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AN APPROXIMATE SOLUTION TO THE LAMM EQUATION

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An approximate solution to the Lamm equation subject to the initial and boundary conditions for conventional sedimentation velocity experiments is derived and compared with the approximate solution of Fujita and MacCosham. Calculations with this solution demonstrate that the half-height method of estimating sedimentation coefficients yields correct values for $\epsilon < 0.02$.

1. Introduction

Previous work [1] has demonstrated that reliable estimates of s/D, but not s, may be obtained by nonlinear regression analysis of approach-to-sedimentation equilibrium data using an approximate solution to the Lamm equation. Of interest is a similar analysis of sedimentation velocity data which could yield estimates for s and s/D using data obtained from sedimentation velocity experiments. With this purpose in mind, a derivation of an approximate solution of the Lamm equation will be developed.

For sedimentation velocity experiments, the solution column height is about 1 cm. The conditions chosen for conventional sedimentation velocity experiments result in a plateau region ($dc/dr = 0$) which exists over the central portion of the solution column during the course of the experiment. This fact allows the use of the Faxen-type boundary condition which considers that the solution column extends indefinitely from $r = r_a$ to $r = \infty$. The initial condition for conventional experiments is that $C_{r,t} = C_0$ for $t = 0, r_a \leqslant r < \infty$. A boundary condition exists which states that no flow of solute occurs at $r = r_a$. Faxen has given a formal exact solution for these conditions [2], but the results appears too complex for use in nonlinear regression analysis. Fujita and MacCosham [3] have derived an approximate solution based on the approximation that the boundary remains close to the upper meniscus ($(r/r_a)^2 \approx 1$). This solution has proved to be of considerable use in extending our understanding of the sedimentation of small solutes. In the analysis which follows both s and D are assumed to be independent of concentration. The angular velocity ω is assumed to be constant during the course of the experiment.

2. Solution of the equation

The Lamm equation for a single homogeneous solute sedimenting in a sector-shaped cell is [4]

$$\frac{\partial C}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left[rD\frac{\partial C}{\partial r} - s\omega^2 rC\right], \quad (1)$$

where C is the concentration of the solute on a volume basis, t is time, r is the radial distance from the center of rotation, ω is the angular velocity, s is the sedimentation constant, and D is the diffusion constant. The initial and boundary conditions are:

$$C = C_0; \quad r_a \leqslant r < \infty, \ t = 0, \quad (2)$$

$$D\,\partial C/\partial r = r\omega^2 sC; \quad r = r_a, \ t > 0. \quad (3)$$

Eq. (1) is converted into an equation with dimensionless variables by the substitutions:

$C/C_0 = \theta$, $X = (r/r_a)^2 - 1$, $\tau = 2s\omega^2 t$, $\epsilon = 2D/s\omega^2 r_a^2$.

Equation (1) now becomes

$$\partial\theta/\partial\tau = (\partial/\partial X)\,[(X+1)(\epsilon\,\partial\theta/\partial X - \theta)]. \quad (4)$$

The initial and boundary conditions become:

$$\theta = 1; \quad 0 < X < \infty, \quad \tau = 0, \tag{5}$$

$$\epsilon\, \partial\theta/\partial X = \theta; \quad \tau > 0, \quad X = 0. \tag{6}$$

It may be shown that under these conditions for X large (the plateau region of the boundary curve) that $\theta = e^{-\tau}$. Thus the substitution $\theta = e^{-\tau} \cdot U$ is made. Eq. (4) becomes with this substitution:

$$\partial U/\partial\tau = \epsilon(X+1)\partial^2 U/\partial X^2 + (\epsilon - X - 1)\,\partial U/\partial X. \tag{7}$$

In the derivation of Fujita's approximate Archibald-type solution for approach-to-sedimentation equilibrium the approximation [5] is made that $X+1$ is replaced by the constant value $(1+(r_b/r_a)^2)/2$. Here the value of $X+1$ will be assumed to be constant and equal to a. The appropriate value for a will be explored subsequently. Under this approximation eq. (7) becomes:

$$\partial U/\partial\tau = \epsilon a\, \partial^2 U/\partial X^2 + (\epsilon - a)\,\partial U/\partial X. \tag{8}$$

The boundary conditions are transformed to:

$$U = e^{\tau}; \quad 0 < X < \infty, \quad \tau = 0, \tag{9}$$

$$\epsilon\, \partial U/\partial X = U; \quad \tau > 0, \quad X = 0. \tag{10}$$

The substitution is now made that:

$$U = V \exp\left(-\frac{2X + \tau(\epsilon - a)}{4\epsilon a/(\epsilon - a)}\right). \tag{11}$$

With this substitution eq. (8) reduces to:

$$\partial V/\partial\tau = \epsilon a\, \partial^2 V/\partial X^2. \tag{12}$$

The boundary and initial conditions become:

$$\left(\frac{2\epsilon a}{\epsilon + a}\right)\frac{\partial V}{\partial X} = V; \quad X = 0, \quad \tau > 0, \tag{13}$$

$$V = \exp\{-X(a - \epsilon)/(2\epsilon a)\}; \quad \tau = 0, \quad 0 < X < \infty. \tag{14}$$

The Laplace transform of eq. (12) subject to the initial condition given in eq. (14) gives the subsidiary equation (15):

$$\frac{d^2 \bar{V}}{dX^2} - q^2 \bar{V} = -\frac{1}{\epsilon a}\exp\left\{-X\left(\frac{a-\epsilon}{2a\epsilon}\right)\right\}, \tag{15}$$

where $\bar{V}$ is the Laplace transform of V and $q^2 = p/(\epsilon a)$. The general solution of this equation is:

$$\bar{V} = \frac{1/(\epsilon a)}{q^2 - [(a-\epsilon)/2a\epsilon]^2}\exp\left\{-X\left(\frac{a-\epsilon}{2a\epsilon}\right)\right\} + C_1 \exp(-qX) + C_2 \exp(qX). \tag{16}$$

Since we require that $\bar{V}$ be bounded as $X \to \infty$, the constant of integration $C_2 = 0$.

The boundary condition (13) allows the determination of C_1 as:

$$C_1 = -\frac{1}{a\epsilon^2}\,\frac{1}{q^2 - [(a-\epsilon)/2a\epsilon]^2}\,\frac{1}{q + (\epsilon + a)/2\epsilon a}. \tag{17}$$

In order to find the inverse transform of $\bar{V}$, eq. (16) is expressed as a sum of partial fractions which simplify to:

$$\begin{aligned}\bar{V} = {} & \frac{1/(\epsilon a)}{q^2 - [(a-\epsilon)/2a\epsilon]^2}\exp\left\{-X\left(\frac{a-\epsilon}{2a\epsilon}\right)\right\} \\ & - \frac{1}{\epsilon}\,\frac{1}{q + (\epsilon + a)/2\epsilon a}\exp(-qX) \\ & + \frac{a}{\epsilon(a-\epsilon)}\,\frac{1}{q + (a-\epsilon)/2\epsilon a}\exp(-qX) \\ & + \frac{1}{(\epsilon - a)}\,\frac{1}{q - (a-\epsilon)/2a\epsilon}\exp(-qX).\end{aligned} \tag{18}$$

Upon replacing q by $\sqrt{p/(\epsilon a)}$ the inverse transform [6] may be simplified to:

$$\begin{aligned}V = {} & \exp\left\{\frac{(a-\epsilon)^2}{4a\epsilon}\tau\right\}\exp\left\{-X\left(\frac{a-\epsilon}{2a\epsilon}\right)\right\} \\ & + \left(\frac{\epsilon + a}{2\epsilon}\right)\exp\left(\frac{2(\epsilon + a)X + (\epsilon + a)^2\tau}{4\epsilon a}\right) \\ & \times\left(1 - \phi\left(\frac{X + (a+\epsilon)\tau}{2\sqrt{\epsilon a\tau}}\right)\right) \\ & - \frac{a}{2\epsilon}\exp\left(\frac{2(a-\epsilon)X + (a-\epsilon)^2\tau}{4\epsilon a}\right) \\ & \times\left(1 - \phi\left(\frac{X + (a-\epsilon)\tau}{2\sqrt{\epsilon a\tau}}\right)\right) \\ & - \frac{1}{2}\exp\left(\frac{2(\epsilon - a)\cdot X + (\epsilon - a)^2\tau}{4\epsilon a}\right) \\ & \times\left(1 - \phi\left(\frac{X + (\epsilon - a)\tau}{2\sqrt{\epsilon a\tau}}\right)\right),\end{aligned} \tag{19}$$

where

$$\phi(X) = \frac{2}{\pi}\int_0^X e^{-t^2}\,dt.$$

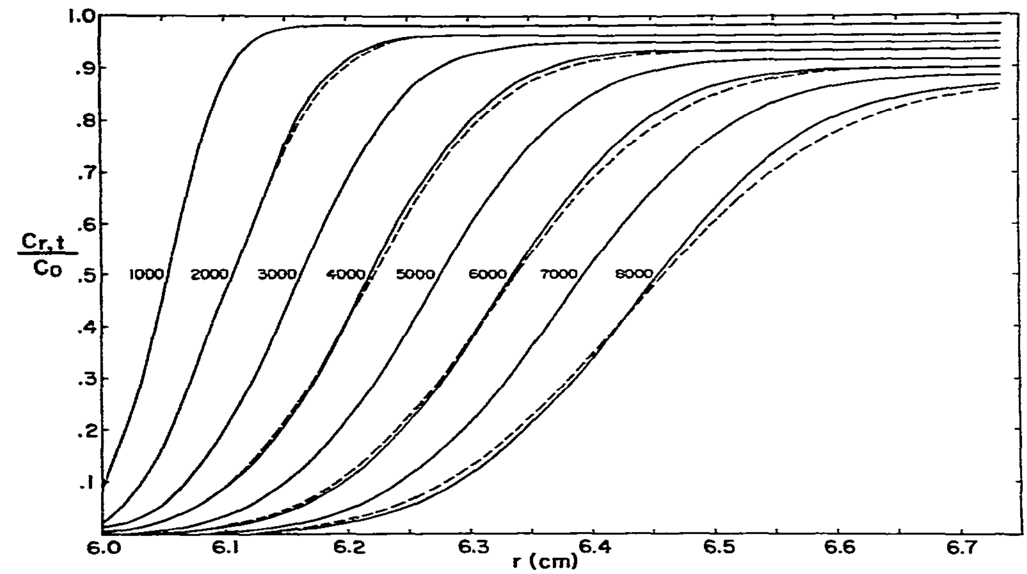

Fig. 1. Calculated boundary curves using the Fujita-MacCosham (dashed line) and derived (solid line) approximate solutions with $s = 2.54 \times 10^{-13}$ s, $D = 9.5 \times 10^{-7}$ cm^2/s, $r_a = 6.0$ cm, and RPM = 56000. The times (in seconds) for the boundary curves are given in the figure adjacent to each curve.

The final solution is:

$$C_{r,t} = C_0 V e^{-\tau} \exp\left(-\frac{2X + \tau(\epsilon - a)}{4\epsilon a/(\epsilon - a)}\right). \tag{20}$$

In the case where $\epsilon \lll a$, eq. (20) simplifies to:

$$C_{r,t} = C_0 e^{-\tau}\left\{1 - \frac{1}{2}\left(1 - \phi\left(\frac{X - a\tau}{2\sqrt{\epsilon a \tau}}\right)\right)\right\}. \tag{21}$$

The problem of the value of a remains. Suppose the experiment has reached some reduced time $\tau = \tau^*$. At the start of the experiment a would have the value $e^{\tau=0} = 1$; at $\tau = \tau^*$, a would have the value e^{τ^*}. The most suitable value for a would appear to be the τ-averaged value. Thus when calculating the shape of the boundary at $\tau = \tau^*$ a is taken to the $(e^{\tau^*} - 1)/\tau^*$, the average value of a between $\tau = 0$ and $\tau = \tau^*$. Essentially the same numerical result is obtained if a is averaged with respect to r between $r = r_a$ and $r = r^*$.

Table 1
Effect of ϵ on estimation of sedimentation coefficients by the half-height method

$s \times 10^{13}$	$D \times 10^6$	ϵ	τ final[a)]	estimated $s \times 10^{13}$
2.54	0.95	0.0060	0.140	2.53
1.82	1.19	0.0207	0.128	1.83
1.00	1.50	0.0242	0.082	1.03
0.50	2.50	0.0808	0.005	0.54

a) Sedimentation coefficients were calculated using data for which $0 < \tau < \tau_{final}$.

3. Numerical results and discussion

Fig. 1 shows graphically the degree of similarity for the two approximate solutions. For $\tau < 0.02$ ($t \leqslant 1000$ s) the two solutions are virtually coincident, but diverge considerably for $\tau > 0.1$ ($t > 6000$ s). The Fujita-MacCosham solution results in a broader boundary. Current practice for the estimation of sedimentation coefficients involves estimating the position of the boundary as the radial distance at which $dc/dr|_{max}$ occurs or at which $C_{r,t}/C_{plateau}$ is 0.5. Fujita and MacCosham showed that for small solutes the location of the boundary as $dc/dr|_{max}$ will yield sedimentation coefficients larger than their true value due to the fact that a time lag exists in the appearance of a maximum in the dc/dr versus r curve.

The results summarized in table 1 show that for small solutes the half-height method will yield results which are erroneously high, while for larger solutes the half-height method will yield accurate estimates for the sedimentation coefficient. A typical sedimentation velocity experiment generates a number of $C_{r,t}$ versus r curves. The half-height method utilizes only one r value from each time point to estimate s. The solution developed herein along with previous work with approach-to-sedimentation equilibrium data suggests that it may be possible to use all the data generated during the time course of a sedimentation velocity experiment to provide estimates for s/D as well as for s.

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