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Enzyme kinetics as "singular perturbation" problem (Michaelis – Menten theory)

1) Basic enzyme reaction:

$$S + E \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SE \xrightarrow{k_2} P + E$$

S – substrate, E – enzyme, SE – complex, P – product

Enzymes are catalysts of bio-chemical Reactions: $S \to \dots \to P$

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2) Concentrations: $s = [S]$; $e = [E]$; $c = [SE]$; $p = [P]$

k_i – reaction rates

$$\begin{cases} \dot{s} = -k_1 s e + k_{-1} c \\ \dot{e} = -k_1 s e + (k_{-1} + k_2) c \\ \dot{c} = k_1 s e - (k_{-1} + k_2) c \\ \dot{p} = k_2 c \end{cases}$$

Mass action (conservation): $\boxed{e + c = e_0}$ – const

Reduced 2D system:

$$\begin{cases} \dot{s} = -k_1 e_0 s + (k_1 s + k_{-1}) c \\ \dot{c} = k_1 e_0 s - (k_1 s + k_{-1} + k_2) c \end{cases}$$

IC/BC

$$\begin{cases} s(0) = s_0 \\ c(0) = 0 \end{cases}$$

Rescaling: $\tau = (k_1 e_0) t$; $u = S/S_0$; $v = C/e_0$

$K - \lambda$

$$\begin{cases} \dfrac{du}{d\tau} = -u + \left(u + \dfrac{k_{-1}}{k_1 S_0}\right) v \\ \underbrace{\dfrac{e_0}{S_0}}_{\varepsilon} \dfrac{dv}{d\tau} = u - \Big(u + \underbrace{\dfrac{k_{-1} + k_2}{k_1 S_0}}_{K}\Big) v \end{cases}$$

D-less constants

$K = \dfrac{k_{-1} + k_2}{k_1} / S_0 = K_m / S_0$

(Menten const)

$\lambda = \dfrac{k_2}{k_1 S_0}$

$\varepsilon = e_0 / S_0 \ll 1$ - small param.

$$(1) \begin{cases} \dot{u} = -u + (u + K - \lambda) v & \text{— "slow"} \\ \varepsilon \dot{v} = u - (u + K) v & \text{— "fast"} \end{cases}$$

i) Any DE/DS with small parameter ε can be expanded in a power series:

$$\dot{u} = f(u, \varepsilon) \Longrightarrow u = u_0 + \varepsilon u_1 + \dots$$

$$\begin{cases} \dot{u}_0 = f_0(u_0); \\ \dots \end{cases} \quad \begin{cases} \dot{u}_1 = \dots \\ \dots \end{cases}$$

} Regular perturb. expansion

ii) Small parameter in highest derivative makes Singular perturbation problem, since Regular perturbation series has no solution at 0-order:

Take expansion: $\begin{cases} u = u_0 + \varepsilon\, u_1 + \dots \\ v = v_0 + \varepsilon\, v_1 + \dots \end{cases}$

substitute in (1) $\Longrightarrow$

0-order DS

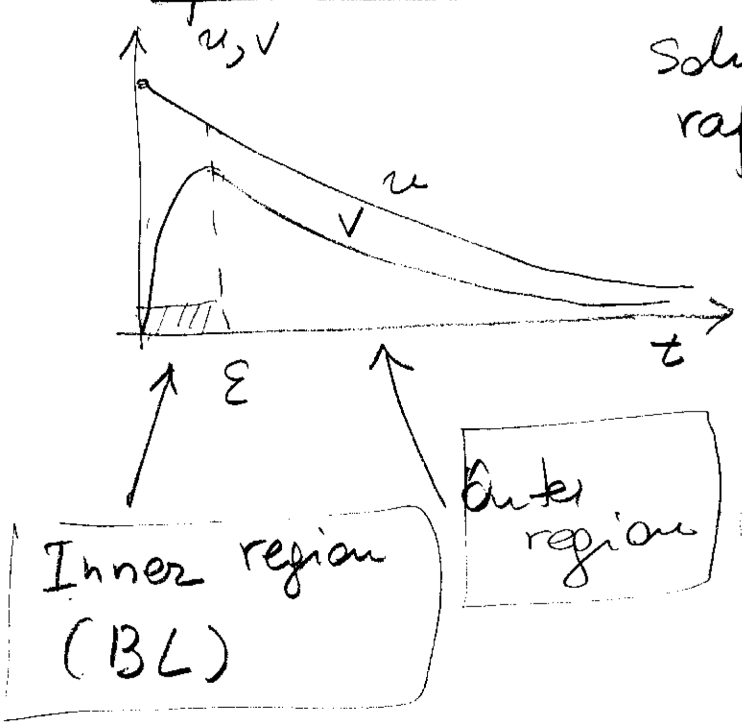
$$\begin{cases} \dot{u}_0 = -u_0 + (u_0 + K - \lambda)\, v_0 \\ 0 = u_0 - (u_0 + K)\, v_0 \end{cases} \Rightarrow \text{Quasi-equilibr. solution}$$

$$\dot{u}_0 = -\frac{\lambda u_0}{u_0 + K}$$

$$v_0 = \frac{u_0}{K + u_0}$$

Inconsistent w. IC: $u_0(0) = 1$, $v_0(0) = 0$

Conclusion: No Regular perturbation expansion for DS (1)!



Solution v(t) undergoes rapid change in the Boundary layer region $(0 < t < \varepsilon)$ before turning into quasi-equilibrium

$$v^* = \frac{u^*}{K + u^*}$$