

# Redbud Notes: Mass Transfer and ...

C.T. Miller, B. Griffith, K.M. Bruning, C.A. Bowers, ...

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## Abstract

The purpose of these notes is to organize activities for microscale and macroscale model development and application to support the simulation of experimental data collected by Redbud Labs.

## 1 Introduction

Our target for the phase I report and proposal is to simulate beads in system with and without flow. We also wish to simulate for both flow conditions, systems in which mass transfer of the target species occurs to beads distributed on the bottom and/or top of the domain and to the actuated posts. This mass transfer process is not currently in the model. Redbud Labs has produced the data needed to understand this process, and this data is of sufficient quality to inform a reasonable first-cut modeling approach.

## 2 Mass Transfer

The motivation for using beads, which was not in the original proposal, is that these are commodity items that can be targeted to a variety of specific species, saving development time. The magnetic beads are distributed in the microfluidic cell and the target species attaches to these beads, providing the separation needed for the applications of concern.

Mass transfer in general has two aspects, a model to determine the equilibrium state if the system is allowed to equilibrate until no net mass transfer is occurring, and a model to describe the rate at which this equilibrium state is approached. Laboratory data is thus collected for both aspects of the process and quantitative descriptions are advanced to represent these aspects.

Rate data is collected in well mixed systems, where a solute originally in the fluid phase attaches to the beads. The extent of attachment increases with time until an equilibrium point is approached. Of concern is the time scale for this approach to an equilibrium state, and the details of the shape of the function describing the solid phase mass fraction

$$\omega^{is} = f(t) , \tag{1}$$

where  $\omega^{is}$  is the macroscale mass fraction of species  $i$  on the solid phase,  $f$  is some unspecified function, and  $t$  is time.

In systems void of reactions and without flow, mass is conserved so the mass of the solute is either in the fluid phase or on the beads (solid phase). This distribution changes with time moving from all of the mass in the fluid phase to the final distribution of mass between the phases. Thus batch experiments are set up and the distribution of the solute between the fluid and bead phases is observed as a function of time. One can use such data to determine the time required to approach an equilibrium state.

Equilibrium data is collected using well-mixed experiments void of flow, batch experiments, in which a distribution of solute mass is placed in a set of batch systems and allowed to equilibrate for a time that is long compared to the time identified from the batch systems to approach equilibrium. The intention here is to determine the monotonic relationship between the solid phase mass fraction and the fluid phase concentration

$$\omega_{\text{eq}}^{is} = f(C_{\text{eq}}^{if}) , \quad (2)$$

where the subscript eq denotes an equilibrium state, and  $C^{if}$  is the solute concentration in the fluid phase. A set of classic models exist to describe both the sorption rate and equilibrium. These classic models are the typical starting point and should be adequate as a first-cut analysis of the data collected.

The equilibrium data collected appears to be consistent with a Langmuir model

$$\omega_{\text{eq}}^{is} = \frac{Q_o b C_{\text{eq}}^{if}}{1 + b C_{\text{eq}}^{if}} , \quad (3)$$

where  $Q_o$  is a parameter related to the capacity, and  $b$  is a parameter related to the shape of the equilibrium relationship. Note that for small values of  $C_{\text{eq}}^{if}$  the relationship between the solid phase mass fraction and the fluid phase concentration is linear, and in the limit of large values of  $C_{\text{eq}}^{if}$  a constant mass fraction of  $\omega_{\text{eq}}^{is}$  is approached. The batch equilibrium data is used to determine these two parameters.

There are a lot of approximations for the mass transfer rate—local equilibrium models, first-order approximations, a set of first-order approximations, and many types of diffusion models. The Redbud Labs data clearly has rate effects that are important, so the assumption of local equilibrium would not be a good assumption. The next simplest thing we can do is to assume a first-order approximation. For a batch system this becomes

$$V^f \frac{dC^{if}}{dt} = -\hat{k} M^s (\omega_{\text{eq}}^{is} - \omega^{is}) , \quad (4)$$

where  $V^f$  is the volume of the fluid phase in the batch system,  $M^s$  is the mass of the solid phase in the batch system, and  $\hat{k}$  is a first-order rate coefficient. For this rate model,  $\omega_{\text{eq}}^{is}$  is computed using Eqn (3) evaluated using  $C^{if}$ , or the solid-phase equilibrium mass fraction corresponding to the current fluid-phase

concentration. At equilibrium, both sides of Eqn (4) vanish. Correspondingly, for constant  $\rho^s$ , it follows from the conservation of mass that

$$\frac{d\omega^{is}}{dt} = \hat{k} (\omega_{\text{eq}}^{is} - \omega^{is}) . \quad (5)$$

This will get us started. If KMB or CAB need more details, then they should review the environmental physics notes. It may turn out that we need a more complicated model for the rate, but we should go with this to get us started and produce results for the report and proposal.

### 3 Macroscale Modeling

Modeling Redbud microfluidic cells at the macroscale is done by using the conservation of mass equation, formulated in the TCAT framework as

$$\frac{\partial \epsilon^{\bar{w}} \rho^w \omega^{i\bar{w}}}{\partial t} + \nabla \cdot (\epsilon^{\bar{w}} \rho^w \omega^{i\bar{w}} \mathbf{v}^{\bar{w}}) + \nabla \cdot (\epsilon^{\bar{w}} \rho^w \omega^{i\bar{w}} \mathbf{u}^{\bar{i}\bar{w}}) - \epsilon^{\bar{w}} r^{iw} - \overset{s \rightarrow w}{M} = 0 , \quad (6)$$

where  $\epsilon^{\bar{w}}$  is porosity,  $\rho^w$  is density,  $\omega^{i\bar{w}}$  is mass fraction of  $i$ ,  $\mathbf{v}^{\bar{w}}$  is the averaged fluid velocity,  $\mathbf{u}^{\bar{i}\bar{w}}$  is the variation velocity of  $i$ ,  $r^{iw}$  is the reaction source term for species  $i$ , and  $\overset{s \rightarrow w}{M}$  is the mass exchange from the  $s$  to the  $w$  phase. Each term in Eqn (6) may be calibrated to match microscale simulation or experimental data by comparing macroscale simulations to precisely defined, averaged microscale quantities.

There are four cases that have been modeled so far: 1.) conserved species transport with no flow; 2.) species transport with no flow and mass transfer between the fluid and solid phases; 3.) perfusion without mass transfer; and 4.) perfusion with mass transfer. In all of the cases, the Redbud posts (RBPs) are present and spinning. Each of the scenarios discussed above are treated in detail in the following sections.

#### 3.1 Conserved transport, no perfusion

The conservation of mass equation for the case of species transport without perfusion or mass transfer is

$$\frac{\partial \epsilon^{\bar{w}} \rho^w \omega^{i\bar{w}}}{\partial t} + \nabla \cdot (\epsilon^{\bar{w}} \rho^w \omega^{i\bar{w}} \mathbf{u}^{\bar{i}\bar{w}}) = 0 . \quad (7)$$

Note that, although the posts are spinning in this case, we are modeling the system with a macroscale phase velocity of zero, reflecting the time-averaged velocity. The deviation velocity was modeled by assuming that effects from RBPs lead to enhanced diffusion that follow Fick's law at the macroscale, thus

$$\rho^w \omega^{i\bar{w}} \mathbf{u}^{\bar{i}\bar{w}} = -\rho^w \hat{\mathbf{D}}^w \cdot \nabla \omega^{i\bar{w}} , \quad (8)$$

where  $\hat{\mathbf{D}}^w$  is enhanced diffusion. For our case of incompressible flow with isotropic diffusion, this makes the conservation of mass equation

$$\rho^w \frac{\partial \omega^{i\bar{w}}}{\partial t} - \rho^w \hat{D}^w \nabla^2 \omega^{i\bar{w}} = 0. \quad (9)$$

Eqn (9) was solved using OpenFOAM.

### 3.2 Species transport with mass transfer, no perfusion

The conservation of mass equation for the case of no perfusion and mass transfer, after applying Eqn (8), is

$$\epsilon^{\bar{w}} \rho^w \frac{\partial \omega^{i\bar{w}}}{\partial t} - \epsilon^{\bar{w}} \rho^w \hat{D}^w \nabla^2 \omega^{i\bar{w}} - \overset{s \rightarrow w}{M} = 0. \quad (10)$$

The mass transfer term is calculated from the sorption rate of the solid phase, which was found to follow the pseudo  $n$ th order rate law

$$\frac{\partial \omega^{i\bar{s}}}{\partial t} = \hat{k}^w (\omega^{i\bar{s}}_{eq} - \omega^{i\bar{s}})^n, \quad (11)$$

where  $\hat{k}^w$  and  $n$  are empirically fit constants, and  $\omega^{i\bar{s}}_{eq}$  is the equilibrium mass fraction given by the Langmuir model,

$$\omega^{is}_{eq} = \frac{Q_0 b C_{eq}^{iw}}{1 + b C_{eq}^{iw}}, \quad (12)$$

where  $C_{eq}^{iw}$  is the equilibrium concentration in the fluid phase and  $Q_0$  and  $b$  are empirically fit constants. We have shown elsewhere that the mass transfer rate can be calculated from

$$\overset{s \rightarrow w}{M} = - \left( 1 + \frac{\omega^{i\bar{s}}}{1 - \omega^{i\bar{s}}} \right)^2 \frac{m_0^s}{V^w} \frac{d\omega^{i\bar{s}}}{dt}, \quad (13)$$

where  $m_0^s/V^w$  is the initial mass-per-fluid-volume of solid in the system, which is one of the design parameters that we may choose.

In cases where mass transfer occurs, we solved Eqn (10) using a split-operator method that we coded into OpenFOAM. This works by solving Eqn (9) for some intermediate value,  $\omega^{i\bar{w}*}$ , first, and then solving for the concentration after reaction using a forward Euler method, given below

$$\rho^w \omega^{i\bar{w}} = \rho^w \omega^{i\bar{w}*} + \overset{s \rightarrow w}{M}. \quad (14)$$

### 3.3 Perfusion cases

The perfusion cases involved solving Eqn (6) when  $\mathbf{v}^{\bar{w}}$  is non-zero. In these cases,  $\mathbf{v}^{\bar{w}}$  was calculated by solving for the velocity potential,  $\phi^{\bar{w}}$ , defined by

$$\mathbf{v}^{\bar{w}} = \nabla \phi^{\bar{w}}. \quad (15)$$

The flow potential itself was calculated from the Laplace equation for the system,

$$\nabla^2 \phi^{\bar{\bar{w}}} = 0 . \quad (16)$$

Eqn (16) was solved using solver utilities that are built into OpenFOAM. All other calculations for the perfusion cases were conducted in the same way as for the cases without perfusion.

## 4 Next Steps

The next steps for getting this process into our models are:

- KMB and CAB should get the equilibrium and rate data from Katelyn and determine  $Q_o$ ,  $b$ , and  $\hat{k}$ .
- BG should review, ask questions as needed, and formulate into both the beads attached to posts and the bottom and top boundaries for the IBAMR code. The inputs will be the coefficients and mass distribution of the beads. We will be interested in evaluating cases where the mass distribution of beads differs among the posts, and top and bottom boundaries.
- CAB should incorporate into the macroscale model, which will require a coupled equation for the solid phase. Review the physics notes, work through the details, and ask questions as needed.