14 Jan 2010 Math Modeling - Crystal Precipitation

First chapter of the book deals with making film, which is facilitated by using silver bromide ($AgBr$) crystals.

Background

photographic emulsion: a suspension of small particles in aqueous gelatin

crystal - three-dimensional atomic or molecular structure consisting of periodically repeated unit cells.

- crystal particles generally have planar external face
- modern film consists of several emulsion layers.

When a picture is taken, film is exposed to light, causing some photons to enter the crystal grains.
↳ this is the photograph.

Turns out (see text) that ~~then~~ size of ~~a~~ crystals determine the film speed.

Also, 'graniness' of a picture is a result of size and distribution of crystals.

The process of manufacturing ~~so~~ crystal grains of a given (approximate) size is based on a process called 'Ostwald ripening'.

The process begins with a dry mixture of small grain sizes that have been 'precipitated' from a sol^{n}.

* Ostwald ripening is based on the following fact:

→ Next, grains are added to a solvent and kept mixed.

→ if we allow the mixture to go on for a long time then one of two things will occur:

1) all crystal grains will dissolve into sol^{n}
2) all grains in sol^{n} will become the same size

Option 2 is the objective by messing with the solvent, or other parameters.

Model

emperical eq^{n}s - equations derived experimentally

- Always begin w/ assumptions:

1a) Assume that all crystal grains have the same shape and differ only in size. For example, boxes w/ edges $\lambda a, \lambda b, \lambda c$, a, b, c = constant, λ = positive.

1b) Assume all grains are cubes w/ variable diameter and orientation.

Given a volume of fluid containing an amount of dissolved matter (solute), there will be in equilibrium a saturation concentration c^* which is the maximum solute per unit volume of fluid that the system can hold.

actual concentration: $c(t)$, t = time (s)

if $c(t)$ exceeds c^*, then there is precipitation.

For our work, to cause precipitation, $c(t)$ must be larger than a quantity C_L, $C_L > C^*$, that is dependent on grain size.

Denote the length of an edge of crystal grains by L (all cubes).

~~For~~ Empirically (from experiment), C_L is given by,

$$C_L = c^* e^{\Gamma/L} \qquad (1)$$

Γ - physical quantity depending on crystal shape, composition, and temperature.

Note that:

- if $c(t) > C_L$, then material will come out of sol^n and deposit crystals characterized by L.
- if $c(t) < C_L$ then material will disolve from the crystals

Using (1), can write

$$② \quad L^*(t) = \frac{\Gamma}{\log_e\left(\frac{c(t)}{c^*}\right)}$$

, $\log() = \ln()$
= natural log
= log base e

From semi-empirical law, crystal size L will grow or dissolve at the rate:

$$\frac{dL}{dt} = G(L, c(t)) \quad ③$$

where,

$$④ \quad G(L, c(t)) = \begin{cases} k_g\left(c(t) - c^* e^{\Gamma/L}\right)^g, & L > L^*(t) \\ -k_d\left(c^* e^{\Gamma/L} - c(t)\right)^d, & L < L^*(t) \end{cases}$$

where k_g, k_d, g, and d are constant, positive, with

$$1 \le g \le 2, \qquad 1 \le d \le 2$$

Note from (3) and (4),

- if $c(t) > C_L$ (or $L > L^*(t)$), then

$$\frac{dL}{dt} > 0 \Rightarrow \text{crystal growth}$$

- if $c(t) < C_L$ $(L < L^*(t))$, then

$$\frac{dL}{dt} < 0, \Rightarrow \text{crystal shrinkage}$$

Assume initially there are N different sizes of crystals, sizes $L = X_j^*$, and numbers μ_j^* per unit volume, where

$$0 < X_1^* < X_2^* < \dots < X_N^*.$$

The sizes will then evolve in time according to (3)

$$\Rightarrow \frac{dx_j}{dt} = G(x_j, c(t)) \quad (5)$$

The concentration $c(t)$ of the solute at time t is given by

$$c(t) = C_0 + \rho K_v \sum_{j=1}^{N} \mu_j^* (x_j^*)^3 - \rho K_v \sum_{j=1}^{N} \mu_j^* x_j(t)^3 \quad (6)$$

C_0 - initial concentration
K_v - geometric parameter (taken, for cubic crystals, $K_v = 1$)
ρ - mass density of solid phase

Subsitute $c(t)$ from 6 into 5, to obtain a system of differential equations.

(7) $$\frac{dx_j}{dt} = G_j(x_1, \dots, x_N) \quad , \ j = 1, \dots, N$$

Also have initial conditions,

(8) $$x_j(0) = x_j^* .$$

Set $\mu_j = \rho k_v \mu_j^*$, $c_1 = c_0 + \sum_{j=1}^{N} \mu_j (x_j^*)^3$

c_1 - represents total amount of silver bromide per unit volume in either crystal or sol^n form.

Special case $N=1$,

$$\frac{dx}{dt} = G(x), \ x(0) = x^*$$

where

$$G(x) = \begin{cases} k_g\left(c_1 - \mu x^3 - c^* e^{\Gamma/x}\right)^g, & c_1 - \mu x^3 > c^* e^{\Gamma/x} \\ -k_d\left(c^* e^{\Gamma/x} - (c_1 - \mu x^3)\right)^d, & c^* e^{\Gamma/x} > c_1 - \mu x^3 \end{cases}$$

Typical physical constants given in book, p. 7.

This is an ordinary diff. eq^n. (ODE)

Note that 7 and 8 are a system ~~s~~ of ODEs, specifically an ~~d~~ initial value problem, or IVP.

7 and 8

Note that sections 1.4, 1.5, and 1.6 contain review material on ODEs and systems of ODEs. These include existence and uniqueness theorems and ~~asso~~ proofs.