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.)

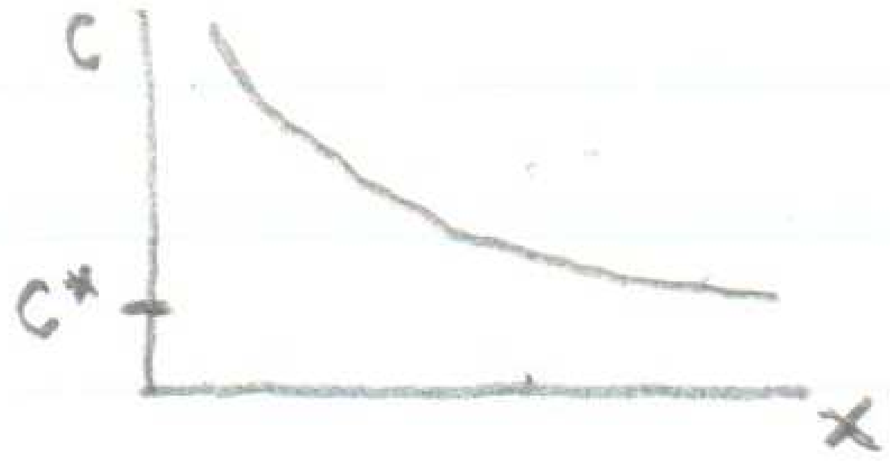
There are various models of the process (involving PDEs)

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) <u>kinetic Law</u> for $x(t)$:

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

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

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

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

$$= C_1 - \sum_{i=1}^{N} \mu_i \, x_i(t)^3$$

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

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

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

Simplest case: <u>Single size crystals</u>: $N = 1$

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

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

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

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

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

Note: time does <u>not</u> appear explicitly, such ODEs are called <u>autonomous</u>.

<u>Equilibria</u> 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?