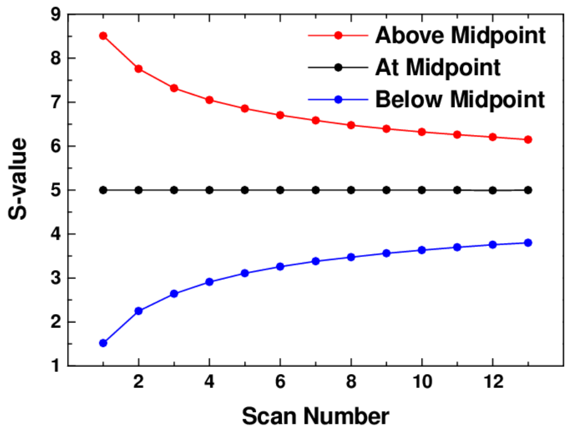
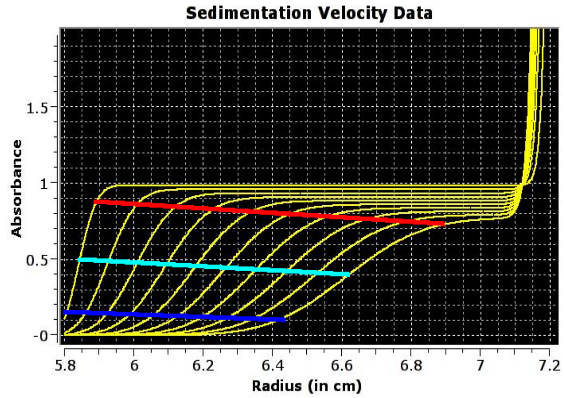
Consider the 2 graphs below:





On the right graph, you see a simulated sedimentation velocity experiment with three colored lines (blue, cyan, red) that intersect the experimental data at different radial positions. For each intersection, an *apparent* sedimentation can be determined by considering how far $(r_b - r_m)$ a particular component in the mixture has moved since the beginning of the experiment $(t - t_0)$, where r_m is the position of the meniscus (top of the solution column), t_0 is the time when the rotor started spinning (you can assume that the rotor started at full speed, which is of course not possible, but it simplifies things now). At some time t later in the experiment, after the experiment has proceeded for $(t - t_0)$ seconds, the particle has moved to the position r_b, a radius somewhere in the boundary. Using the formula below, it is possible to calculate an apparent sedimentation coefficient, s_b, for that point in the boundary, using the time of the scan and the radial distance moved as observed in the experiment.

$$\hat{s}_b = \ln\left(\frac{r_b(t)}{r_m(t_0)}\right)\left(\omega^2(t - t_0)\right)^{-1}$$

When measuring the radial positions of all the intercepts of the colored lines with the experimental data and calculating and plotting the apparent s-values for those points, you will get the graph on the left. We would expect that a particle sedimenting at a particular point in the boundary has a constant sedimentation speed, but curiously, there is an unexpected result: Apparently, the answer is different dependent on where in the boundary the measurement is made. Furthermore, the measurements above the midpoint are sedimenting slower over time, while the measurements at the midpoint are actually constant, and measurements below the midpoint are actually increasing in speed. Please explain these contradictions:

1. Why is the discrepancy the largest for the early scans? (10 points)

Answer: When the particles start to sediment upon rotor acceleration, ALL the particles move towards the bottom, increasing concentration at the bottom as particles pile up there, and depleting the concentration of particles near the meniscus. This creates an infinitely steep concentration gradient near the meniscus, which initially is just as vertical as the meniscus. Nature doesn't like any gradients and tries to equilibrate them. It does so by diffusion. Diffusion transport flow is proportional to the steepness of the gradient (see Fick's law), so when the boundary is the steepest, the diffusional flow is the fastest. When a steep concentration gradient exists as in this case, you will have a large chemical potential, that Nature is trying to minimize. Diffusion flow in such cases is so strong, it causes some of the particles to be transported *against* the sedimentation direction, back towards the meniscus. Those particles will no longer be recorded to the right of the moving boundary. On the bottom of the boundary you will see molecules with an apparently slower sedimentation coefficient, the opposite at the top of the boundary.

2. What will happen at infinite time, if we had an infinitely large rotor and an infinitely long cell, and an infinite amount of time to wait for the sample to sediment to infinity? (5 points)

Answer: As the plot on the left suggests, the later the scans, the more similar the sedimentation coefficients from the three boundary positions become. If one waits long enough, the red and the blue lines will converge with the black line and all show the same values at infinity.

3. What would the result look like if there were two components in the mixture with different sedimentation coefficients? (10 points)

Answer: There would be two boundaries that would sediment with different speeds. For each species, a different boundary would show up, and the plots would look the same, but they would be vertically shifted, and the black lines would point to the sedimentation coefficients of each species. Of course, you would need to calculate 3 more boundary fractions, and each black line would need to be centered at the midpoints of each boundary.

4. How should one correct for this observation? (20 bonus points if you figure this one out correctly!)

Answer: In order to answer this question one needs to understand Fick's second law, which describes the time dependence of the flow of diffusing particles as a function of chemical potential (or gradient steepness). The solution to Ficks second law suggests that diffusion transport has a $\sqrt{t}$ dependence on time. To cancel the effect of this dependence, one could plot these sedimentation coefficients not against the scan number as we did here, but against the inverse square-root of time of each scan. In such a plot, the square-root dependence would be converted to a linear dependence of time, and each boundary position could be plotted as a linear extrapolation to zero, which on the inverse time scale reflects infinity.

Note: ignore the fact that there are 13 scans shown in the graph on the left and only 10 in the graph on the right, the principle still holds. You do not need to make any calculations to answer this question. Please no collaboration, and please type your response.

Don't forget to send me your RSA public key and your IP4 address if you want to connect from home. (no points, but you will need it for future homework assignments).