MODELLING BIOLOGICAL MACROMOLECULES IN SOLUTION: THE GENERAL TRI-AXIAL ELLIPSOID

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CHAPTER 2

The Viscosity Increment for a Dilute, Newtonian Suspension of Tri-axial Ellipsoids

2.1. Hydrodynamic Forces and Brownian Motion

Although the forces and torques exerted upon a suspended particle by a fluid are all ultimately of molecular origin, it is convenient to distinguish those that can be explained by continuum hydrodynamics from those, due to molecular fluctuations, that give rise to Brownian motion. If we first completely neglect the Brownian motion, it is clear that, once a steady state has been attained, suspended particles free of any external imposed impressed forces or torques must move in such a way that the net hydrodynamic force and torque, T_H acting upon them are zero, i.e. $T_H = 0$.

Let us consider a steady simple shearing flow (section 1.3.), as in, for example, a simple capillary or Ubbelohde viscometer experiment (Yang, 1961). The motion of the fluid in the neighbourhood of any point can be decomposed into three components; a translational velocity which varies from point to point, an angular velocity which for this type of flow is the same for all points, and a pure straining motion which again is the same for all points. If now a single, neutrally bouyant, rigid ellipsoidal particle is introduced the flow will be disturbed, although at large distances from the ellipsoid the disturbance will tend to zero. We shall assume that the motion of the ellipsoid and of the fluid is such that the Reynold's number (Batchelor, 1967) is very small. Then it is possible on the basis of work by Oberbeck (1876) and Jeffrey (1922) to say what the hydrodynamic forces and torques acting upon the particle are. In particular it is known that the force will be zero when the translational velocity of the particle is the same as the translational velocity of the point in the undisturbed flow at which the point is suspended. The situation for angular velocity is more complicated since two factors come into play; one gives a torque if the angular velocity of the particle differs from the angular velocity defined by the undisturbed flow (or, equivalently, by the actual flow at infinity), whilst the other gives a torque if the principal axes of the ellipsoid have a different orientation from the principal axes of the straining motion defined by the undisturbed flow. Taken together, these mean that the angular motion of the particle under zero hydrodynamic torque conditions is very complicated (Chwang, 1975) and a complete solution for it is not known.

Turning to the Brownian motion which is in the nature of fluctuations the simplest question we can ask is what is the average velocity and the average angular velocity of the particle? By the average we mean in the first instance the time average, although in practice this will be assumed equal to the volume average taken over an ensemble over a very large number of particles suspended in unit volume (see Batchelor, 1970 for a detailed discussion of various methods of averaging). Ignoring for the moment the hydrodynamic forces, we can answer the question by saying that on average the particle is at rest in the local frame of reference defined by the undisturbed flow. In other words it is on average moving with the translational velocity of the point in the undisturbed flow at which it is suspended and with the angular velocity defined by the undisturbed flow (Kuhn & Kuhn, 1945, Brinkman et al, 1949, Scheraga, 1955).

When we come to consider the combined effect of the hydrodynamic forces and the Brownian motion no problem arises with the translational motion since both effects tend in the same direction - motion with the translational velocity of the flow. But for the angular motion the situation is less simple, the two effects do not have the same tendancy and we must consider a range of possibilities depending on the relative strengths of the two. This range is represented by the Peclet number

$\alpha = G/\theta$ (Brenner, 1972a) where G is the shear rate and θ the mean rotational diffusion coefficient. We shall only be considering the case of overwhelming Brownian motion ($\alpha \to 0$) in which the hydrodynamic effects are completely negligible compared with the Brownian motion effects. Thus we shall take it that on average the particles are rotating with the local angular velocity of the ambient flow; and we may additionally assume that the orientation of the particles will be random. This last fact would not be so if hydrodynamic forces and torques were not negligible for they introduce systematic motions and hence preferred orientations.

2.2. The Simha Model of Overwhelming Brownian Motion

We consider a homogeneous dilute suspension of identical rigid ellipsoids randomly oriented in an incompressible Newtonian fluid in which they are neutrally buoyant. The ambient flow is taken to be a slow simple shearing flow, whilst the suspended particles are taken to be moving with the velocity and the angular velocity of the ambient flow appropriate to the point at which each is suspended. Near each particle this ambient flow is disturbed but is still taken to be a slow (low Reynold's number) flow so that we may apply the classical results of Jeffrey (1922).

This model, which is taken to be appropriate for the case of overwhelming Brownian motion derives from Simha (1940) although in his original work doubt is left about whether or not the particles are rotating with the local angular velocity of the fluid. An attempt to clear this difficulty is made below (section 2.6.). The key simplifying feature of the model introduced by Simha is that it eliminates the complicated statistical problem presented by the Brownian motion by substituting an assembly of particles all moving with the average motion. This, together with the assumptions of diluteness and random orientation, allows us to compute the effect of the suspended particles by simply summing their individual effects. The isotropy of the particle distribution in the model means that non-Newtonian behaviour will not appear, and also allows us to use the energy dissipation method of computing the viscosity (Batchelor, 1970, Brenner, 1972b, p93).

The simplifications of the model are achieved, however, at a price. Non-Newtonian and concentration dependent effects, which to the theoretical rheologist are of the greatest interest, have been deliberately discarded; and the model can say nothing about lesser degrees of Brownian motion. In effect we shall be calculating the first term of a series; nevertheless this is of great value to the molecular biologist who can deliberately arrange the conditions of a viscosity experiment so that the model is applicable:

(i) Giesekus (1962) has shown that non-Newtonian normal stress effects are of 2nd order, and can thus be neglected for very low shear rates as in, for example, a capillary viscometer (Yang, 1961);

(ii) Viscosity coefficients are normally extrapolated to 'infinite dilution' i.e. zero concentration-dependent effects, to give the 'intrinsic viscosity' (Van Holde, 1971), related to the viscosity increment by equation (8).

2.3. The Viscosity Increment

We let η be the viscosity measured in an experiment on a dilute suspension of particles in a fluid of viscosity η_o. If ϕ is the volume concentration - the total volume of the particles in unit volume of the suspension - then the viscosity increment ν is defined, from equation (7), by

$$\frac{\eta}{\eta_o} = 1 + \nu\phi \tag{65}$$

where, when ν is independent of ϕ, the linear dependence of η/η_o upon ϕ gives the empirical characteristic of a dilute suspension. From the theoretical point of view however, a dilute suspension is one in which there are no hydrodynamic interactions between the particles and thus one in which each particle independently contributes to the viscosity the same amount it would were it alone present. This contribution for a general ellipsoidal particle was first calculated by Jeffrey (1922) using the simple energy dissipation analysis for averaging over the particle ensemble (Batchelor, 1970) and it is a straightforward matter to extend his results to cover the case of ellipsoids rotating with the local angular velocity of the ambient flow as required by our model.

2.4. The Flow Velocity and Pressure

In order to calculate the additional dissipation of energy caused by introducing the particle into a given flow, we compare that given flow with the consequent disturbed flow within a suitable sphere, S, of radius R, centred on the particle position. We impose two requirements upon S: first, that it is small compared with the scale of spatial variations in the given flow, and thus within it that flow is effectively given as a linear variation of velocity with position; secondly, that it is large compared with the size of the particle, and thus that the disturbed flow will not appreciably differ from the given flow by the time the surface of S is reached. Naturally, these requirements can only be met when the particle is, as we have assumed, very much smaller than the scale of spatial variations in the velocity field of the given flow.

For our purposes then, the disturbed flow may be taken to be the flow of an incompressible fluid in the region between the rotating ellipsoidal surface of the particle and the concentric spherical surface S. On the inner surface we impose the usual no-slip boundary condition, whilst on S we require the velocity field to be equal to its value in the original flow. We give the velocity components of the two flows with respect to rectangular Cartesian axes fixed in the rotating particle so that its ellipsoidal surface will always be given by

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1 \tag{66}$$

The undisturbed flow is given, within S, by

$$u_i^o = g_{ij}\, x_j$$

where g_{ij} are the components of the velocity gradient tensor which are by our assumptions, independent of position within S. In this equation and in subsequent equations, the indices range over the values 1,2,3 and the summation convention is used whereby when an index is repeated within a term a summation is indicated over the three values of that index.

Using ellipsoidal harmonics, Jeffrey was able to give the flow velocity and pressure in the region of S for R large, but finite. He gives the result under the assumption that the angular velocity is such that no net hydrodynamic torque acts on it, i.e. hydrodynamic effects alone affect the motion of the particle. In order to consider the Brownian motion we follow Simha in dropping this restriction whence the flow near S is found, to leading order, to be

$$u_i = u_i^o - 4\Phi x_i \left(\frac{1}{r^5} - \frac{1}{R^5}\right) + \frac{5\partial\Phi}{\partial x_i} \left(\frac{1}{R^3} - \frac{r^2}{R^5}\right) \tag{67}$$

In this equation, $\Phi = A_{ij}x_ix_j$, whilst the A_{ij} themselves are coefficients independent of position but dependent on the g_{ij} and the components, ω_i of the angular velocity of the particle; their explicit values are given by Jeffrey (see Table 4 for the relationship between his notation and ours). We consider the values of the A_{ij} below.

On the assumption that terms of second order in the velocity may be neglected and that the particle spins are of the same order as the fluid velocities, the dynamical equation for the fluid reduces to

$$\eta \nabla^2 \underline{u} = \nabla p \tag{68}$$

from which the pressure, p, can be found. For the disturbed flow we find the pressure on S to be

$$p = p_o - \frac{50\,\eta\,\Phi}{R^5} \tag{69}$$

where p_o is a constant.

2.5. The Dissipation of Energy

Assuming a steady state, we can compare the rates of dissipation of energy within S in the two flows by comparing the corresponding rates for working of the viscous stresses on the surface S. This rate of working, dW/dt, is given by

$$\frac{dW}{dt} = \int_S u_i^o \sigma_{ij} n_j \, dS \tag{70}$$

where

$$\sigma_{ij} = - p\,\delta_{ij} + \eta \left(\frac{\partial u_j}{\partial x_i} + \frac{\partial u_i}{\partial x_j} \right) \tag{71}$$

are the components of the stress tensor, and

$$n_j = \frac{x_j}{R} \tag{72}$$

are the components of the unit normal to S.

For the disturbed flow we find

$$\frac{dW}{dt} = \frac{8}{3}\pi\eta\, a_{ij} a_{ij} R^3 + \frac{32}{3}\pi\eta\, A_{ij} g_{ij} \tag{73}$$

where the $a_{ij} = \frac{1}{2}(g_{ij} + g_{ji})$ are the components of the local distortion in the undisturbed flow. On the other hand, the well-known formula of Stokes gives, for the undisturbed flow

$$\frac{dW}{dt} = \frac{8}{3}\pi\eta\, a_{ij} a_{ij} R^3 \tag{74}$$

We thus obtain an expression for Δ , the extra dissipation of energy when the particle is present, namely

$$\Delta = \frac{32}{3}\pi\eta\, A_{ij} g_{ij} \tag{75}$$

If we split g_{ij} into its symmetric and skew-symmetric parts, we have

$$\Delta = \frac{32}{3}\pi\eta\, (A_{ij} a_{ij} + A_{ij} \xi_{ij}) \tag{76}$$

where $\xi_{ij} = \frac{1}{2}(g_{ij} - g_{ji})$. Jeffrey, as a consequence of the dynamical assumption mentioned above, was working with symmetrical A_{ij}, and so naturally obtained only the first term in our expression for Δ; and it appears that Simha, although he removed the restriction on A, failed to find the second term. The consequence of this for his calculation will now be discussed.

2.6. The Particle Rotation

Simha takes the average angular velocity to be zero and on this basis calculates his well known formula for ν (equation 9), a formula which has been shown to give good agreement with observations (Mehl, Oncley & Simha, 1940, Tanford, 1961). A few years later, Saito (1951) using the assumption that the particles should rotate on average with the local undisturbed rotation of the fluid obtained precisely the same result; he suggested that Simha "has committed some errors in calculation" but does not investigate the matter further. Using Jeffrey's notation (Table 4) we have:

$$A_{ij}a_{ij} = (A\underline{a} + B\underline{b} + C\underline{c}) + (F + F')\underline{f} + (G + G)\underline{g} + (H + H')\underline{h} \tag{77}$$

$$A_{ij}\xi_{ij} = (F' - F)\xi + (G' - G)\eta + (H' - H)\zeta \tag{78}$$

whilst the values of, for example, F and F' are

$$F = \frac{\beta_o \underline{f} - c^2\alpha'_o(\xi - \omega_1)}{2\alpha'_o (b^2\beta_o + c^2\gamma_o)} \tag{79}$$

$$F' = \frac{\gamma_o \underline{f} + b^2\alpha_o' (\xi - \omega_1)}{2\alpha_o' (b^2\beta_o + c^2\gamma_o)} \tag{80}$$

In Jeffrey's paper the α_o' etc. in the numerators of the above expressions are misprinted as α_o etc.

We can thus deduce that

$$(F + F')\underline{f} = \frac{\frac{2\alpha_o''}{\alpha_o'} \underline{f}^2 + (b^2 + c^2)\underline{f}^2 + (b^2 - c^2)(\xi - \omega_1)\underline{f}}{2(b^2\beta_o + c^2\gamma_o)} \tag{81}$$

$$(F' - F)\xi = \frac{(b^2 - c^2)\underline{f}\xi + (b^2 + c^2)(\xi - \omega_1)\xi}{2(b^2\beta_o + c^2\gamma_o)} \tag{82}$$

where we have utilised the various relations between α_o, β_o etc. that are given by Jeffrey.

Now Simha apparently did not find the $A_{ij}\,\xi_{ij}$ term and thus would not have had terms like $(F' - F)$ in his calculation. We can see, however, that taking $\omega_1 = 0$ as he apparently did, in the $(F + F')\underline{f}$ term gives the same final result as taking $\omega_1 = \xi$ in the sum of the $(F + F')\underline{f}$ and the $(F' - F)\xi$ terms. Since the same argument applies to the other terms we conclude that Simha's formula (equation 9) although incorrect for $\omega_i = 0$ on account of the omission of the term $A_{ij}\,\xi_{ij}$, is, by a lucky coincidence, actually correct if $\omega_1 = \xi$, $\omega_2 = \eta$, $\omega_3 = \zeta$.

It is worth noting that if one does take $\omega_1 = 0$ and includes the $A_{ij}\,\xi_{ij}$ term, one obtains for spherical particles $\nu = 4$, in contrast to Einsteins (1906, 1911) value of 2.5. The result $\nu = 4$ for $\omega_i = 0$ agrees with that previously found by Brenner (1970). In all that follows we take the assumption that $\omega_1 = \xi$ etc. i.e. that the particles are on average rotating with the local angular velocity of the fluid.

2.7. The Calculation of ν

To complete our calculation we take, as before, the given flow to be locally a simple shearing flow with shear rate G. The principal axes of any particular particle will not in general coincide with the shear axes but, using the Euler angles to describe relative orientation of the two sets of axes, we can calculate the components g_{ij} relative to the particle axes in terms of G and the Euler angles θ, ϕ and ψ. Hence we can obtain Δ for that particle as a function of these variables; the details can be found at least for a special case in Jeffrey's paper (1922). Since Jeffrey's calculations show that the A_{ij} are linear in the g_{ij}'s, it follows that Δ will involve G^2 as a factor and hence that the total dissipation will be of the form ηG^2 as originally asserted.

To find the total dissipation in unit volume we average the effects of the N particles on the assumption that they are randomly oriented, obtaining

$$\bar{\Delta} = \frac{N}{2\pi}\int_0^{2\pi}\left\{\frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi}\Delta(\theta,\phi,\psi)\,\sin\theta\,d\theta\,d\phi\right\}d\psi \tag{83}$$

The integrations yield

$$\bar{\Delta} = \frac{32}{3}\,\pi\,\eta\,NG^2 Z \tag{84}$$

where

$$Z = \frac{1}{30}\left(\frac{\alpha_o'' + \beta_o'' + \gamma_o''}{\beta_o''\gamma_o'' + \gamma_o''\alpha_o'' + \alpha_o''\beta_o''}\right)$$

$$+ \frac{1}{40}\left(\frac{\beta_o + \gamma_o}{\alpha_o'(b^2\beta_o + c^2\gamma_o)} + \frac{\gamma_o + \alpha_o}{\beta_o'(c^2\gamma_o + a^2\alpha_o)} + \frac{\alpha_o + \beta_o}{\gamma_o'(a^2\alpha_o + b^2\beta_o)}\right) \quad (85)$$

Thus ν is determined from

$$\eta\nu V G^2 = \eta\nu N\frac{4}{3}\pi abc G^2 = \frac{32}{3}\pi\eta N G^2 Z \quad (86)$$

as

$$\nu = \frac{8Z}{abc} \quad (87)$$

Hence on substituting for Z we obtain

$$\nu = \frac{1}{abc}\left\{\frac{4(\alpha_o'' + \beta_o'' + \gamma_o'')}{15(\beta_o''\gamma_o'' + \gamma_o''\alpha_o'' + \alpha_o''\beta_o'')} + \frac{1}{5}\left[\frac{\beta_o + \gamma_o}{\alpha_o'(b^2\beta_o + c^2\gamma_o)} + \frac{\gamma_o + \alpha_o}{\beta_o'(c^2\gamma_o + a^2\alpha_o)} + \frac{\alpha_o + \beta_o}{\gamma_o'(a^2\alpha_o + b^2\beta_o)}\right]\right\} \quad (88)$$

where a,b,c are the semi-axes, and the elliptic integrals α_o etc. now depend on a,b and c (Appendix I).

The formula reduces to the Simha-Saito formula (equation 9) when b=c, and gives Einstein's value of 2.5 when a=b=c. It may be of interest to note that had we followed Simha in taking $\omega_i = 0$ then Z would have contained the following term in addition to those given above,

$$\frac{1}{24}\left\{\frac{b^2 + c^2}{b^2\beta_o + c^2\gamma_o} + \frac{c^2 + a^2}{c^2\gamma_o + a^2\alpha_o} + \frac{a^2 + b^2}{a^2\alpha_o + b^2\beta_o}\right\} \tag{89}$$

It is the presence of this added term that gives the value of $\nu = 4$ for spheres rather than the Einstein value $\nu = 2.5$ which is obtained when it is absent. The value of 2.5 has been confirmed experimentally for polystyrene latex spheres by Cheng & Schachman (1955).

2.8. Discussion

An equation similar to (88) was given by Batchelor (1970) on the assumption that the suspended particles, although randomly oriented, moved so that zero hydrodynamic torque acted upon them. His result was

$$\nu = \frac{1}{abc}\left\{\frac{4(\alpha_o'' + \beta_o'' + \gamma_o'')}{15(\beta_o''\gamma_o'' + \gamma_o''\alpha_o'' + \alpha_o''\beta_o'')} + \frac{2}{5}\left[\frac{1}{\alpha_o'(b^2 + c^2)} + \frac{1}{\beta_o'(c^2 + a^2)} + \frac{1}{\gamma_o'(a^2 + b^2)}\right]\right\} \tag{90}$$

when written in the same notation as we have used before. It does not seem likely that (90) would be applicable to the case of overwhelming Brownian motion since one would need to include the Brownian torque T_B as well as the purely hydrodynamic torque, T_H in satisfying the condition of zero net torque, i.e.

$$T_B + T_H = 0 \tag{91}$$

Random orientation alone is not a sufficient characterisation of overwhelming Brownian motion since one also needs to describe correctly the distribution of the angular velocity. Both (88) and (90) are obtained by methods that avoid the full statistical treatment of the angular motion but as explained earlier we consider the simplified model underlying (88) to be the appropriate one for overwhelming Brownian motion. In effect, formula (88) generalises the Simha-Saito equation for ellipsoids of revolution, whilst (90) generalises formulae of Jeffrey for ellipsoids of revolution. In general the two formulae give quite different results as can be seen from Figure 25 and Table 5, both of which are for convenience restricted to the case of ellipsoids of revolution. Since (90) does not reduce to the classical Simha-Saito formula the classic experimental evidence on macromolecules which favours the latter (Mehl, et al, 1940, Lauffer, 1942) strengthens the view that (90) is incorrect. More recent experimental evidence is given by Tanford (1961) who allows for particle swelling due to solvation and Table 6 extends his tables to include a comparison with the Jeffrey-Batchelor equation. The table compares the axial ratio inferred from translational diffusion experiments with that inferred from viscometric experiments on the basis first of the Simha-Saito equation and secondly of the Jeffrey-Batchelor equation. Tanford (1961) says "within the accuracy of the measurements, the description of globular proteins in aqueous solution provided by the (Simha-Saito) equation is identical with that provided by (translational) diffusion". On the other hand we see that the Jeffrey-Batchelor equation gives values of the axial ratio that are consistently too high and outside the expected experimental error bounds. We conclude that (90) is not applicable to the cases of interest to the molecular biologist.

As previously stated, we have avoided the full statistical treatment of the angular motion but have made the assumption of particles being on average at rest in the local referential frame in which they are suspended to be appropriate for the case of overwhelming Brownian motion. Although this has been rigorously proved only for axisymmetric particles (Brenner, 1972), we have made the assumption that it will be a good approximation for general tri-axial ellipsoids, at least for low axial ratios.

Since the derivation of equation (88) a general analysis using the full statistical treatment of the angular motion has been given by Rallison (1978). His results for the case of overwhelming Brownian motion show that to first-order in the shear rate the non-Newtonian stress effects vanish, which is consistent with our assumption of Newtonian behaviour for very low shear rates. He also gives an expression for ν correct to first-order in the shear rate, although not in the form of a simple formula like equation (88), but by using numerical methods Rallison is able to give a plot of ν for various axial ratios; the results are clearly very close to those obtained from equation (88) - compare my Figure 26 with Rallison's Figure 7. However, an exact comparison (personal communication by J.M. Rallison) shows a very slight discrepancy between values from equation (88) and Rallison's procedure, although no difference at levels likely to be experimentally significant for globular particles (i.e. a/b: 1.0 - 3.0, b/c: 1.0 - 3.0) is observed, and the discrepancy is not apparent within four significant figures for a/b: 1.0 $\rightarrow$ 2.0, b/c: 1.0 $\rightarrow$ 2.0. The values given in Table 7 are therefore definitive.

It has been indicated to us (J.M. Rallison, H. Brenner, private communications of unpublished work) that our formula requires the addition of a very small term related to the deviation from our assumed condition of non-axisymmetric particles rotating on average with the local angular velocity of the fluid:

$$-\frac{1}{5abc}\left\{\frac{\left[\frac{a^2-b^2}{a^2\alpha_o+b^2\beta_o}+\frac{b^2-c^2}{b^2\beta_o+c^2\gamma_o}+\frac{c^2-a^2}{c^2\gamma_o+a^2\alpha_o}\right]^2}{\left[\frac{a^2+b^2}{a^2\alpha_o+b^2\beta_o}+\frac{b^2+c^2}{b^2\beta_o+c^2\gamma_o}+\frac{c^2+a^2}{c^2\gamma_o+a^2\alpha_o}\right]}\right\} \qquad (88b)$$

The numerical results show our approximation to be extremely accurate for 'globular' particles, as noted above, but for certain particles of higher asymmetry calculations suggest that deviations of up to 1% in ν can arise. It is clear though that our formula provides a good approximation over the entire molecular range. Of particular interest is the fact that the discrepancy tends asymptotically to zero for ellipsoids whose axes are all substantially different in length (i.e. $a \gg b \gg c$ - "tapes").

Table 4. The relation between the notation used in this study and that used by Jeffrey (1922)

$$(A_{ij}) = \begin{pmatrix} A & H & G' \\ H' & B & F \\ G & F' & C \end{pmatrix},$$

$$(a_{ij}) = \begin{pmatrix} \underset{\sim}{a} & \underset{\sim}{h} & \underset{\sim}{g} \\ \underset{\sim}{h} & \underset{\sim}{b} & \underset{\sim}{f} \\ \underset{\sim}{g} & \underset{\sim}{f} & \underset{\sim}{c} \end{pmatrix},$$

$$(\xi_{ij}) = \begin{pmatrix} 0 & -\zeta & \eta \\ \zeta & 0 & -\zeta \\ -\eta & \xi & 0 \end{pmatrix}.$$

Table 5

ν for an ellipsoid of revolution calculated from the Simha - Saito equation and the Batchelor - Jeffrey equation

Axial Ratio	Prolate Model		Oblate Model	
	S - S	B - J	S - S	B - J
1.0	2.500	2.500	2.500	2.500
2.0	2.908	2.583	2.854	2.610
3.0	3.685	2.786	3.431	2.868
4.0	4.663	3.077	4.059	3.198
5.0	5.806	3.434	4.708	3.563
6.0	7.099	3.844	5.367	3.947
7.0	8.533	4.302	6.032	4.342
8.0	10.103	4.804	6.700	4.744
9.0	11.804	5.346	7.371	5.151
10.0	13.634	5.928	8.043	5.562

Table 6

Extension of Tanford's Tables ("Physical Chemistry of Macromolecules", 1961, Wiley & Sons, p 359 and 395) to compare the axial ratios predicted by the Simha-Saito equation and the Batchelor-Jeffrey equation, using a 0.2 grams/gram solvation for four globular proteins.

		Prolate			Oblate		
		Diffusion	S-S	B-J	Diffusion	S-S	B-J
	υ	a/b	a/b	a/b	a/b	a/b	a/b
Ribonuclease	3.6	2.1	2.9	5.5	2.2	3.4	5.3
β-lactoglobulin	3.6	3.7	2.9	5.5	4.0	3.4	5.3
Serum albumin	4.0	4.9	3.3	6.5	5.0	4.0	6.3
Hemoglobin	3.8	2.1	3.1	6.0	2.2	3.6	5.8

Table 7. Values of ν as a function of (a/b, b/c) for a general tri-axial ellipsoid (a>b>c)

(on the basis of equation 88)

	a/b \ b/c	1.0 (Prolate Ellipsoid)	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
Oblate Ellipsoid	1.0	2.500	2.507	2.524	2.550	2.583	2.620	2.661	2.706	2.753	2.803	2.854
	1.1	2.507	2.520	2.544	2.576	2.614	2.656	2.702	2.751	2.803	2.857	2.913
	1.2	2.525	2.545	2.575	2.612	2.655	2.703	2.754	2.808	2.865	2.923	2.983
	1.3	2.553	2.579	2.615	2.658	2.706	2.579	2.815	2.874	2.935	2.998	3.063
	1.4	2.588	2.621	2.662	2.711	2.764	2.822	2.883	2.947	3.013	3.081	3.151
	1.5	2.630	2.668	2.716	2.770	2.829	2.892	2.958	3.027	3.098	3.171	3.245
	1.6	2.677	2.722	2.775	2.834	2.899	2.967	3.039	3.113	3.189	3.267	3.346
	1.7	2.729	2.779	2.839	2.904	2.974	3.047	3.124	3.204	3.285	3.368	3.453
	1.8	2.785	2.842	2.907	2.978	3.053	3.132	3.215	3.300	3.386	3.475	3.565
	1.9	2.844	2.908	2.978	3.055	3.137	3.222	3.310	3.400	3.492	3.586	3.681
	2.0	2.908	2.977	3.054	3.137	3.224	3.315	3.408	3.504	3.602	3.702	3.803

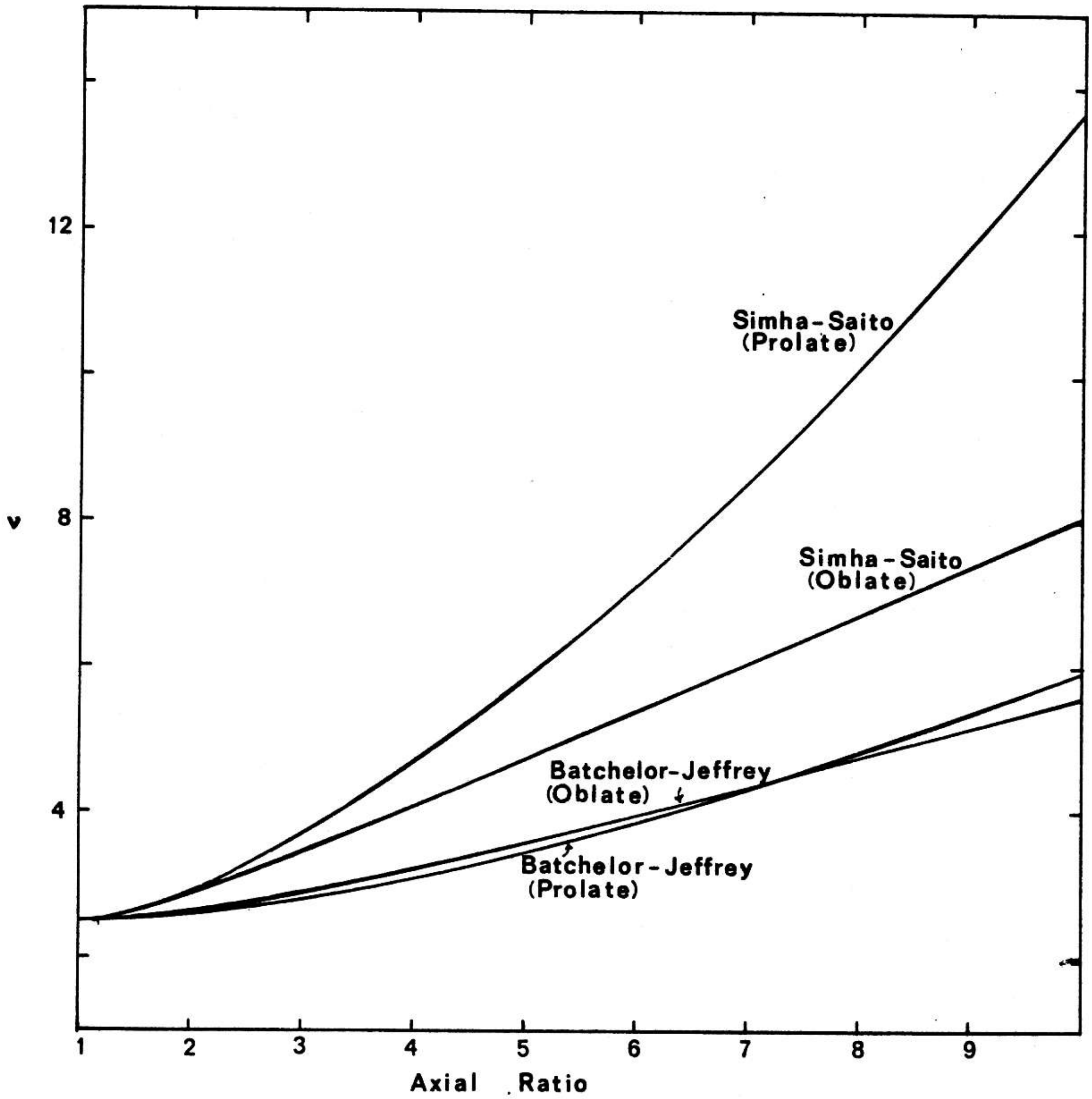

Figure 25. A comparison of the values of ν as a function of axial ratio predicted by the Simha - Saito and Batchelor - Jeffrey equations for ellipsoids of revolution

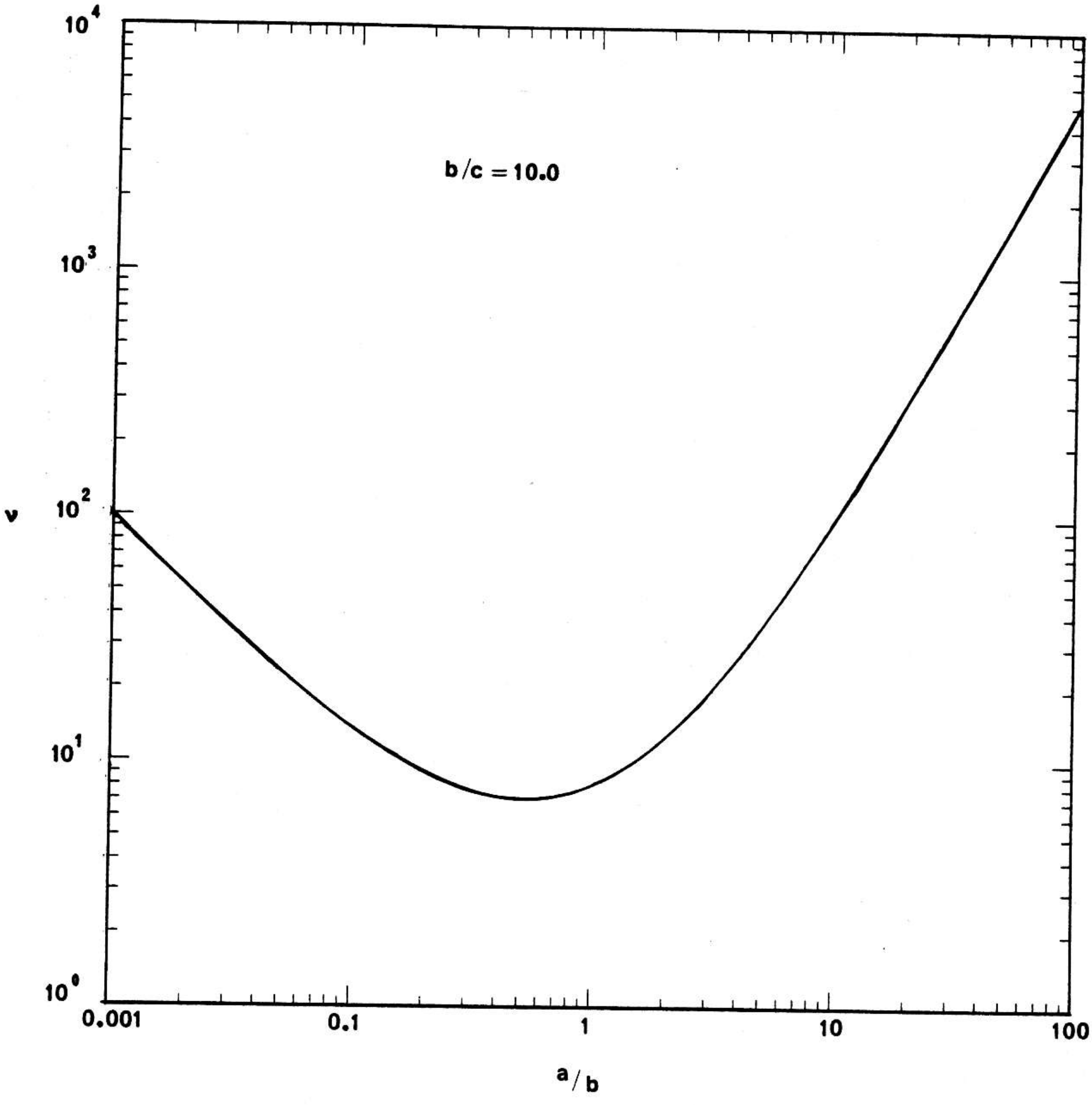

Figure 26. Plot of $\overline{\nu}$ as a function of a/b when b/c = 10.0 (a>b>c) determined from equation (88). This plot agrees very closely with that from the numerical procedure of Rallison (Figure 7, 1978)

N.B. Rallison has c>a>b

B I B L I O G R A P H Y

Alexander, A.E. and Johnson, P. (1949)

'Colloid Science', Volume 2, Oxford University Press

Alpert, S.S. and Banks, G. (1976)

Biophysical Chem. 4, 287

Baghurst, P.A., Nichol, L.W., Ogston, A.G., Winzor, D.J. (1975)

Biochem. J. 147, 575

Ballinger, K.W.A. and Jennings, B.R. (1979)

Nature 282, 699

Batchelor, G.K. (1967)

'An Introduction to Fluid Mechanics', Cambridge University Press

Batchelor, G.K. (1970)

J. Fluid Mech. 41, 545

Batchelor, G.K. and Green, J.T. (1972)

J. Fluid Mech. 56, 375

Beeman, W.W., Koesberg, P., Anderegg, J.W. and Webb, M.B. (1957)

in 'Handbuck der Physik', (Flugge, S. ed.), 32, 321, Springer-Verlagg (Berlin)

Benoit, H. (1951)

Ann. Physik. 6, 561

Berne, P.J. and Pecora, R. (1974)
Ann. Rev. Phys. Chem. 25, 233

Blake, C.C.F. (1975)
Essays in Biochem. II, 37

Blake, C.C.F., Geisow, M.J. and Oatley, S.J. (1978)
J. Mol. Biol. 121, 339

Blake, C.C.F., Koenig, D.F., Mair, G.A., North, A.C.T., Phillips, D.C. and Sarma, V.R. (1965)
Nature 206, 757

Bloomfield, V.A., Dalton, W.O. and Van Holde, K.E. (1967)
Biopolymers 5, 135

Bresler and Talmud (1944)
CR Acad. Sci. URSS, 43, 310

Brinkman, H.C., Hermans, J.J., Oosterhoff, L.J., Overbeek, J. Th. G., Polder, D., Staverman, A.J. and Wiebenga, E.H. (1949)
Proc. Int. Rheol. Congress (Schveningen) II, 77

Brenner, H. (1970)
J. Coll. Int. Sci. 32, 141

Brenner, H. (1972a)

<u>Chem. Eng. Sci.</u> <u>27</u>, 1069

Brenner, H. (1972b)

<u>Progr. Heat and Mass Transfer</u> <u>5</u>, 93

Cantor, C.R. and Tao, T. (1971)

<u>Proc. Nucl. Acid Res.</u> <u>2</u>, 31

Cerf, R. and Scheraga, H.A. (1952)

<u>Chem. Revs.</u> <u>51</u>, 185

Chapman, P.F. (1913)

<u>Phil. Mag.</u> <u>25</u>, 475

Cheng, P.Y. and Schachman, H.K. (1955)

<u>J. Polymer Sci.</u> <u>16</u>, 19

Chu, B. (1974)

'<u>Laser Light Scattering</u>', Academic, New York

Chwang, A.T. (1975)

<u>J. Fluid Mech.</u> <u>72</u>, 17

Clenshaw, C.W. and Curtis, A.R. (1960)

<u>Num. Math.</u> <u>2</u>, 197

Creeth, J.M. and Knight, C.G. (1965)
Biochim. Biophys. Acta 102, 549

Cummings, H.Z. and Pike, E.R. (1973)
(eds.) 'Photon Correlation and Light Beating Spectroscopy', Plenum,
New York

Dickerson, R.E. and Geiss, I. (1969)
'The Structure and Action of Proteins', Benjamin, California

Dougherty, J. and Kreiger, I.M. (1972)
in Kreiger, Adv. Colloid Sci. 3, 111

Edsall, J.T. (1953)
in 'The Proteins' (Neurath, H. and Bailey, K. eds) 1B, Chapter 7,
Academic, New York

Edwardes, D. (1892)
Quart. J. Math. 26, 70

Einstein, A. (1905)
Ann. Physik 17, 549

Einstein, A. (1906)
Ann. Physik 34, 591

Einstein, A. (1911)
Ann Physik 34, 591

Emes, C.H. (1977)

Ph. D. thesis, University of Leicester

Emes, C.H. and Rowe, A.J. (1978a)

Biochim. Biophys. Acta 537, 110

Emes, C.H. and Rowe, A.J. (1978b)

Biochim. Biophys. Acta 537, 125

Farrant, J.L. (1954)

Biochim. Biophys. Acta 13, 569

Feldman, R.J. (1976)

'Atlas of Macromolecular Structure on Microfiche', Traco Jitco Int., Rockville, Md. USA

Gans, R. (1928)

Ann. Physik 86, 628

Garcia Bernal, J.M. and Garcia de la Torre, J. (1980)

Biopolymers 19, 628

Garcia de la Torre, J. and Bloomfield, V.A. (1977a)

Biopolymers 16, 1747

Garcia de la Torre, J. and Bloomfield, V.A. (1977b)

Biopolymers 16, 1765

Garcia de la Torre, J. and Bloomfield, V.A. (1977c)
Biopolymers 16, 1779

Garcia de la Torre, J. and Bloomfield, V.A. (1978)
Biopolymers 17, 1605

Gardner, D.G., Gardner, J.C., Laush, G. and Meinke, W.W. (1959)
J. Chem. Phys. 31, 978

Giesekus, H. (1962)
Rheol. Acta 2, 50

Gill, P.E. and Murray, W. (1976)
Nat. Phys. Lab. report NAC 72

Gold, O. (1937)
Ph. D. thesis, University of Vienna

Goodwin, J.W. (1975)
Colloid Science 2 (Chemical Society), 246

Guoy, L.G. (1910)
J. Phys. Chem. 9, 457

Hall, C.E. and Slayter, H.S. (1959)
J. Biophys. Cytol. 5, 11

Harding, S.E. (1980a)

Biochem. J. 189 (in press)

Harding, S.E. (1980b)

mss. submitted to J. Phys. Chem.

Harrison, P.M. (1959)

J. Mol. Biol. 1, 69

Herzog, R.O., Illig, R. and Kudar, H. (1934)

Z. Phys. Chem. A167, 329

Holtzer, A. and Lowey, S. (1956)

J. Am. Chem. Soc. 78, 5954

Jablonski, A. (1961)

Naturforsch 169, 1

Jeffrey, G.B. (1922)

Proc. Roy. Soc. (London) A102, 476

Johnson, P. and Mihalyi, E. (1965)

Biochim. Biophys. Acta 102, 476

Jost, J.W. and O'Konski, C.T. (1978)

in 'Molecular Electro Optics' (O'Konski, C.T. ed.) Volume 2, 529

Kartha, G., Bello, J. and Harker, D. (1967)
Nature 213, 862

Kendrew, J.C., Bodo, G., Dintzis, H.M., Parrish, R.G., Wycoff, H. and Phillips, D.C. (1958)
Nature 181, 665

Kim, S.H. (1974)
in 'Biochemistry' (Stryer, L.) 653, Freeman, San Francisco

Kirkwood, J.G. (1967)
'Macromolecules' (Aueur, P.L. ed.), Gordon and Breach

Koenig, S.H. (1975)
Biopolymers 14, 2421

Kratky, O., Leopold, H. and Stabinger, H. (1969)
Z. Angew. Phys. 27, 273

Kratky, O., Leopold, H. and Stabinger, H. (1969)
in 'Methods in Enzymology' (Hirs, C.H.W. and Timasheff, S.N. eds.), 27, 98, Academic, London

Krause, S. and O'Konski, C.T. (1959)
J. Am. Chem. Soc. 81, 5082

Kuff, E.J. and Dalton, A.L. (1957)
J. Ultrastructure Res. 1, 62

Kuhn, W. and Kuhn, H. (1945)
Helvetica Chimica Acta 38, 97

Kynch, G.J. (1956)
Proc. Roy. Soc. (London) A237, 90

Labaw, L.W. and Wycoff, R.W.G. (1957)
Biochim. Biophys. Acta 25, 263

Lauffer, M.A. (1942)
Chem. Rev. 31, 561

Laurent, T.C. and Killander, J. (1964)
J. Chromatog. 14, 317

Lipscomb, W.N. (1971)
Proc. Robert A. Welch Found. Conf. Chem. Res. 15, 134

Lloyd, P.H. (1974)
'Optical Methods in Ultracentrifugation, Electrophoresis and Diffusion',
Clarendon Press, Oxford

Lucas, C.W. and Terrill, C.W. (1970)
Collected Algorithms from CACM, No. 404

Manley, R. and Mason, S. G. (1954)
Canad. J. Chem. 32, 763

Martin, R.B. (1964)
'Introduction to Biophysical Chemistry' Chap. 11, McGraw-Hill, New York

McCammon, J.A., Deutch, J.M. and Bloomfield, V.A. (1975)
Biopolymers 14, 2479

Mehl, J.W., Oncley, J.L. and Simha, R. (1940)
Science 92, 132

Mendelson, R. and Hartt, J. (1980)
EMBO Workshop on Muscle Contraction, Alpbach Conf. Austria

Mihalyi, E. and Godfrey, J. (1963)
Biochim. Biophys. Acta 67, 90

Memming, R. (1961)
Z. Physik. Chem. (Frankfurt) 28, 169

Mooney, M. (1951)
J. Coll. Sci. 6, 162

Mooney, M. (1957)
J. Coll. Sci. 12, 575

Munro, I., Pecht, I. and Stryer, L. (1979)
Proc. Nat. Acad. Sci. (USA) 76, 56

Nichol, L.W., Jeffrey, P.D., Turner, D.R. and Winzor, D.J. (1977)
J. Phys. Chem. 81, 776

Nisihara, T. and Doty, P. (1958)
Proc. Nat. Acad. Sci. (USA) 44, 411

Oberbeck, A. (1876)
J. reine. angew. Math. 81, 62

O'Connor, D.V., Ware, W.R. and Andre, J.C. (1979)
J. Phys. Chem. 83, 1333

Offer, G., Moos, C. and Starr, R. (1973)
J. Mol. Biol. 74, 653

O'Hara and Smith (1968)
Comp. Journal 11, 213

O'Konski, C.T. and Haltner, A.J. (1956)
J. Am. Chem. Soc. 78, 3604

Oliver, J. (1972)
Comp. Journal 15, 141

Oncley, J.L. (1940)
J. Phys. Chem. 44, 1103

Oncley, J.L. (1941)
Ann. New York Acad. Sci. 41, 121

Paradine, C.G. and Rivett, B.H.P. (1960)
'Statistical Methods for Technologists', English Universities Press, London

Pearce, T.C., Rowe, A.J. and Turnock, G. (1975)
J. Mol. Biol. 97, 193

Perrin, F. (1934)
J. Phys. Radium 5, 497

Perrin, F. (1936)
J. Phys. Radium 7, 1

Perutz, M.F., Rossmann, M.G., Cullis, A.F., Muirhead, H., Will, G. and North, A.C.T. (1960)
Nature 185, 416

Powell, D.R. and MacDonald, J.R. (1972)
Comp. Journal 15, 148

Pytkowickz, R.M. and O'Konski, C.T. (1959)
J. Am. Chem. Soc. 81, 5082

Rallison, J.M. (1978)
J. Fluid Mech. 84, 237

Riddiford, C.L. and Jennings, B.R. (1967)
Biopolymers 5, 757

Ridgeway, D. (1966)
J. Am. Chem. Soc. 88, 1104

Ridgeway, D. (1968)
J. Am. Chem. Soc. 90, 18

Rowe, A.J. (1977)
Biopolymers 16, 2595

Rowe, A.J. (1978)
Techniques in Protein and Enzyme Biochem. B105a, 1

Saito, N. (1951)
J. Phys. Soc. (Japan) 6, 297

Scheraga, H.A. (1955)
J. Chem. Phys. 23, 1526

Scheraga, H.A. (1961)
'Protein Structure', Academic, New York

Scheraga, H.A. and Mandelkern, L. (1953)
J. Am. Chem. Soc. 79, 179

Simha, R. (1940)

J. Phys. Chem. 44, 25

Simha, R. (1952)

J. Appl. Phys. 23, 1020

Shaw, D.J. (1970)

'Introduction to Colloid and Surface Chemistry' (2nd edn.), Butterworths

Small, E.W. and Isenberg, I. (1977)

Biopolymers 16, 1907

Sorenson, N.A. (1930)

CR Lab. Carlsberg 18, No. 5

Squire, P.G. (1970)

Biochim. Biophys. Acta 221, 425

Squire, P.G. (1978)

in 'Molecular Electro Optics' (O'Konski, C.T. ed.) Volume 2, 565

Squire, P.G., Moser, L. and O'Konski, C.T. (1968)

Biochemistry 7, 4261

Stacey, K.A. (1956)

'Light Scattering in Physical Chemistry', Butterworths, London

Stokes, Sir G. (1851)

Trans. Cambridge Phil. Soc. 9, 8

Stokes, Sir G. (1880)

'Mathematical and Physical Papers', Cambridge University Press

Svedberg, T. and Pedersen, K.O. (1940)

'The Ultracentrifuge', Oxford University Press

Tanford, C. (1955)

J. Phys. Chem. 59, 798

Tanford, C. (1961)

'Physical Chemistry of Macromolecules', Wiley, New York

Theorell, H. (1934)

Biochem. Z. 268, 46

Vand, V. (1948)

J. Phys. Coll. Chem. 52, 277

Van de Hulst, H.C. (1957)

'Light Scattering by Small Particles', Wiley, New York

Van Holde, K.E. (1971)

'Physical Biochemistry', Prentice Hall, New Jersey

Wahl, P. (1966)

Compt. Rend. Acad. Sci. (Paris) 263D 1525

Wales, M. and Van Holde, K.E. (1954)

J. Polymer Sci. 14, 81

Wilde, D.J. (1964)

'Optimum Seeking Methods', Prentice Hall, New Jersey

Williams, R.C., Ham, W.T. and Wright, A.K. (1976)

Anal. Biochem. 73, 52

Wilson, R.W. and Bloomfield, V.A. (1979a)

Biopolymers 18, 1205

Wilson, R.W. and Bloomfield, V.A. (1979b)

Biopolymers 18, 1543

Yang, J.T. (1961)

Adv. Protein Chem. 16, 323

Zimm, B.H. (1948)

J. Chem. Phys. 16, 1093

Zimm, B.H. (1956)

J. Chem. Phys. 24, 269