Topic 1: Crystal Precipitation
in batch crystalizer
Ostwald Ripening process

Batch crystalization – used in making many products...
– big business in chemical industry
pharmaceutical

Very often, crystals of certain sizes are desired.
This is done in a crystalizer, based on Ostwald Ripening:

- mix crystals of any sizes (produced by precipitation from solution) into appropriate solvent
- keep mixed, usually by stirring, to promote Ostwald Ripening:
  Larger crystals grow at the expense of smaller ones (via diffusion)
  "thermodynamic capitalism"!
  slower and slower...
- when crystals are about the desired size, remove them (often by drying out solvent.)

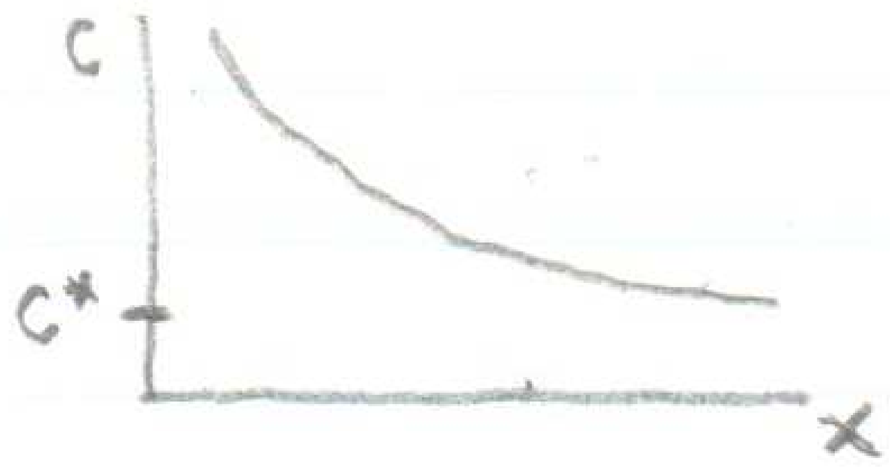
There are various models of the process (involving PDEs)

We will discuss a simple but successful one, involving ODEs.

A simple model for Ostwald Ripening

- Assume crystals of same shape, say cubes, of size x, for simplicity

- A solute-solvent equilibrium is governed by a



solubility curve

c = solute concentration

c_{crit} = saturation concentration

= max the system can hold in solution at T, P

if $c > c_{crit}$ then the excess precipitates out as solid (crystals)

if $<$ then crystals dissolve into the solvent

- Gibbs-Thomson relation: $c_{crit} = c^* e^{\frac{\Gamma}{x}}$

$$\Gamma = \frac{4 \sigma v}{RT}$$

σ = surface energy $\left[\frac{J}{m^2}\right]$

v = molar volume of solute $\left[\frac{m^3}{mol}\right]$

R = gas constant $\left[\frac{J}{mol\ K}\right]$

T = temperature $[K]$

c^* = saturation conc. at ∞ dilution

so, the larger the size x, the lower the triggering value

so, larger crystals grow easier! "thermodynamic capitalism"!

- solute concentration in solution: $c = c_0 + \mu (x^*)^3 - \mu x^3$

x^* = initial size (at time zero)

c_0 = initial concentration of solute in solution

- $c^*, \Gamma, \mu, c_0, x^*$: given constants (parameters)

$x(t)$ time-dependant unknown

need a law (rule) for how $x(t)$ evolves in time...

Empirical (phenomenological) Kinetic Law for $x(t)$:

$$\frac{dx}{dt} = \begin{cases} k_g (c - c_{crit})^g & \text{if } c > c_{crit} \\ -k_d (c_{crit} - c)^d & \text{if } c < c_{crit} \end{cases}$$

for some parameters $k_g, k_d > 0$, $1 \leq g, d \leq 2$.

So, if $c > c_{crit}$ then $\frac{dx}{dt} > 0$ so x grows
if $c < c_{crit}$ < 0 decays
if $c = c_{crit}$ $= 0$ no change

This is an ODE for $x(t)$, of 1^{st} order

$$\frac{dx}{dt} = G(x)$$

with initial condition: $x(0) = x^* =$ initial size.

For simplicity (and convenience) we take $g = d = 1$
and $k_g = k_d =: k$
in which case $G(x)$ simplifies to

$$G(x) = k(c - c_{crit})$$
$$= k\left[c_0 + \mu(x^*)^3 - \mu x^3 - c^* e^{\frac{\Gamma}{x}}\right]$$

Evolution model for crystals of $\boxed{N \text{ sizes}}$

Assume initially there are N different sizes

$$0 < x_1^* < \dots < x_N^*$$

They evolve according to our kinetic law to sizes $x_1(t), \dots, x_N(t)$ governed by

$$(\text{IVP}) \begin{cases} \dfrac{dx_j}{dt} = G_j(x_1, \dots, x_N) = k\left[c(t) - c_{crit,j}\right] \\ x_j(0) = x_j^* \end{cases} \qquad j = 1, 2, \dots, N$$

$$\text{where} \quad c(t) = c_0 + \sum_{j=1}^{N} \mu_j (x_j^*)^3 - \sum_{i=1}^{N} \mu_i (x_i(t))^3$$

$$= \underbrace{c_0 + \sum_{j=1}^{N} \mu_j (x_j^*)^3}_{\substack{= C_1 \\ \text{(constant)}}} - \sum_{i=1}^{N} \mu_i x_i(t)^3$$

$$c_{crit,j} = c^* e^{\frac{\Gamma}{x_j}} \quad , \quad j = 1:N$$

This is an Initial Value Problem (IVP) for a system of N first order ODEs.

Very nonlinear, x_j's appear in x_j^3 and e^{Γ/x_j}

In vector notation, setting $\vec{X} = \begin{bmatrix} x_1 \\ \vdots \\ x_N \end{bmatrix}$, $\vec{G} = \begin{bmatrix} G_1 \\ \vdots \\ G_N \end{bmatrix}$, $\vec{X}^* = \begin{bmatrix} x_1^* \\ \vdots \\ x_N^* \end{bmatrix}$

$$(\text{IVP}) \quad \frac{d\vec{X}}{dt} = \vec{G}(\vec{X}) \quad , \quad \vec{X}(0) = \vec{X}^*$$

Simplest case: Single size crystals: $N = 1$

Consider crystals of a single size $x(t)$ evolving from initial size x^*:
cubic shape

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

where $$G(x) = k\left[c - c_{crit}\right] = k\left[c_1 - \mu x^3 - c^* e^{\frac{\Gamma}{x}}\right]$$

with $$c(t) = \underbrace{c_0 + \mu(x^*)^3}_{} - \mu x(t)^3 \quad , \quad c_{crit} = c^* e^{\frac{\Gamma}{x(t)}}$$

$$= c_1 - \mu x^3$$

Note: time does not appear explicitly, such ODEs are called autonomous.

Equilibria are constant (steady-state) solutions of an ODE $\frac{dx}{dt} = G(x)$

so must satisfy $G(x) = 0$, so they are zeros (roots) of $G(x)$.

Are there any? how many?

About ODEs - core ideas

General <u>n-th order ODE</u> for $y(t)$: $F(t, y, y', y'', \dots, y^{(n)}) = 0$

Useful form: can solve for highest order derivative

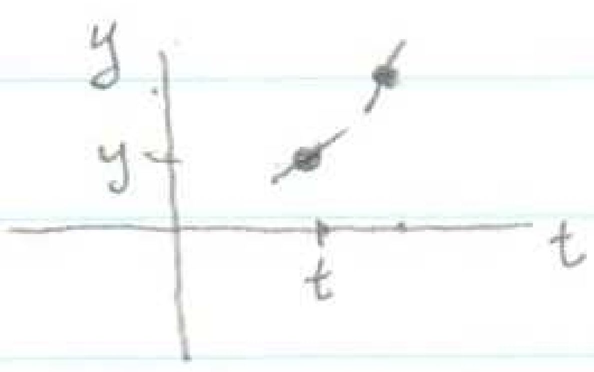
most important (by far...): 1^{st} and 2^{nd} order in "standard form":

$$y' = f(t,y) \quad , \quad y'' = f(t,y,y')$$

and 1^{st} order systems:
$$\begin{cases} y_1' = f_1(t, y_1, \dots, y_n) \\ y_2' = f_2(t, y_1, \dots, y_n) \\ \vdots \\ y_n' = f_n(t, y_1, \dots, y_n) \end{cases} \quad \text{or} \quad \vec{y}\,' = \vec{f}(t, \vec{y})$$

<u>1^{st} order</u>: $y' = f(t,y)$: find a <u>curve</u> $y = y(t)$ given its slope $y'(t)$

At each point (t, y) the ODE specifies the direction (slope) of $y = y(t)$



To solve it: pick a starting point (t_0, y_0)
and follow the <u>direction field</u>

To get a unique solution curve, need to specify a starting point
so need an <u>Initial Condition</u> (IC): $y(t_0) = y_0$

Operationally, must somehow "integrate" to find $y(t)$ from $y'(t)$
so there will be an arbitrary constant of integration,
so need an IC to find the constant.

standard form of 1^{st} order (IVP): $\begin{cases} y' = f(t,y) \\ y(t_0) = y_0 \end{cases}$ find solution curve through (t_0, y_0)

<u>Well-posed problem</u> if
1. existence: a solution exists
2. uniqueness: only one solution
3. continuous dependence on data
   (small change in data $\Rightarrow$ small change in solution)
   (stability under perturbations)