^2\hat{e}_z + \frac{16\pi}{15}\sigma^2\hat{e}_r\cos\theta$$

To order σ^2

$$\int_0^{2\pi} d\Phi \int_0^{\pi} \sin\Theta \, d\Theta \, A^3 \begin{pmatrix} \sin\Theta\cos\Theta\cos\Phi \\ \sin\Theta\cos\Theta\sin\Phi \\ 1+\cos^2\Theta \end{pmatrix} \cos\Theta$$

$$= -12\sigma \int_0^{2\pi} d\Phi \int_0^{\pi} \sin\Theta\cos\Theta \, (8 - 6\sigma^2 + 12\sigma^2\cos^2\beta - 12\sigma\cos\beta) \begin{pmatrix} \sin\Theta\cos\Theta\cos\Phi \\ \sin\Theta\cos\Theta\sin\Phi \\ 1+\cos^2\Theta \end{pmatrix}$$

$$= -12\sigma \left(\frac{28}{15}\cos\theta\,\hat{e}_z + \frac{4\pi}{15}\hat{e}_r \right)$$

With these results then, the integral to zero order in σ' is

$$\frac{cM\omega^2(1-\bar{v}\rho)}{8\pi\eta N}\left[\frac{n^2b^2}{2}(Z_0 - nb\sigma\cos\theta)\left(\frac{64\pi}{3}\hat{e}_z - \frac{32}{15}\pi\sigma^2\hat{e}_z + \frac{16\pi}{15}\sigma^2\hat{e}_r\cos\theta\right) + \frac{n^3b^3}{3}\,12\sigma\left(\frac{28\pi}{15}\cos\theta\,\hat{e}_z + \frac{4\pi}{15}\hat{e}_r\right)\right]$$

$$= \frac{cM\omega^2n^2b^2(1-\bar{v}\rho)}{8\eta N}\left\{Z_0\left(\frac{32}{3}\hat{e}_z - \frac{32}{15}\sigma^2\hat{e}_z + \frac{16}{15}\sigma^2\hat{e}_r\cos\theta\right) + nb\sigma\left(-\frac{16}{5}\cos\theta\,\hat{e}_z + \frac{8}{15}\hat{e}_r\right)\right\}$$

The next important term after σ'^0 is σ'^2. A calculation such as that just demonstrated has been performed for this case and the results indicate that this contribution is quite negligible (about 1%) compared to the σ'^0 contribution. It and higher terms in σ' will be neglected, as will small terms in the σ'^0 part. Thus, the velocity perturbation is approximately

$$\frac{4}{3}\,\frac{Z_0cM\omega^2n^2b^2(1-\bar{v}\rho)}{N\eta}\hat{e}_z + \frac{cM\omega^2n^3b^3\sigma(1-\bar{v}\rho)}{8\eta N}\left(-\frac{16}{5}\cos\theta\,\hat{e}_z + \frac{8}{15}\hat{e}_r\right)$$

or, since $2nb = \mathcal{L}$,

$$\frac{Z_0cM\omega^2\mathcal{L}^2}{3\eta N}\hat{e}_z + \frac{cM\omega^2\mathcal{L}^3\sigma}{64\eta N}\left(-\frac{16}{5}\cos\theta\,\hat{e}_z + \frac{8}{15}\hat{e}_r\right)$$

To scale this down as was mentioned in the text, multiply by $3d/4\mathcal{L}$. Also, since the $\hat{e}_r$ terms do not give any contribution to physical observables, they are neglected, and the velocity perturbation becomes

$$\vec{v}(\sigma) = \frac{cM\omega^2 \mathcal{L} d(1-\bar{v}\rho)}{4\eta N}\left(Z_0 \hat{e}_z - \frac{3\sigma\mathcal{L}}{2o}\cos\theta\, \hat{e}_z\right)$$

APPENDIX B

The integral desired is

$$\frac{cm\omega^2(1-\bar{v}\rho)}{8\pi\eta N}\int_0^{2\pi}d\Phi\int_0^{\pi}\sin\Theta\,d\Theta\int_{-1}^{1}d\sigma'\int_0^{2\pi}d\phi'\int_0^{\pi}\sin\theta'd\theta'\int_0^{L}R'dR'\,\Big(Z_0-nb\sigma\cos\theta$$

$$-R'\cos\Theta+nb\sigma'\cos\theta'\Big)f(\theta')\left\{\frac{\psi^{(1)}(\sigma')}{\Omega^{(1)}(1)}\left(\underset{\sim}{I}+\hat{e}_R\hat{e}_R\right)-\right.$$

$$\left.-\left(\hat{e}_{r'}\hat{e}_{r'}+\hat{e}_{R'}\hat{e}_{r'}\cos\gamma\right)\left(\frac{\psi^{(1)}(\sigma')}{\Omega^{(1)}(1)}-\frac{\psi^{(2)}(\sigma')}{\Omega^{(2)}(1)}\right)\right\}\begin{pmatrix}0\\0\\-1\end{pmatrix}$$

Since L does not depend on any variables also integrated over, the angular parts can be done first. Thus, the integral becomes

$$\frac{cM\omega^2(1-\bar{v}\rho)\,(Z_0-nb\sigma\cos\theta)}{8\pi\eta N}\int_0^{2\pi}d\Phi\int_0^{\pi}\sin\Theta\,d\Theta\int_0^{L}R'dR'\,(1+\cos^2\Theta)$$

Since this is the same integral as in equation 114, the result is

$$-\frac{CM\omega^2(1-\bar{v}\rho)(Z_0-nb\sigma\cos\theta)a^2}{9\eta}$$

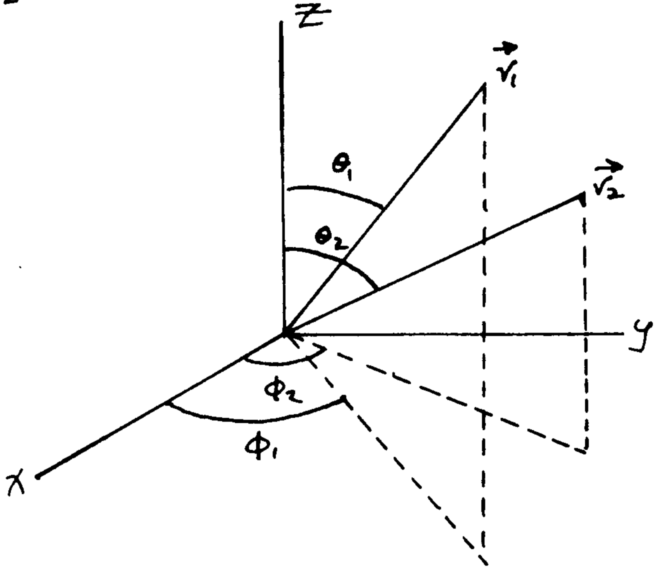
APPENDIX C

The integral of interest is

$$\int_0^{2\pi} d\phi_2 \int_0^{\pi} \sin\theta_2\, d\theta_2 \sin\gamma \sin^2\theta_2 \sin^2\phi_2 = \int_0^{2\pi} d\phi_2 \int_0^{\pi} \sin\theta_2\, d\theta_2 \left(\hat{e}_y \cdot \hat{e}_{r_2}\right)^2$$

where

$$\hat{e}_{r_2} = \hat{e}_x \sin\theta_2 \cos\varphi_2 + \hat{e}_y \sin\theta_2 \sin\varphi_2 + \hat{e}_z \cos\theta_2$$



It is convenient to transform to a new coordinate system whose z axis is along r_1, and to express $\hat{e}_y$ in terms of this coordinate system. The transformation matrix is the same as equation 15 of the text.

$$\underset{\sim}{\alpha} = \left\{ \begin{array}{ccc} \cos\theta_1 \cos\varphi_1 & -\sin\varphi_1 & \sin\theta_1 \cos\varphi_1 \\ \cos\theta_1 \sin\varphi_1 & \cos\varphi_1 & \sin\theta_1 \sin\varphi_1 \\ -\sin\theta_1 & 0 & \cos\theta_1 \end{array} \right\}$$

Therefore,

$$(0\ 1\ 0)\begin{Bmatrix}\hat{e}_x\\ \hat{e}_y\\ \hat{e}_z\end{Bmatrix}=(0\ 1\ 0)\begin{Bmatrix}\cos\theta_1\ \cos\varphi_1 & -\sin\varphi_1 & \sin\theta_1\ \cos\varphi_1\\ \cos\theta_1\ \sin\varphi_1 & \cos\varphi_1 & \sin\theta_1\ \sin\varphi_1\\ -\sin\theta_1 & 0 & \cos\theta_1\end{Bmatrix}\begin{Bmatrix}\hat{e}_{x'}\\ \hat{e}_{y'}\\ \hat{e}_{z'}\end{Bmatrix}$$

or

$$\hat{e}_y = (\cos\theta_1\ \sin\varphi_1 \quad \cos\varphi_1 \quad \sin\theta_1\ \sin\varphi_1)\begin{Bmatrix}\hat{e}_{x'}\\ \hat{e}_{y'}\\ \hat{e}_{z'}\end{Bmatrix}$$

and

$$\hat{e}_y\cdot\hat{e}_{r_2} = \cos\theta_1\ \sin\varphi_1\ \sin\gamma\ \cos\chi + \cos\varphi_1\ \sin\gamma\ \sin\chi + \sin\theta_1\ \sin\varphi_1\ \cos\gamma$$

$$\int_0^{2\pi} d\chi \int_0^{\pi} \sin^2\gamma\ d\gamma\ (\hat{e}_y\cdot\hat{e}_{r_2})^2 = \frac{\pi^2}{8}(3 - \sin^2\theta_1\ \sin^2\varphi_1)$$

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PROPOSITION I

A new method of handling chronopotentiometric data by the method of least squares is proposed.

In the theory of totally irreversible chronopotentiometric processes, the equation relating the various parameters is (1)

$$E = \frac{RT}{\alpha n_a F} \ln \frac{nFC^\circ k^\circ_{f,n}}{i_o} + \frac{RT}{\alpha n_a F} \ln \left[1 - \sqrt{\frac{t}{\tau}}\right] \qquad (1)$$

where E = voltage

α = transfer coefficient

n_a = number of electrons transferred in rate-determining step

i_o = current density

F = Faraday

C^o = concentration of material in solution reacting at the electrode

$k^o_{f,n}$ = rate constant

t = time

τ = time at which reacting component is used up at the electrode surface.

Experimentally, the measured quantities are E and t. A characteristic of the recording apparatus is that t is more accurately measured than E. From the experimentally produced data, the parameters in the equations are adjusted to fit the data as well as possible, and are thus considered to be determined. This is usually done graphically by fiddling with $\sqrt{\tau}$ until a sensibly linear plot is obtained for E versus $\ln(1 + \sqrt{t}/\sqrt{\tau})$; the slope gives $RT/\alpha n_a F$ and the intercept $(RT/\alpha n_a F)\ln(nFC^o k^o_{fn}/i_o)$.

A scheme is developed here which points out the feasibility of accomplishing this more accurately by computer methods, using a least squares technique.

Define

$$\begin{aligned} y &= E \\ a &= RT/\alpha n_a F \\ b &= -1/\sqrt{\tau} \\ c &= (RT/\alpha n_a F)\ln(nFC^o k^o_{fn}/i_o) \\ x &= \sqrt{t} \end{aligned} \tag{2}$$

Then

$$y = a \ln(1 + bx) + c \tag{3}$$

Suppose there are n pieces of experimental data. It is desired to compute from these data the quantities a, b, and c such that the principle of least squares is satisfied.

Define

$$\Delta_i = y_i - a \ln(1 + bx_i) - c \tag{4}$$

where the experimental quantities y_i and x_i are used in this evaluation of Δ_i. The least squares condition is

$$\frac{\partial \Sigma \Delta_i^2}{\partial a} = \frac{\partial \Sigma \Delta_i^2}{\partial b} = \frac{\partial \Sigma \Delta_i^2}{\partial c} = 0 \tag{5}$$

or

$$\frac{\partial \Sigma \Delta_i^2}{\partial a} = -2\sum \Delta_i \ln(1+bx_i) = 0 \tag{6a}$$

$$\frac{\partial \Sigma \Delta_i^2}{\partial b} = -2\sum \Delta_i \frac{a x_i}{1+bx_i} = 0 \tag{6b}$$

$$\frac{\partial \Sigma \Delta_i^2}{\partial c} = -2\sum \Delta_i = 0 \tag{6c}$$

These conditions lead immediately to

$$\sum y_i \ln(1+bx_i) = a \sum \ln^2(1+bx_i) + c \sum \ln(1+bx_i) \tag{7a}$$

$$\sum \frac{y_i x_i}{1+bx_i} = a \sum \frac{x_i \ln(1+bx_i)}{1+bx_i} + c \sum \frac{x_i}{1+bx_i} \tag{7b}$$

$$\sum y_i = a \sum \ln(1+bx_i) + nc \tag{7c}$$

For conciseness of notation, define the following quantities

$$\alpha = \Sigma \ln^2 (1 + bx_i)$$

$$\gamma = \Sigma \ln (1 + bx_i)$$

$$\xi = \Sigma \frac{x_i y_i}{1 + bx_i}$$

$$\tau = \Sigma \frac{x_i}{1 + bx_i}$$

$$\beta = \Sigma \frac{x_i \ln (1 + bx_i)}{1 + bx_i}$$

$$\lambda = \Sigma y_i \ln (1 + bx_i)$$

$$\Omega = \Sigma y_i$$

Then equations 7 become

$$a\alpha + c\gamma = \lambda \tag{8a}$$

$$a\beta + c\rho = \xi \tag{8b}$$

$$a\gamma + cn = \Omega \tag{8c}$$

If 8b and 8c are solved for a and c, the results are

$$a = \frac{n\xi - \beta\Omega}{n\beta - \varsigma\gamma} \tag{9a}$$

$$C = \frac{\beta\Omega - \gamma\xi}{n\beta - \varsigma\gamma} \tag{9b}$$

When these quantities are substituted into equation 8a, the result is

$$\alpha(n\xi - \varsigma\Omega) + \gamma(\beta\Omega - \gamma\xi) - \lambda(n\beta - \varsigma\gamma) = 0 \tag{10}$$

Equation 10 is an implicit transcendental expression for the parameter b, which equation can be solved. The most convenient way is by computer techniques.

For computation, a more convenient form of equation 10 is

$$\sum_{i} \sum_{k} \frac{x_k \ln(1+bx_i)}{1+bx_k} \Big[y_k \ln(1+bx_i) - y_i \ln(1+bx_k) + \frac{\Omega}{n}\big(\ln(1+bx_k) - \ln(1+bx_i)\big) + \frac{\gamma}{n}(y_i - y_k) \Big] \tag{11}$$

Using this form of the equation determining b, the tendency to accumulate very large numbers and then take differences is somewhat mitigated. A trial calculation carried out indicated that numbers with fourteen necessary significant figures may be involved unless the summation order suggested by equation 11 is used. Once b has been determined by solving equation 11, a and c are easily computed via 9a and 9b.

A program to solve equation 11 and to compute a and c has been written for the Burroughs 220 computer. Several trial calculations have been performed with quite reasonable results.

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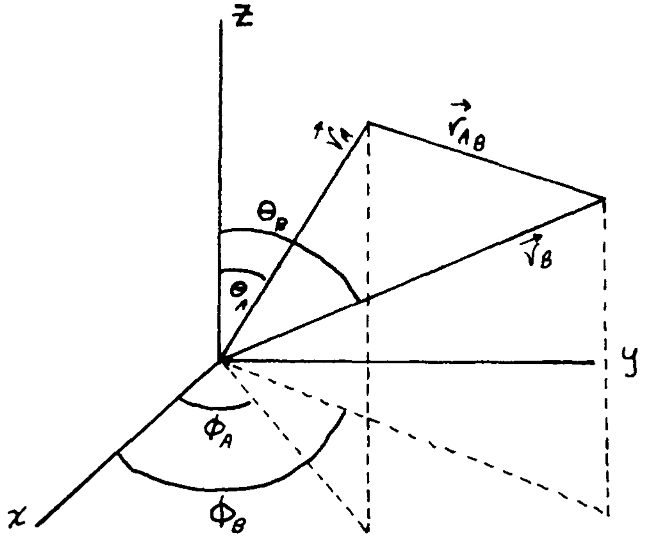
PROPOSITION II

A table of associated Legendre polynomials expressed as the unassociated Legendre polynomials is presented. In this form certain integrals which arise involving Legendre polynomials are easier to evaluate when a table such as this is available.

As an example of the simplifications intended, the following is considered.



From the formula to be found in Morse and Feshback (1),

$$\frac{2^{\beta}}{(1+t^2-2tz)^{\beta+\frac{1}{2}}} = \frac{\pi^{\frac{1}{2}}}{\Gamma(\beta+\frac{1}{2})}\sum_{n=0}^{\infty} t^n T_n^{\beta}(z)$$

where the $T_n^{\beta}(z)$ are Gegenbauer polynomials, can be derived the following expressions:

$$\frac{1}{|\vec{r}_A-\vec{r}_B|} = \frac{1}{r_B}\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\left(\frac{r_A}{r_B}\right)^{\ell}\frac{(\ell-|m|)!}{(\ell+|m|)!}\,P_\ell^m(\cos\theta_A)\,P_\ell^m(\cos\theta_B)\,e^{im(\phi_A-\phi_B)}$$

$$\frac{1}{|r_A - r_B|^3} = \frac{2}{r_B^3} \sum_{n=1}^{\infty} \sum_{m=1}^{n} \left(\frac{r_A}{r_B}\right)^{n-1} \frac{m\,(n-m)!}{(n+m)!} \; \frac{P_n^m(\cos\theta_A)}{\sin\theta_A} \; \frac{P_n^m(\cos\theta_B)}{\sin\theta_B} \; \frac{\sin m\,(\phi_A - \phi_B)}{\sin\,(\phi_A - \phi_B)}$$

The first formula is fairly well known, the second possibly not so much so. Here $r_A < r_B$. If $r_A > r_B$, the positions of r_A and r_B in the formulae are to be interchanged.

The usefulness of the table presented occurs in integrals with $|\vec{r}_A - \vec{r}_B|^{-3}$ as a factor in the integrand. As a specific example, consider the integral

$$\int_0^{2\pi} d\phi_B \int_0^{\pi} \sin\theta_B \, d\theta_B \quad \frac{\cos\theta_B}{|\vec{r}_A - \vec{r}_B|^3}$$

The φ_B integration gives $2\pi\,\delta_m^{\text{odd}}$, and it is immediately apparent that the situation is complicated compared to an integral involving $|\vec{r}_A - \vec{r}_B|^{-1}$, where the only contribution is $m = 0$.

Since $\cos\theta = P_1^0(\cos\theta)$, the integral becomes

$$\frac{4\pi}{r_B^3} \sum_{n=1}^{\infty} \sum_{m=1}^{n} \left(\frac{r_A}{r_B}\right)^{n-1} \frac{m\,(n-m)!}{(n+m)!} \; \frac{P_n^m(\cos\theta_A)}{\sin\theta_A} \; \delta_m^{\text{odd}} \int_0^{\pi} P_1^0(\cos\theta_B)\, P_n^m(\cos\theta_B)\, d\theta_B$$

Now since m is odd, n must be even or the integral vanishes because for n odd and m odd the integrand is an odd function about $\pi/2$. The table gives odd m entries as a product of $\sin\theta$ and a sum of Legendre polynomials, so the factor $\sin\theta$ is restored to the integrand and allows use of the orthogonal properties of Legendre polynomials.

The purpose of the example is to show how interest in the table may arise, and now that this has been done, the evaluation will be taken no further. It is clear that an infinite series is involved, and the terms are much easier to compute when the $P_1^0(\cos\theta)$ projections on the $P_n^m(\cos\theta)$ are known.

The table gives values from n = 1 to n = 10. All entries have been double-checked for accuracy. They were calculated by fitting the highest power of $\cos\theta$ in $P_n^m(\cos\theta)$ to the highest power of $\cos\theta$ in the $P_n(\cos\theta)$ or the $P_{n-1}(\cos\theta)$, depending on whether m happened to be even or odd. Then the next highest power of $\cos\theta$ was fit, and so on.

$P_0^0 = P_0$

$P_1^0 = P_1$

$P_1^1 = \sin\theta\ P_0$

$P_2^0 = P_2$

$P_2^1 = \sin\theta(3P_1)$

$P_2^2 = -2P_2 + 2P_0$

$$P_3^0 = P_3$$

$$P_3^1 = \sin\theta\ (5P_2 + P_0)$$

$$P_3^2 = -6P_3 + 6P_1$$

$$P_3^3 = \sin\theta\ (-10P_2 + 10P_0)$$

$$P_4^0 = P_4$$

$$P_4^1 = \sin\theta\ (7P_3 + 3P_1)$$

$$P_4^2 = -12P_4 + 10P_2 + 2P_0$$

$$P_4^3 = \sin\theta\ (-42P_3 + 42P_1)$$

$$P_4^4 = 24P_4 - 80P_2 + 56P_0$$

$$P_5^0 = P_5$$

$$P_5^1 = \sin\theta\ (9P_4 + 5P_2 + P_0)$$

$$P_5^2 = -20P_5 + 14P_3 + 6P_1$$

$$P_5^3 = \sin\theta\ (-108P_4 + 52P_2 + 56P_0)$$

$$P_5^4 = 120P_5 - 336P_3 + 216P_1$$

$$P_5^5 = \sin\theta\ (216P_4 - 720P_2 + 504P_0)$$

$$P_6^0 = P_6$$

$$P_6^1 = \sin\theta\ (11P_5 + 7P_3 + 3P_1)$$

$$P_6^2 = -30P_6 + 18P_4 + 10P_2 + 2P_0$$

$$P_6^3 = \sin\theta\ (-220P_5 + 112P_3 + 108P_1)$$

$$P_6^4 = 360P_6 - 864P_4 + 360P_2 + 144P_0$$

$$P_6^5 = \sin\theta\ (1320P_5 - 3696P_3 + 2376P_1)$$

$$P_6^6 = -720P_6 + 3888P_4 - 7920P_2 + 4752P_0$$

$P_7^0 = P_7$

$P_7^1 = \sin\theta \ (13P_6 + 9P_4 + 5P_2 + P_0)$

$P_7^2 = -42P_7 + 22P_5 + 14P_3 + 6P_1$

$P_7^3 = \sin\theta \ (-390P_6 + 126P_4 + 210P_2 + 54P_0)$

$P_7^4 = 840P_7 - 1760P_5 + 392P_3 + 528P_1$

$P_7^5 = \sin\theta \ (4680P_6 - 11016P_4 + 3960P_2 + 2376P_0)$

$P_7^6 = -5040P_7 + 23760P_5 - 39312P_3 + 20592P_1$

$P_7^7 = \sin\theta \ (-9360P_6 + 50544P_4 - 102960P_2 + 61776P_0)$

$P_8^0 = P_8$

$P_8^1 = \sin\theta \ (15P_7 + 11P_5 + 7P_3 + 3P_1)$

$P_8^2 = -56P_8 + 26P_6 + 18P_4 + 10P_2 + 2P_0$

$P_8^3 = \sin\theta \ (-630P_7 + 110P_5 + 322P_3 + 198P_1)$

$P_8^4 = 1680P_8 - 3120P_6 + 216P_4 + 960P_2 + 264P_0$

$P_8^5 = \sin\theta \ (12600P_7 - 25080P_5 + 2184P_3 + 10296P_1)$

$P_8^6 = -20160P_8 + 84240P_6 - 112752P_4 + 28080P_2 + 20592P_0$

$P_8^7 = \sin\theta \ (-75600P_7 + 1029600P_5 - 1262880P_3 + 308880P_1)$

$P_8^8 = 40320P_8 - 299520P_6 + 933120P_4 - 1497600P_2 + 823680P_0$

$$P_9^0 = P_9$$

$$P_9^1 = \sin\theta\ (17P_8 + 13P_6 + 9P_4 + 5P_2 + P_0)$$

$$P_9^2 = -72P_9 + 30P_7 + 22P_5 + 14P_3 + 6P_1$$

$$P_9^3 = \sin\theta\ (-952P_8 + 52P_6 + 432P_4 + 380P_2 + 88P_0)$$

$$P_9^4 = 3024P_9 - 5040P_7 - 264P_5 + 1344P_3 + 936P_1$$

$$P_9^5 = \sin\theta\ (28560P_8 - 48360P_6 - 7344P_4 + 20280P_2 + 6864P_0)$$

$$P_9^6 = -60480P_9 + 226800P_7 - 245520P_5 - 5040P_3 + 84240P_1$$

$$P_9^7 = \sin\theta\ (-342720P_8 + 1422720P_6 - 1866240P_4 + 374400P_2 + 411840P_0)$$

$$P_9^8 = 362880P_9 - 2419200P_7 + 6462720P_5 - 8225280P_3 + 3818880P_1$$

$$P_9^9 = \sin\theta\,(685440P_8 - 5091840P_6 + 15863040P_4 - 25459200P_2 + 14002560P_0)$$

$$P_{10}^0 = P_{10}$$

$$P_{10}^1 = \sin\theta\,(19P_9 + 15P_7 + 11P_5 + 7P_3 + 3P_1)$$

$$P_{10}^2 = -90P_{10} + 34P_8 + 26P_6 + 18P_4 + 10P_2 + 2P_0$$

$$P_{10}^3 = \sin\theta\,(-1368P_9 - 60P_7 + 528P_5 + 588P_3 + 312P_1)$$

$$P_{10}^4 = 5040P_{10} - 7616P_8 - 1144P_6 + 1584P_4 + 1720P_2 + 416P_0$$

$$P_{10}^5 = \sin\theta\,(57456P_9 - 83160P_7 - 30096P_5 + 27720P_3 + 28080P_1)$$

$$P_{10}^6 = -151200P_{10} + 514080P_8 - 449280P_6 - 120960P_4 + 151200P_2 + 56160P_0$$

$$P_{10}^7 = \sin\theta\,(-1149120P_9 + 4233600P_7 - 4308480P_5 - 685440P_3 + 1909440P_1)$$

$$P_{10}^8 = 1814400P_{10} - 10967040P_8 + 25309440P_6 - 24675840P_4 + 3427200P_2 + \\ + 5091840P_0$$

$$P_{10}^9 = \sin\theta\,(6894720P_9 - 45964800P_7 + 122791680P_5 - 156280320P_3 + \\ + 72558720P_1$$

$$P_{10}^{10} = -3628800P_{10} + 34272000P_8 - 142272000P_6 + 334886400P_4 - 465120000P_2 + \\ + 241862400P_0$$

$f(\varphi_2)$	$\int_0^{2\pi} \frac{\sin m(\phi_2-\phi_1)}{\sin(\phi_2-\phi_1)} \; f(\phi_2)\, d\phi_2$
1	$2\pi\,\delta_m^{\text{odd}}$
$\sin^2\varphi_2$	$\pi\delta_m^1 + 2\pi\sin^2\phi_1\,\delta_m^{\text{odd}>1}$
$\cos^2\varphi_2$	$\pi\delta_m^1 + 2\pi\cos^2\phi_1\,\delta_m^{\text{odd}>1}$
$\sin\varphi_2$	$2\pi\sin\phi_1\,\delta_m^{\text{even}>0}$
$\cos\varphi_2$	$2\pi\cos\phi_1\,\delta_m^{\text{even}>0}$
$\sin\varphi_2\cos\varphi_2$	$2\pi\sin\phi_1\cos\phi_1\,\delta_m^{\text{odd}>1}$
$\sin^2\varphi_2\cos\varphi_2$	$\frac{\pi}{2}\cos\phi_1\,\delta_m^2 + 2\pi\sin^2\phi_1\cos\phi_1\,\delta_m^{\text{even}>2}$
$\sin\varphi_2\cos^2\varphi_2$	$\frac{\pi}{2}\sin\phi_1\,\delta_m^2 + 2\pi\sin\phi_1\cos^2\phi_1\,\delta_m^{\text{even}>2}$
$\sin^3\varphi_2$	$\frac{3\pi}{2}\sin\phi_1\,\delta_m^2 + 2\pi\sin^3\phi_1\,\delta_m^{\text{even}>2}$
$\cos^3\varphi_2$	$\frac{3\pi}{2}\cos\phi_1\,\delta_m^2 + 2\pi\cos^3\phi_1\,\delta_m^{\text{even}>2}$

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PROPOSITION III

There are two parts to this proposition; both are concerned with the change of viscosity of solutions of long flexible molecules with rate of shear. It is first proposed that Kirkwood's theory of viscosity be applied to flexible molecules which are just beginning to deform, and secondly, it is proposed that the radius of gyration of random coil molecules can be related to the rate of shear by using viscosity versus shear rate data for DNA.

Part I

There exist no theoretical predictions concerning the dependence of viscosity on shear rate for macromolecular solutions except for the case of ellipsoidal molecules (1, 2) and infinitely long rods (3). A formal theory has been developed by Kirkwood (4) which is powerful enough to handle systems with molecules of any shape, but mathematical complexity has so far discouraged any application other than to rigid-rod type molecules.

Zimm and Crothers (5) have measured the change of viscosity of DNA solutions with rate of shear, and came up with results which look qualitatively like the results predicted by Scherega (2) for rigid ellipsoids. Both display zero slope for viscosity as a function of shear rate at zero shear.

The mechanism of viscosity versus shear rate in the case of rigid-rod type molecules is the tendency of the shear to align the molecules parallel to the flow lines, which alignment decreases the effective viscosity. The reason the viscosity decreases steadily versus increasing shear rate is the counterbalancing randomising effect of brownian motion, which becomes less intense as more torque is applied.

The mechanism of viscosity variation with shear rate in DNA solutions is probably much different, for DNA is by no means a rigid molecule. It possesses rod-like characteristics, but is rather long and flexible. Professor S. G. Mason and coworkers have performed measurements on long flexible rayon fibers and have observed their physical behavior as a function of rate of shear (6, 7). Long flexible filaments were noted to form "snake turns," "S-turns," and coils. Geometrically the simplest of these is the snake turn.

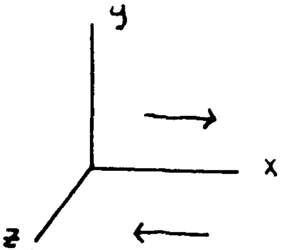
An application of Kirkwood's theory to snake turns approximated as ellipses looks difficult but feasible. It should be of interest as a first step toward understanding the behavior of flexible molecules such as DNA under shear. From Mason's measurements the diameter of a snake turn decreases as the rate of shear increases, which change will have an effect on the viscosity. The necessary relationships for this model will now be set up and the Kirkwood-Riseman equation written down.

The essential approximations, aside from those inherent in the Kirkwood theory, are

1. The particles will be treated as ellipses with $2n + 1$ hydrodynamic elements a distance b apart, and each possessing the same friction factor ζ. Mason's measurements show that this approximation may not be too bad as an average non-linear configuration.

2. The effect of brownian motion will be neglected. Including brownian motion would make an already complicated mathematical problem prohibitively difficult. DNA molecules are anyway quite large, though not as large as rayon fibers, and the diffusion constants are correspondingly quite small in comparison with smaller systems such as TMV or other molecules manifesting rigid-rod characteristics.

Consider the following situation



The arrows denote the direction of laminar motion of fluid. The fluid velocity is

$$v_x = \dot{\epsilon} y$$

The dissipation of energy is $\eta_0 \dot{\epsilon}^2$ (4). If a macromolecular particle is introduced whose center of mass is at the origin of the coordinate system, the dissipation of energy increases to some new value $\eta \dot{\epsilon}^2$. If the molecule has 2n+ 1 hydrodynamic elements, each with a characteristic friction factor ζ, the increase of energy dissipation is given by (4)

$$(\eta - \eta_0)\, \dot{\epsilon}^2 = \sum_{\ell=-n}^{n} \langle \vec{F}_\ell \cdot \vec{v}_\ell^{\,\circ} \rangle \tag{1}$$

where $\vec{F}_\ell$ is the force which the ℓ^{th} particle exerts on the fluid, and

$$\vec{v}_\ell^{\,\circ} = \dot{\epsilon}\, (\vec{R}_\ell^{\,\circ} \cdot \hat{e}_y)\, \hat{e}_x \tag{2}$$

where $\vec{R}_\ell^{\,o}$ is the vector from the center of mass of the particle to element ℓ.

Substitution of 2 into 1 gives

$$(\eta - \eta_0)\, \dot{\epsilon}^2 = \dot{\epsilon} \sum_{\ell=-n}^{n} (\vec{F}_\ell \cdot \hat{e}_x)(\vec{R}_\ell^{\,\circ} \cdot \hat{e}_y) \tag{3}$$

Hence

$$\frac{\eta - \eta_0}{\eta_0} = \frac{1}{\dot{\epsilon}\, \eta_0} \sum_{\ell=-n}^{n} (\vec{F}_\ell \cdot \hat{e}_x)(\vec{R}_\ell^{\,\circ} \cdot \hat{e}_y) = \frac{\zeta G}{\eta_0} \tag{4}$$

where G is clearly

$$G = \frac{1}{\dot{\epsilon}\, \zeta} \sum_{\ell=-n}^{n} (\vec{F}_\ell \cdot \hat{e}_x)(\vec{R}_\ell^{\,\circ} \cdot \hat{e}_y) \tag{5}$$

This gives the increase in specific viscosity for one particle, or equivalently the intrinsic viscosity when the concentration is expressed in number of particles per unit volume. Since the concentration usually used in intrinsic viscosity is grams solute per 100 grams solvent,

$$[\eta] = \lim_{c \to 0} \frac{\eta - \eta_0}{c\,\eta_0} = \frac{N \zeta G}{100 M \eta_0} \tag{6}$$

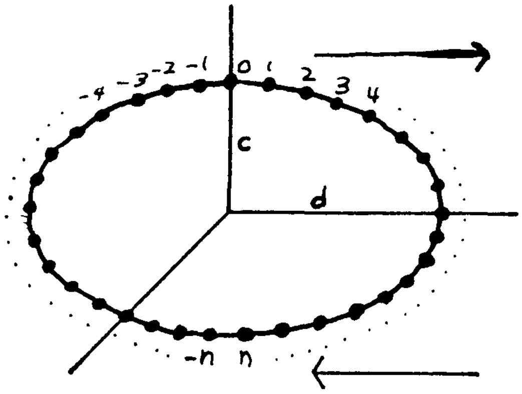
This is the relationship used in Kirkwood's theory.

If $[\eta]$ is a function of rate of shear, s, then

$$\frac{[\eta(s)]}{[\eta(o)]} = \frac{\eta_{sp}(s)}{\eta_{sp}(o)} = \frac{G(s)}{G(o)} \tag{7}$$

This is the relationship of interest in the study of shear dependence.

The model is an ellipse whose circumference is L.



The location of the beads is

$$c^2 x_\ell^{\,2} + d^2 y_\ell^{\,2} = c^2 d^2 \tag{8}$$

The circumference is

$$L = 4d \int_0^{\frac{\pi}{2}} \left(1 - \sin^2\varphi \sin^2\theta\right)^{\frac{1}{2}} d\theta = 4d\, E(\sin\varphi) \tag{9}$$

where E(x) is the complete elliptic integral of the second kind, and $\cos\varphi = c/d$. d and φ are thus not independent, but are related by equation 9.

Since brownian motion will be neglected, the hydrodynamic torques will be zero if the loop rotates such that the velocity of the particle, O, located at (O, c, O) is

$$\vec{u}_o = \frac{cd}{c+d}\,\dot{\epsilon}\,\hat{e}_x = \frac{d\,\dot{\epsilon}\cos\varphi}{1+\cos\varphi}\,\hat{e}_x \tag{10}$$

Each element, of course, has the same speed, given by the absolute value of 10. The velocity of other elements is

$$\begin{aligned}\vec{u}_\ell &= \frac{cd\dot{\epsilon}}{d+c}\;\frac{\hat{e}_x\, d^2 y_\ell + \hat{e}_y\, c^2 x_\ell}{(c^4 x_\ell^2 + d^4 y_\ell^2)^{1/2}} \\ &= \frac{d\,\dot{\epsilon}\cos\varphi}{1+\cos\varphi}\;\frac{\hat{e}_x\sqrt{d^2-x_\ell^2} + \hat{e}_y\cos\varphi\, x_\ell}{(d^2+\sin^2\varphi\, x_\ell^2)^{1/2}}\end{aligned} \tag{11}$$

The forces $\vec{F}_\ell$ necessary to determine the quantity G are derived from the equation

$$\vec{F}_\ell = \zeta(\vec{v}_\ell^{\,\circ} - \vec{u}_\ell) - \zeta\sum_{\substack{s=-n\\ \neq\ell}}^{n} \underset{\sim}{T}_{\ell,s}\cdot\vec{F}_s \tag{12}$$

The signs differ from Kirkwood's equation because of a slightly different convention in defining the $\vec{F}_\ell$. The Oseen tensor here is

$$\underset{\sim}{T}_{\ell,s} = \frac{\underset{\sim}{\mathbb{1}} + \hat{e}_{\vec{R}_s^\circ - \vec{R}_\ell^\circ}\,\hat{e}_{\vec{R}_s^\circ - \vec{R}_\ell^\circ}}{|\vec{R}_s^\circ - \vec{R}_\ell^\circ|} \tag{13}$$

where

$$\hat{e}_{\vec{R}_s^o - \vec{R}_\ell^o} = |\vec{R}_s - \vec{R}_s^o|^{-1}\left((x_s - x_\ell)\,\hat{e}_x + (y_s - y_\ell)\,\hat{e}_y\right) \tag{14}$$

Further

$$|\vec{R}_s^o - \vec{R}_\ell^o| = \sqrt{(x_s - x_\ell)^2 - (y_s - y_\ell)^2} \tag{15}$$

The coordinate x_ℓ is determined from the condition

$$\ell b = \int_0^{\sin^{-1}\left(\frac{x_\ell}{d}\right)} (1 - \sin^2\varphi \sin^2\theta)\,d\theta = E\left(\sin^{-1}\left(\frac{x_\ell}{d}\right), \varphi\right) \tag{16}$$

where $E(y,z)$ is the incomplete elliptic integral of the second kind.

The necessary relationships for determining the $\vec{F}_\ell$ as functions of d have been presented. The solution of equation 12 is feasible but obviously not simple.

It is now necessary to relate the rate of shear to the quantity d. Once this is done, the viscosity as a function of rate of shear can be calculated from equation 6. The relationship between d and the rate of shear is established by balancing the components of the $\vec{F}_\ell$ perpendicular to the elliptical perimeter and the forces arising from the tendency of the ellipse to revert to a circle, which can be calculated by knowing the bending moment per unit length of the molecule.

Part II

If it is assumed that the DNA molecule has the configuration of a random coil above shear rates of about 0.5 sec^{-1}, the data relating shear rate and specific viscosity advanced by Zimm and Crothers (5) can be used along with the viscosity theory of Kirkwood for random coil molecules to relate the average radius of gyration of a DNA molecule to shear rate.

According to Forgacs and Mason (7), very long flexible thread-like molecules tend to coil into knots upon application of shear. This leads to the conclusion that DNA molecules perhaps coil into tight knots on application of shear, with the tightness related to the magnitude of the shear. The data of Zimm demonstrate that the viscosity of DNA suspensions decreases with shear rate increase, so the above conclusion is at least not unreasonable.

According to Kirkwood and Riseman (8), the intrinsic viscosity for a random coil molecule is given by

$$[\eta] = \frac{N \zeta b^2}{3600 \eta_0 M_0} Z F(\lambda_0, Z^{\frac{1}{2}}) \qquad (1)$$

where N = Avogadro's number

ζ = friction constant for a monomeric unit on the coil

η_o = viscosity of medium

M_o = molecular weight of monomeric unit

Z = total number of monomeric units = M/M_o

$\lambda_o = \zeta/(6\pi^3)^{\frac{1}{2}}\ \eta_o b$

$$F(x) = \frac{6}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{K^2} \frac{1}{1 + x/\sqrt{K}}$$

For large Z, the following relationship holds

$$\lim_{\lambda_o Z^{\frac{1}{2}} \to \infty} \lambda_o Z^{\frac{1}{2}} F(\lambda_o Z^{\frac{1}{2}}) = 1.588 \qquad (2)$$

The radius of gyration of a random coil molecule is (9)

$$r_g = bz^{\frac{1}{2}} \qquad (3)$$

Combining 1, 2, and 3 gives

$$[\eta] = \frac{1.588\, N\, (6\pi^3)^{\frac{1}{2}}}{3600\, M}\ r_g^3 \qquad (4)$$

The important thing here is that the intrinsic viscosity is proportional to r_g^3. Thus, log $[\eta]$ should vary with log r_g^3 the same as with log $\eta_{sp}^{(s)}/\eta_{sp}^{(o)}$, which is the quantity given by Zimm and Crothers as a function of shear rate.

It is now assumed that

$$r_g(s) = s^m\, r_g(S) \qquad (5)$$

in the range of interest, which, according to Zimm and Crothers' data, lies between shear rates of about 0.5 $\sec^{-1}$ and some unspecified upper limit greater than 18.3 $\sec^{-1}$. The relationship defined clearly cannot hold as the shear rate vanishes, and this is the reason $r_g(S)$ is introduced, which is the radius of gyration at the bend of the viscosity versus shear rate curve, which is presumed to lie at the beginning of the range of validity.

A plot of $\log \eta_{sp}^{(s)}/\eta_{sp}^{(o)}$ versus log s is given on the graph. The line connecting the points is remarkably straight and thus indicates that the assumption of the type of dependence of the radius of gyration on shear rate is valid in this region. The slope of this line is about -1/5. Hence,

$$\begin{aligned} \log [\eta] &= \text{constant} + \log r_g^3(S) \\ &= \text{constant} + 3 \log r_g(S) + 3m\log s \end{aligned} \qquad (6)$$

or, as just stated,

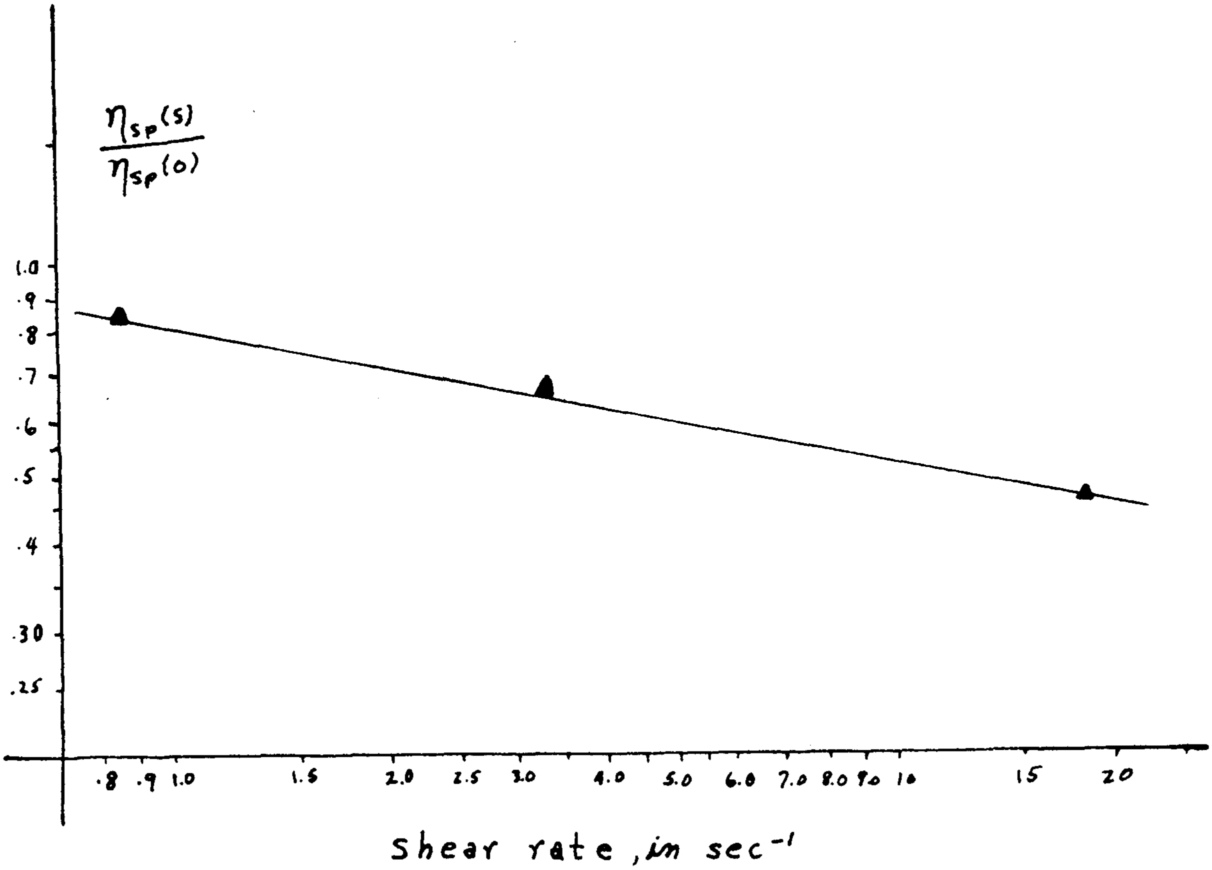
$$3m = -1/5$$

$$m = -1/15$$

Therefore,

$$r_g(s) = s^{-1/15}\, r_g(S) \qquad (7)$$

From the looks of Zimm and Crothers' graph, a good value of $r_g(S)$ is the radius of gyration at zero shear, which can be determined from viscosity data and the formula of Kirkwood and Riseman.


ηsp(s) / ηsp(0)
1.0
.9
.8
.7
.6
.5
.4
.30
.25
.8
.9
1.0
1.5
2.0
2.5
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
15
20
Shear rate, in sec⁻¹

It might be pointed out that an error was discovered in the work of Kirkwood and Riseman (9). When it was investigated, these authors were unable to immediately predict the magnitude of its correction. Their best guess was that it would alter somewhat the numerical constants. The original theory agreed excellently with experiments on polystyrene. In any event, changing the numerical constants will not alter equation 7, but may make $r_g(S)$ somewhat ill-defined.

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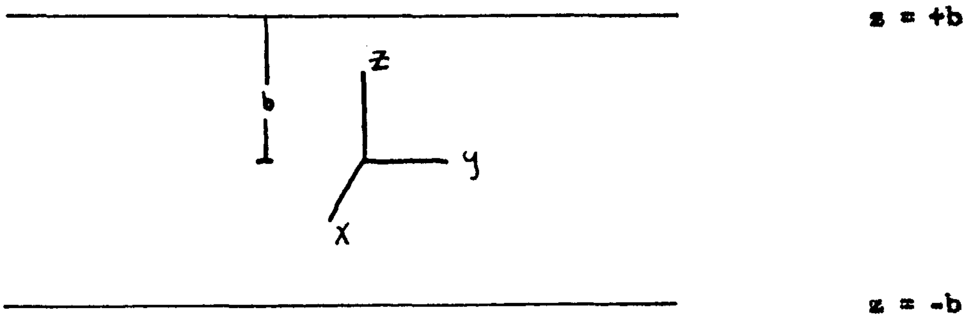
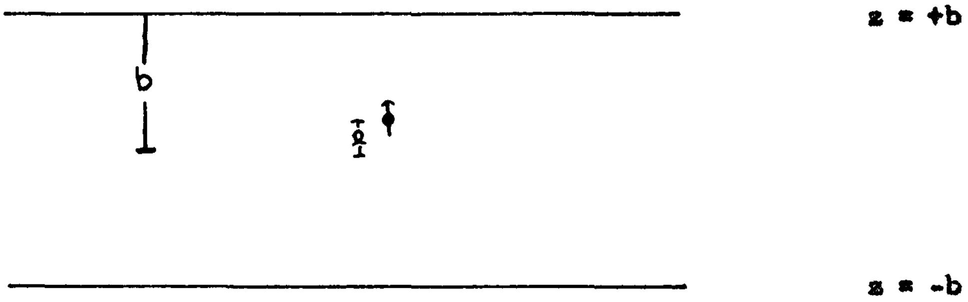
PROPOSITION IV

A method of calculating fluid velocity perturbations due to a small sphere moving perpendicularly between two infinite plane horizontal walls is presented. The sphere is approximated by a point force.

Consider a pair of parallel planes extending infinitely in the x and y directions and separated by a distance 2b. Define the z axis perpendicular to the planes, with the origin exactly halfway between them. The space between the planes is filled with a viscous fluid of viscosity η, and the fluid is at rest.



Introduce at the point $z = \ell$, $x = y = 0$ a point force $\vec{F}$ operating in the +z direction.



The components of induced velocity will now be derived.

The solution for the case of one plane was given by Lorentz (1), by noticing that if the quantities $v_x^{(1)}$, $v_y^{(1)}$, $v_z^{(1)}$, satisfy the hydrodynamic equations, so do the quantities

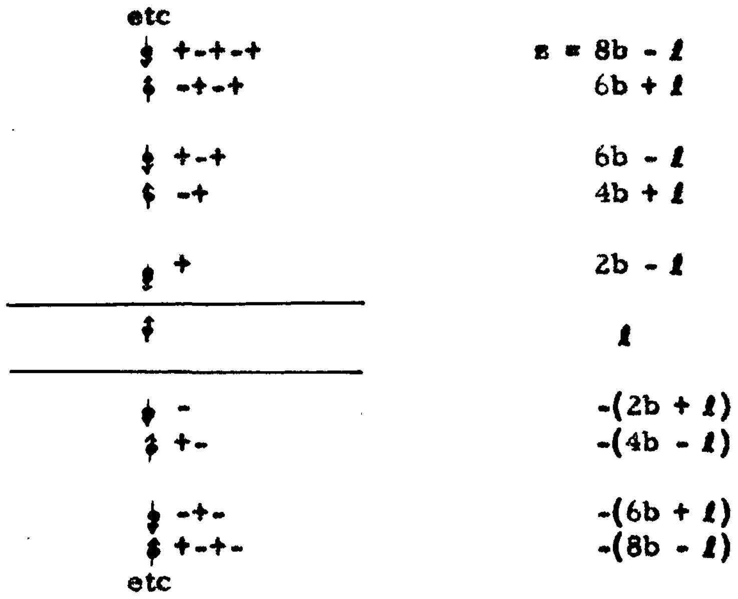
$$v_x^{(2)} = -v_x^{(1)} - 2(z+\alpha)\frac{\partial v_z^{(1)}}{\partial x} + (z+\alpha)^2\,\nabla^2 v_x^{(1)} \qquad (1a)$$

$$v_y^{(2)} = -v_y^{(1)} - 2(z+\alpha)\frac{\partial v_z^{(1)}}{\partial y} + (z+\alpha)^2\,\nabla^2 v_y^{(1)} \qquad (1b)$$

$$v_z^{(2)} = v_z^{(1)} - 2(z+\alpha)\frac{\partial v_z^{(1)}}{\partial z} + (z+\alpha)^2\,\nabla^2 v_z^{(1)} \qquad (1c)$$

In the case of two planes, it is possible to build up a series of images, in the spirit of electrostatic potential theory, to satisfy the boundary condition $\vec{v} = 0$ at $z = +b$ and $z = -b$. However, as might be expected, since the functions to be added onto the original infinite medium solution are vector functions, things are considerably more complicated than in electrostatic potential theory.

It is clear that the image forces are to be installed as follows:



The question now is how to transform the infinite medium solutions for these images in order to satisfy the boundary conditions.

The images are located at the points $(0, 0, z_i)$, where the z_i are given in the column to the right of the image diagram. The + and - notation by the arrows refers to which image is under consideration. For example, -refers to the image of the real force across the negative, or $z = -b$, plane. + carries the analogous meaning across the positive, or $z = +b$, plane. +- means similarly the image of the image - across the positive plane. The same rules apply for the images +-+, -+-; -+-+, +-+-; etc.

The components of velocity which are induced by a point force in the +z direction acting at the origin of an infinite medium are

$$v_x = \frac{F}{8\pi\eta} \frac{xz}{r^3} \tag{2a}$$

$$v_y = \frac{F}{8\pi\eta} \frac{yz}{r^3} \tag{2b}$$

$$v_z = \frac{F}{8\pi\eta} \left(\frac{1}{r} + \frac{z^2}{r^3} \right) \tag{2c}$$

These may also be written

$$v_x = \frac{F}{8\pi\eta} \left(- \frac{\partial^2}{\partial x \partial z} \right) r \tag{3a}$$

$$v_y = \frac{F}{8\pi\eta} \left(- \frac{\partial^2}{\partial y \partial z} \right) r \tag{3b}$$

$$v_z = \frac{F}{8\pi\eta}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) r \tag{3c}$$

where $r^2 = x^2 + y^2 + z^2 = \rho^2 + z^2$.

In the particular case of a point force at $z = \ell$, these become

$$v_x = \frac{F}{8\pi\eta}\left(-\frac{\partial^2}{\partial x\,\partial z}\right) r_0 \tag{4a}$$

$$v_y = \frac{F}{8\pi\eta}\left(-\frac{\partial^2}{\partial y\,\partial z}\right) r_0 \tag{4b}$$

$$v_z = \frac{F}{8\pi\eta}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) r_0 \tag{4c}$$

where $r_0 = \sqrt{\rho^2 + (z - \ell)^2}$.

It becomes particularly advantageous to work with the undifferentiated quantity r, since the modifications of the infinite field solutions for the images can be done with this parameter, leaving the differential operators unchanged.

It is now convenient to define the matrix $\underset{\sim}{R}(-\alpha)$

$$\underset{\sim}{R}(-\alpha) = \left\{\begin{matrix} -1 + (z+\alpha)^2\nabla^2 & 0 & -2(z+\alpha)\frac{\partial}{\partial x} \\ 0 & -1 + (z+\alpha)^2\nabla^2 & -2(z+\alpha)\frac{\partial}{\partial y} \\ 0 & 0 & 1 + 2(z+\alpha)\frac{\partial}{\partial z} + (z+\alpha)^2\nabla^2 \end{matrix}\right\} \tag{5}$$

and the column matrix

$$\underset{\sim}{\star} = \begin{Bmatrix} -\dfrac{\partial^2}{\partial x \partial z} \\ -\dfrac{\partial^2}{\partial y \partial z} \\ \dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} \end{Bmatrix} \tag{6}$$

so that equations 1 become

$$\vec{v}^{\,(2)} = \frac{F}{8\pi\eta}\, \underset{\sim}{R}(-\alpha) \cdot \underset{\sim}{\star}\; r \tag{7}$$

In terms of the quantities $\underset{\sim}{R}$ and $\underset{\sim}{\star}$, the velocities induced by the images + and - are

$$\vec{v}^{\,+} = -\frac{F}{8\pi\eta}\, \underset{\sim}{R}(b) \cdot \underset{\sim}{\star}\; r_{+} \tag{8a}$$

$$\vec{v}^{\,-} = -\frac{F}{8\pi\eta}\, \underset{\sim}{R}(-b) \cdot \underset{\sim}{\star}\; r_{-} \tag{8b}$$

The requirements on these, namely that $\vec{v}^{\,+}$ exactly cancel the effects from the real force at z = +b, and that $\vec{v}^{\,-}$ exactly cancel the effects from the real force at z = -b, are clearly satisfied.

The velocities arising from the images +- and -+ are derived by double use of the matrix operator $\underset{\sim}{R}$. The results are

$$\vec{v}^{\,+-} = \frac{F}{8\pi\eta}\, \underset{\sim}{R}(-b) \cdot \underset{\sim}{R}(-3b) \cdot \underset{\sim}{\star}\; r_{+-} \tag{9a}$$

$$\vec{v}^{\,-+} = \frac{F}{8\pi\eta}\, \underset{\sim}{R}(b) \cdot \underset{\sim}{R}(3b) \cdot \underset{\sim}{\star}\; r_{-+} \tag{9b}$$

The non-obvious part here is that the argument of the first modification operator $\underset{\sim}{R}$ is $\underset{-}{+}3b$. That this is indeed the case can be most easily demonstrated by direct substitution and verifying that v^{+-} exactly cancels v^{+} at $z = -b$, and that v^{-+} exactly cancels v^{-} at $z = +b$. Similarly,

$$\vec{v}^{\,+-+} = -\frac{F}{8\pi\eta}\,\underset{\sim}{R}(b)\cdot\underset{\sim}{R}(3b)\cdot\underset{\sim}{R}(5b)\cdot\underset{\sim}{\bigstar}\,r_{+-+} \tag{10a}$$

$$\vec{v}^{\,-+-} = -\frac{F}{8\pi\eta}\,\underset{\sim}{R}(-b)\cdot\underset{\sim}{R}(-3b)\cdot\underset{\sim}{R}(-5b)\cdot\underset{\sim}{\bigstar}\,r_{-+-} \tag{10b}$$

The z components of some of the images are, less the factor $\frac{F}{8\pi\eta}$

$$\begin{array}{l|l}
0 & \left\{\frac{1}{r_0} + \frac{(z-l)^2}{r_0{}^3}\right\} \\[2ex]
+ & -\left\{\frac{1}{r_+} + \frac{(z-2b+l)^2}{r_+{}^3} - \frac{2(z-b)(b-l)}{r_+{}^3}\left(1-3\,\frac{(z-2b+l)^2}{r_+{}^2}\right)\right\} \\[2ex]
- & -\left\{\frac{1}{r_-} + \frac{(z+2b+l)^2}{r_-{}^3} + \frac{2(z+b)(b+l)}{r_-{}^3}\left(1-3\,\frac{(z+2b+l)^2}{r_-{}^2}\right)\right\} \\[2ex]
+- & \left\{\frac{1}{r_{+-}} + \frac{(z+4b-l)^2}{r_{+-}^3} - \frac{4b(z+2b-l)}{r_{+-}^3}\left(1-3\,\frac{(z+4b-l)^2}{r_{+-}^3}\right)\right. \\[2ex]
 & \qquad\left. - \frac{8b(z+b)(z+4b-l)(b-l)}{r_{+-}^5}\left(9-15\,\frac{(z+4b-l)^2}{r_{+-}^2}\right)\right\}
\end{array} \tag{11}$$

In general, the total velocity is given by

$$\begin{aligned}\vec{v} = \frac{F}{8\pi\eta}\Bigg\{ -\sum_{\mu=1,3,\dots}^{\infty}\Bigg(&\left[\prod_{i=0}^{\frac{\mu-1}{2}} \underset{\sim}{R}(\mu b-2ib)\right]\cdot\underset{\sim}{\bigstar}\left(\rho^2+(2\mu b-\ell-z)^2\right)^{\frac{1}{2}}\\ &+\left[\prod_{i=0}^{\frac{\mu-1}{2}} \underset{\sim}{R}(2ib-\mu b)\right]\cdot\underset{\sim}{\bigstar}\left(\rho^2+(2\mu b+\ell+z)^2\right)^{\frac{1}{2}}\Bigg)\\ +\sum_{\mu=0,2,\dots}^{\infty}\Bigg(&\left[\prod_{i=0}^{\mu/2} \underset{\sim}{R}(\mu b+2ib+\ell)\right]\cdot\underset{\sim}{\bigstar}\left(\rho^2+(z-2\mu b-\ell)^2\right)^{\frac{1}{2}}\\ &+\left[\prod_{i=0}^{\mu/2} \underset{\sim}{R}(-\mu b+2ib-\ell)\right]\cdot\underset{\sim}{\bigstar}\left(\rho^2+(z+2\mu b-\ell)^2\right)^{\frac{1}{2}}\Bigg)\Bigg\}\end{aligned} \qquad (12)$$

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PROPOSITION V

Criticisms of a paper (1) concerning the concentration dependence of friction factors of random coil molecules are presented. These comments should be of importance since concentration-dependent friction factors for macromolecules are not well understood theoretically (2). Specifically, it will be shown that although Yamakawa's results regarding flexible molecules are probably valid, the basic theory which led to the relationship used to calculate these results is highly questionable. A more satisfactory basis for the results is presented.

The friction factor which Yamakawa presents is that one relative to the macroscopic average velocity of the fluid with respect to the laboratory. Of course, for such a case no infinities arise, but there is no interest in this friction constant unless the average velocity with respect to the laboratory is known. The Stokes theory which Yamakawa uses will predict infinity for this velocity; however, since such is not the case physically, Yamakawa implicitly assumes that this velocity is zero. Such an assumption is not very enlightening physically.

To see why Yamakawa's equation 14

$$\langle F_i^{\alpha} \rangle = \zeta \vec{u} - \zeta \sum_{\substack{j=1 \\ \neq i}}^{n} \langle \underset{\sim}{T}_{ij}^{\alpha\alpha} \rangle \cdot \langle \vec{F}_j^{\alpha} \rangle + \zeta \sum_{\substack{\beta=1 \\ \neq \alpha}}^{N} \sum_{j=1}^{n} \left[\langle T_{\bullet j}^{\alpha\beta} \rangle' - \langle T_{ij}^{\alpha\beta} \rangle \right] \cdot \langle F_j^{\beta} \rangle$$

is valid if $\vec{u}$ is defined as the velocity of the center of mass of the macromolecule with respect to the laboratory, rather than the fluid, it is only necessary to develop the ideas presented in the text of the thesis concerning concentration-dependent phenomena. There it was found that the effects with respect to the laboratory at the site of one molecule due to all the other molecules was of the form

$$c\int_{\substack{\text{volume}\\\text{allowed}}} \underset{\sim}{T} \cdot \vec{F}\, dv$$

where $\underset{\sim}{T}$ was some appropriate Oseen tensor (<u>not</u> the infinite medium tensor used by Yamakawa). For both types of Oseen tensor considered (rigid wall and hypothetical concentric sphere), this integral has the properties

$$c\int_{\substack{\text{TOTAL}\\\text{VOLUME}}} \underset{\sim}{T}\cdot\vec{F}\, dv = c\int_{\substack{\text{excluded}\\\text{volume}}} \underset{\sim}{T}\cdot\vec{F}\, dv + c\int_{\substack{\text{volume}\\\text{allowed}}} \underset{\sim}{T}\cdot\vec{F}\, dv \approx 0$$

The Oseen tensor actually used by Yamakawa is (equation 21)

$$[\, g(\vec{R}) - 1\,]\ \underset{\sim}{T}(\infty)$$

where $g(\vec{R})$ is the radial distribution function and $T(\infty)$ is the infinite medium Oseen tensor. Now if $g(\vec{R})$ is unity except in the excluded volume where it is zero, we get

$$\int_{\substack{\text{TOTAL}\\\text{VOLUME}}} (g(\vec{R})-1)\ \underset{\sim}{T(\infty)}\cdot\vec{F}\, dv = -c\int_{\substack{\text{excluded}\\\text{volume}}} \underset{\sim}{T(\infty)}\cdot\vec{F}\, dv$$

where in both integrals infinite medium Cseen tensors are used. In the general case when $g(\vec{R})$ is a more realistic radial distribution function, we have firstly

$$0 \approx c\int_{\substack{\text{excluded}\\ \text{volume}}} \underset{\sim}{T}\cdot\vec{F}\,dv + c\int_{\substack{\text{allowed}\\ \text{volume}}} g(\vec{R})\,\underset{\sim}{T}\cdot\vec{F}\,dv - c\int_{\substack{\text{allowed}\\ \text{volume}}} [g(\vec{R})-1]\,\underset{\sim}{T}\cdot\vec{F}\,dv$$

Now in the region where $[g(\vec{R})-1]$ is nonzero, $T \approx T(\infty)$, so that

$$c\int_{\substack{\text{allowed}\\ \text{volume}}} g(\vec{R})\,\underset{\sim}{T}\cdot\vec{F}\,dv \cong c\int_{\substack{\text{allowed}\\ \text{Volume}}} [g(\vec{R})-1]\,\underset{\sim}{T(\infty)}\cdot\vec{F}\,dv - c\int_{\substack{\text{excluded}\\ \text{volume}}} \underset{\sim}{T}\cdot\vec{F}\,dv \approx c\int_{\substack{\text{TOTAL}\\ \text{VOLUME}}} [g(\vec{R})-1]\,\underset{\sim}{T(\infty)}\cdot\vec{F}\,dv$$

which is Yamakawa's result.

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