

# Modeling of a centrifuge experiment: the Lamm equations

O. Gonzalez and J. Li

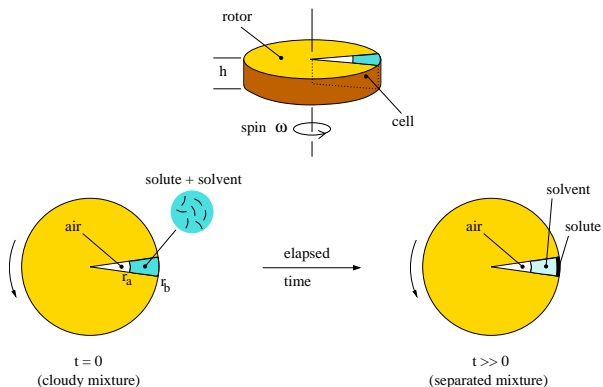
UT-Austin

29 October 2008

# Problem statement

# Setup

Consider an experiment in which a 2-component solution (solute + solvent) is separated in a centrifuge.



# Goals

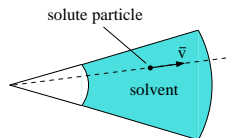
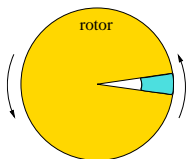
- Derive model for concentration of solute particles.
- Use model to estimate shape from concentration data.
- Begin with simple case of spherical particles.
- Generalize to particles of arbitrary shape.

# Simplifying assumptions

# Assumption 1

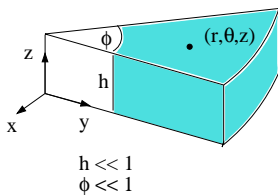
In a coord system attached to and rotating with the rotor, assume:

- (time-averaged) velocity  $\bar{v}$  of a solute particle due to centrifugal force is small and in radial direction,
- solvent is macroscopically stationary.



## Assumption 2

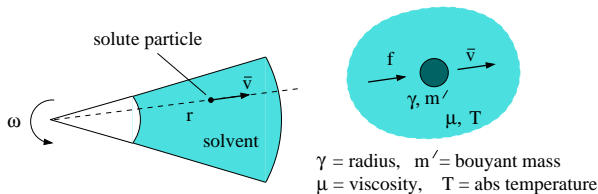
Assume solute concentration  $\rho$  and velocity  $\bar{v}$  depend only on radial coordinate  $r$  and time  $t$ .



$$\rho = \rho(r, t), \quad \bar{v} = \bar{v}(r, t).$$

## Assumption 3

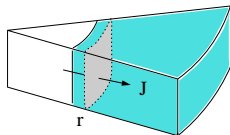
Assume particles are spherical and independent, with velocity proportional to centrifugal force (Stokes law).



$$\bar{v} = \frac{f}{6\pi\gamma\mu}, \quad f = m'\omega^2 r \quad \implies \quad \bar{v} = S\omega^2 r, \quad S = \frac{m'}{6\pi\gamma\mu}.$$

## Assumption 4

Assume mass flux  $J$  of solute particles across radial surface at  $r$  can be decomposed into two parts (diffusion + convection).



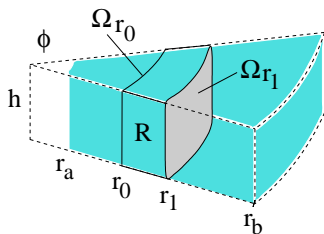
$$J(r, t) = -D \frac{\partial \rho}{\partial r} + \rho \bar{v} \quad \left[ \frac{\text{Mass}}{\text{Area Time}} \right].$$

For spherical particles in a fluid  $D = \frac{kT}{6\pi\gamma\mu}$  (Stokes-Einstein).

# Governing equations

# Setup

Consider the region  $R$  between two radial surfaces  $\Omega_{r_0}$  and  $\Omega_{r_1}$  where  $r_0 < r_1$  are arbitrary.



# Conservation of mass

For the region  $R$  we have

$$\frac{\partial}{\partial t} \left( \begin{array}{l} \text{mass of solute} \\ \text{inside of } R \end{array} \right) = \left( \begin{array}{l} \text{mass flow} \\ \text{in to } R \end{array} \right) - \left( \begin{array}{l} \text{mass flow} \\ \text{out of } R \end{array} \right)$$

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$$\frac{\partial}{\partial t} \int_{r_0}^{r_1} \rho(r, t) \text{Area}(\Omega_r) dr = J(r_0, t) \text{Area}(\Omega_{r_0}) - J(r_1, t) \text{Area}(\Omega_{r_1})$$

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$$\frac{\partial}{\partial t} \int_{r_0}^{r_1} \rho(r, t) \text{Area}(\Omega_r) dr = - \int_{r_0}^{r_1} \frac{\partial}{\partial r} \left[ J(r, t) \text{Area}(\Omega_r) \right] dr.$$

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Substituting  $\text{Area}(\Omega_r) = h\phi r$  and rearranging gives

$$\int_{r_0}^{r_1} \left[ h\phi r \frac{\partial \rho}{\partial t} + \frac{\partial}{\partial r} (h\phi r J) \right] dr = 0, \quad \forall r_0 < r_1.$$

# Localization

Assuming the integrand is continuous, we deduce by the arbitrariness of  $r_0$  and  $r_1$

$$\phi hr \frac{\partial \rho}{\partial t} + \frac{\partial}{\partial r} (\phi hr J) = 0, \quad r_a < r < r_b.$$

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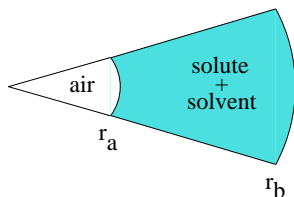
$$\phi hr \frac{\partial \rho}{\partial t} + \frac{\partial}{\partial r} (\phi hr J) = 0, \quad r_a < r < r_b.$$

Substituting  $J = -D \frac{\partial \rho}{\partial r} + \rho \bar{v}$  and  $\bar{v} = S\omega^2 r$  gives, after cancelling factors

$$\frac{\partial \rho}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} \left( S\omega^2 r^2 \rho - rD \frac{\partial \rho}{\partial r} \right) = 0, \quad r_a < r < r_b.$$

# Boundary conditions

Solute particles cannot cross surfaces at  $r_a$  and  $r_b$ .



$$J(r, t) = -D \frac{\partial \rho}{\partial r} + \rho \bar{v} = 0, \quad r = r_a, r_b.$$

# Summary of model

For spherical particles in dilute solution we obtain the *Lamm equations*

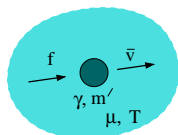
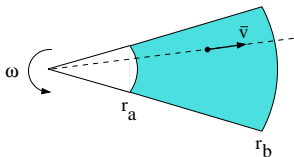
$$\frac{\partial \rho}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r D \frac{\partial \rho}{\partial r} - S \omega^2 r^2 \rho \right), \quad r_a < r < r_b, \quad t > 0$$

$$D \frac{\partial \rho}{\partial r} = S \omega^2 r \rho, \quad r = r_a, \quad t > 0$$

$$D \frac{\partial \rho}{\partial r} = S \omega^2 r \rho, \quad r = r_b, \quad t > 0$$

$$\rho(r, 0) = \rho_0(r), \quad r_a \leq r \leq r_b, \quad t = 0$$

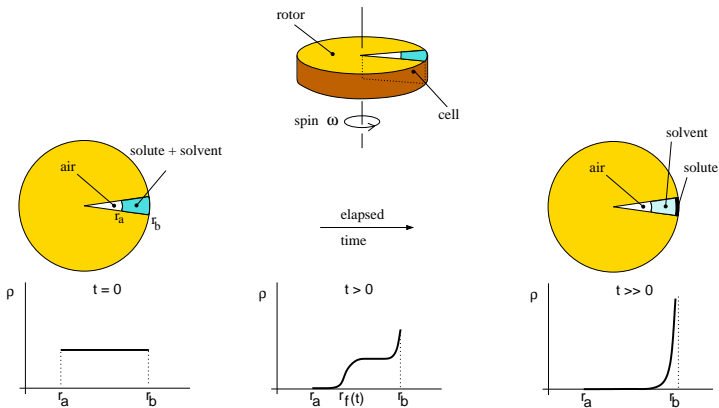
$$D = kT/6\pi\gamma\mu, \quad S = m'/6\pi\gamma\mu.$$



# Analysis of experiment

# Problem

Deduce particle radius  $\gamma$  from experimental data on solute concentration  $\rho$ .



# Simplification of Lamm equations

In experiments,  $D \ll S\omega^2 r_a^2$  ( $\omega$  is large). Thus it is reasonable to ignore  $D \frac{\partial \rho}{\partial r}$  in regions where  $\frac{\partial \rho}{\partial r}$  is moderate (away from  $r = r_b$ ):

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= \frac{1}{r} \frac{\partial}{\partial r} \left( r D \frac{\partial \rho}{\partial r} - S\omega^2 r^2 \rho \right), & r_a < r < r_b, & t > 0 \\ D \frac{\partial \rho}{\partial r} &= S\omega^2 r \rho, & r = r_a, & t > 0 \\ D \frac{\partial \rho}{\partial r} &= S\omega^2 r \rho, & r = r_b, & t > 0 \\ \rho(r, 0) &= \rho_0(r), & r_a \leq r \leq r_b, & t = 0. \end{aligned}$$

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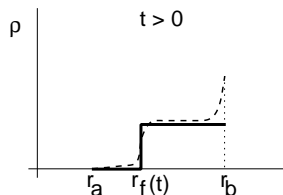
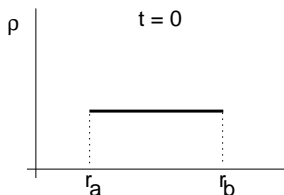
The leading-order equations away from  $r = r_b$  are:

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= -\frac{1}{r} \frac{\partial}{\partial r} \left( S\omega^2 r^2 \rho \right), & r > r_a, & t > 0 \\ 0 &= S\omega^2 r \rho, & r = r_a, & t > 0 \\ \rho(r, 0) &= \rho_0(r), & r \geq r_a, & t = 0. \end{aligned}$$

# Solution of leading-order equations

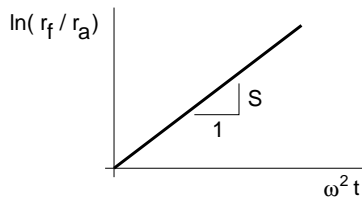
Using the method of characteristics we obtain, for a general initial condition  $\rho_0(r)$

$$\rho(r, t) = \begin{cases} 0, & r < r_a e^{S\omega^2 t} \\ e^{-2S\omega^2 t} \rho_0\left(r e^{-S\omega^2 t}\right), & r \geq r_a e^{S\omega^2 t}. \end{cases}$$



## Estimation of radius

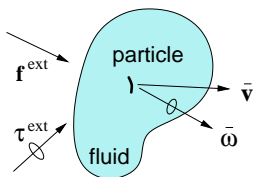
The leading-order solution implies that the location of the moving front is  $r_f(t) = r_a e^{S\omega^2 t}$ . Thus  $S$  can be determined from data on the front location  $r_f$ .



Thus: experiment  $\longrightarrow S = \frac{m'}{6\pi\gamma\mu} \longrightarrow$  particle radius.

# Generalization

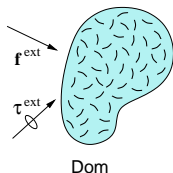
# Stokes law



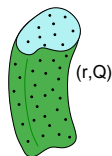
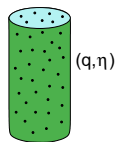
$$\begin{bmatrix} \bar{v} \\ \bar{\omega} \end{bmatrix} = \underbrace{\begin{bmatrix} M_1 & M_3 \\ M_2 & M_4 \end{bmatrix}}_M \begin{bmatrix} f \\ \tau \end{bmatrix}^{\text{ext}}.$$

$M \in \mathbb{R}^{6 \times 6}$  Stokes mobility matrix  
determined by shape of solute particle.

# Conservation of mass



Dom

Dom x SO<sub>3</sub> $\Omega \times A$ 

$$\sigma_t + g^{-1} \nabla \cdot (gJ) = 0$$

$$J \cdot n = 0$$

$$J \cdot n \text{ periodic}$$

$$\sigma = \sigma_0$$

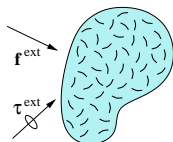
$$\text{in } \Omega \times A, \quad t > 0$$

$$\text{on } (\partial\Omega) \times A, \quad t \geq 0$$

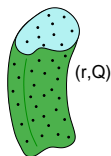
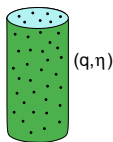
$$\text{on } \Omega \times (\partial A), \quad t \geq 0$$

$$\text{in } \Omega \times A, \quad t = 0.$$

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Dom x SO<sub>3</sub> $\Omega \times A$ 

$$\begin{array}{lll}
 \sigma_t + g^{-1} \nabla \cdot (gJ) = 0 & \text{in} & \Omega \times A, \quad t > 0 \\
 J \cdot n = 0 & \text{on} & (\partial\Omega) \times A, \quad t \geq 0 \\
 J \cdot n \text{ periodic} & \text{on} & \Omega \times (\partial A), \quad t \geq 0 \\
 \sigma = \sigma_0 & \text{in} & \Omega \times A, \quad t = 0.
 \end{array}$$

$\sigma$  = mass concentration in config space.

$$J = -D\nabla\sigma + \sigma Ch^{\text{ext}}, \quad D = \beta b M b^T, \quad C = b M c.$$

$\beta$  = Boltzmann factor.

$g, b, c$  = geometric factors.

$M$  = Stokes mobility matrix.

$h^{\text{ext}} = (f, \tau)^{\text{ext}}$  = external loads.

## Averaging result

**Result.** Due to a time-scale separation, the general balance of mass equation  $\sigma_t + g^{-1} \nabla \cdot (gJ) = 0$  reduces to the Lamm equation

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

where  $\rho = \int_{SO_3} \sigma dV$ ,  $D = \frac{kT}{3} \text{tr}(M_1)$ ,  $S = \frac{m'}{3} \text{tr}(M_1)$ .

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### Remarks.

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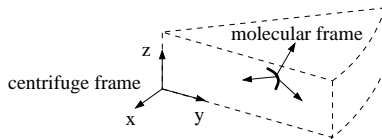
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- $\rho$  is usual concentration per unit volume of physical domain.
- Result follows by averaging over fast rotational time-scale.
- Recover classic results in case of spherical particles.
- As before, experiment  $\rightarrow S \rightarrow$  info on shape.

# Intuitive explanation

In terms of components in the molecular frame, assuming  $\tau^{\text{ext}} = 0$ , we have

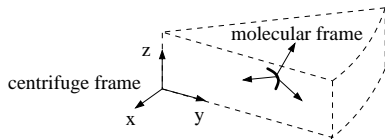
$$\begin{bmatrix} \bar{v} \\ \bar{\omega} \end{bmatrix} = \begin{bmatrix} M_1 & M_3 \\ M_2 & M_4 \end{bmatrix} \begin{bmatrix} f \\ \tau \end{bmatrix}^{\text{ext}} \quad \Rightarrow \quad \bar{v} = M_1 f^{\text{ext}}.$$



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Let  $[\bar{v}]_c$  and  $[f^{\text{ext}}]_c$  be components in the centrifuge frame, and let  $Q \in SO_3$  be the rotation from the centrifuge to molecular frame.

Then

$$[\bar{v}]_c = [M_1]_c [f^{\text{ext}}]_c, \quad [M_1]_c = Q M_1 Q^T.$$

## Intuitive explanation

Due to fast rotational diffusion,  $Q$  wanders uniformly over  $SO_3$ . Averaging the previous relation, assuming  $[f^{\text{ext}}]_c$  is fixed, yields

$$[\bar{v}]_c^{\text{avg}} = [M_1]_c^{\text{avg}} [f^{\text{ext}}]_c,$$

where

$$[M_1]_c^{\text{avg}} = \frac{\int_{SO_3} Q M_1 Q^T dV}{\int_{SO_3} dV} = \frac{1}{3} \text{tr}(M_1) I.$$

Since  $[\bar{v}]_c^{\text{avg}} \propto [f^{\text{ext}}]_c$ , the molecule behaves as if it were spherical.

# The End