ULTRACENTRIFUGE SIMULATION USING CUBIC COLLOCATION

by

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INTRODUCTION

During the last fifteen years a number of methods for simulating the behavior of a sedimenting solute or system of solutes have been developed and presented in the literature. These include the distorted grid model of Cox(1-8), the countercurrent analogue of Bethune and Kegeles(9-10), the finite difference models of Dishon et. al. and Cann and Goad(11-13), and the finite element model of Claverie(14-16).

The method presented here offers three significant improvements over earlier models. It has automatic control over temporal integration errors. All terms of the continuity equation(s), including nonlinear coupling terms, are addressed simultaneously. The method has been implemented as an option in a sophisticated software package which is available for general distribution. For these reasons it deserves careful consideration.

Automatic control of temporal errors is an important feature of this method. It gives the user a great deal of control over errors which are committed in the course of the simulation. The time step is taken to be as large as is prudent in order to keep temporal integration errors below a specified maximum.

The fact that all terms of the continuity equation are addressed together makes the method extremely flexible. Models presented previously have generally required one or more intermediate steps in each step of time integration. Cox's model, for example, uses separate rounds of sedimentation and diffusion for each step of time integration. Claverie's model, on the other hand, employs a sedimentation-diffusion operator but requires an intervening perturbation on the concentrations in order to accomplish relaxation to chemical equilibrium. Since all terms of the continuity equation are addressed together, the model presented here can account for virtually any physical effect that can be incorporated into the continuity equation(s).

The method presented here is available as an option in the code, PDECOL, which has been developed by Madsen and Sincovec(17). This code is available for a nominal distribution charge from the Association for Computing Machinery. PDECOL is currently in use in several hundred installations and no errors have been discovered in it since its release. Some penalty must, of course, be paid in overhead because of the generality of the methods employed in PDECOL. The user is relieved of such an extensive programming burden, however, that the overhead cost is nominal by comparison.

The method presented here is applicable to a wide range of transport experiments. It is presented in the context of centrifugation because this is the area in which the author has the most experience. It is anticipated that in the future this method will play an important role in research involving solutions of the continuity equations which govern transport phenomena.

CONTINUITY EQUATIONS

The continuity equation for the ultracentrifuge is a partial differential equation which governs the behavior of a sedimenting solute. In a fairly general form it is given by

$$c_{t_k} = \frac{1}{r}\frac{\partial}{\partial r}(-rJ_k) + f_k \,, \qquad 1 \leq k \leq K \,,\ t \geq 0 \,,\ r_m < r < r_b \,, \tag{1}$$

$$J_k = s_k \omega^2 r c_k - D c_{r_k} \,. \tag{2}$$

Or, using a more general notation, by

$$c_{t_k} = L_k(r,\ t,\ \vec{c},\ \vec{c}_r,\ \vec{c}_{rr}),\ 1 \leq k \leq K \,,\ t \geq 0,\ r_m < r < r_b \,, \tag{3}$$

where

r is the spatial variable,

t is the temporal variable,

r_m is the value of r at the meniscus,

r_b is the value of r at the cell bottom,

c_{t_k} denotes $\frac{\partial c_k}{\partial t}$

c_{r_k} denotes $\frac{\partial c_k}{\partial r}$

c_{rr_k} denotes $\frac{\partial^2 c_k}{\partial r^2}$

$\vec{c}$ denotes $(c_1,\ c_2,\ \ldots,\ c_K)$

$\vec{c}_r$ denotes $(\frac{\partial c_1}{\partial r},\ \frac{\partial c_2}{\partial r},\ \ldots,\ \frac{\partial c_K}{\partial r})$

$\vec{c}_{rr}$ denotes $(\frac{\partial^2 c_1}{\partial r}, \frac{\partial^2 c_2}{\partial r}, \ldots, \frac{\partial^2 c_K}{\partial r})$

J represents the flux,

K denotes the number of species present,

ω is the angular velocity and is a function of time t ,

s_k and D_k are the sedimentation and diffusion coefficients respectively and are usually functions of $\vec{c}$,

f_k is a chemical coupling term and is a function of $\vec{c}$.