Chemical kinetics HW

Part 0

- write correct kinetic equations
- approximate solns numerically, e.g. Euler's method
- try <u>multiple</u> ICs

  $\Rightarrow$ do they converge to different steady states?

  $\Rightarrow$ defining steady state, plotting solutions $[A](t)$ vs. t

Part 1

- write correct kinetic equations
- Use data where $[A], [B] \ll [C]$:

(backward reaction) $$\frac{d[C]}{dt} \sim -\ell \beta [C]^{\ell}$$

$\Longrightarrow$ ℓ is slope of $\log\left(\frac{d[C]}{dt}\right)$ & $\log([C])$

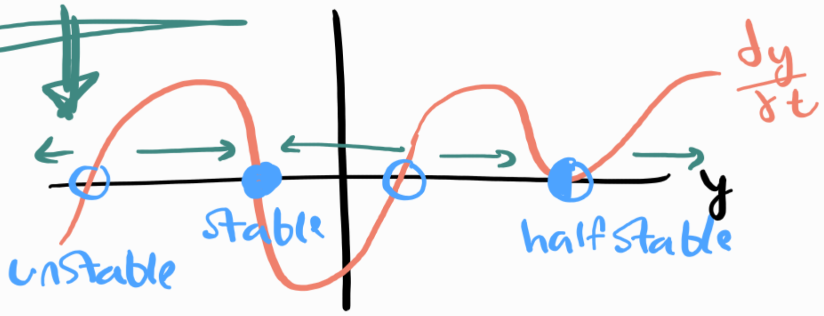
- notice: $\begin{cases} [\mathring{A}]/[\mathring{B}] = \gamma/k \\ [\mathring{B}]/[\mathring{C}] = k/\ell \\ [\mathring{A}]/[\mathring{C}] = \gamma/\ell \end{cases} \Longrightarrow$ use <u>different</u> data to find γ and k

Last time:

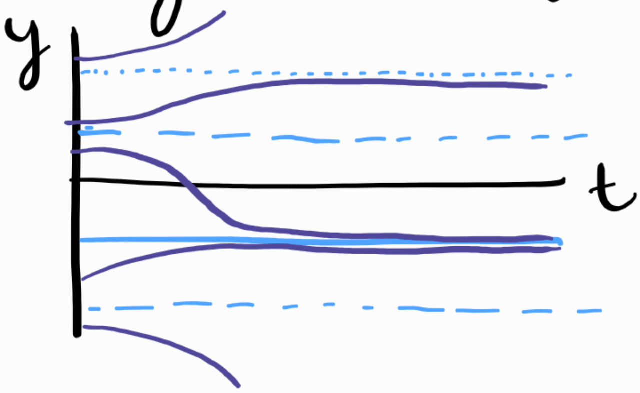
1D autonomous ODEs: $\frac{dy}{dt} = f(y)$

$\Rightarrow$ fixed points y^* s.t. $f(y^*) = 0$

$\Rightarrow$ phase line



$\Rightarrow$ Sketching solutions $y(t)$



$\Rightarrow$ linear stability analysis

small perturbation ε_0 near y^*

$\longrightarrow$ evolves, to $O(\varepsilon^2)$, like

$$\frac{d\varepsilon}{dt} = f'(y^*)\varepsilon \Longrightarrow \varepsilon(t) = \varepsilon_0 \exp(f'(y^*)t)$$

↳ $f'(y^*) > 0$ unstable

↳ $f'(y^*) < 0$ stable

↳ $f'(y^*) = 0$ inconclusive

Autonomous ODEs in 2D

General form: in higher dimensions

$$\begin{cases} \frac{dx_1}{dt} = F_1(x_1, x_2, \ldots, x_N) \\ \frac{dx_2}{dt} = F_2(x_1, x_2, \ldots, x_N) \\ \vdots \\ \frac{dx_N}{dt} = F_N(x_1, x_2, \ldots, x_N) \end{cases}$$

Example: (Linear)

$$\begin{cases} \frac{dx}{dt} = -2x - y \\ \frac{dy}{dt} = -2x - 3y \end{cases} \Rightarrow \frac{d\bar{x}}{dt} = \underline{\underline{A}}\,\bar{x} \text{ with } \underline{\underline{A}} = \begin{bmatrix} -2 & -1 \\ -2 & -3 \end{bmatrix}$$

$\Rightarrow$ X-nullclines: (x,y) s.t. $\frac{dx}{dt} = 0$

Y-nullclines: (x,y) s.t. $\frac{dy}{dt} = 0$

if both true, fixed point

↳ i.e. fixed points are where nullclines intersect

X-nullcline: $y = -2x$ Y-nullcline: $y = -\frac{2}{3}x$

$\Rightarrow$ plot in phase plane ⇝ MATLAB example

⇝ What do solns look like?

⇝ want solns like

growth rate

direction

$$\boxed{\bar{x}(t) = \exp(\lambda t)\,\bar{v}}$$

Notice:

$$\frac{d\bar{x}}{dt} = \lambda \cancel{\exp(\lambda t)} \bar{v} = \underline{\underline{A}}\,\bar{x} = \cancel{\exp(\lambda t)}\, \underline{\underline{A}}\,\bar{v}$$

$$\Longrightarrow \quad \underline{\underline{A}}\,\bar{v} = \lambda \bar{v} \rightsquigarrow \begin{pmatrix}\text{eigenvector} \\ \text{eigenvalue}\end{pmatrix} \text{pair}$$

In $\mathbb{R}^2$, $\bar{v}_1$ & $\bar{v}_2$ are linearly independent so

$$\bar{x}_0 = c_1 \bar{v}_1 + c_2 \bar{v}_2 \quad \text{initial cond.}$$

$$\Downarrow \text{consider}$$

$$x(t) = c_1 \exp(\lambda_1 t)\bar{v}_1 + c_2 \exp(\lambda_2 t)\bar{v}_2$$

$\Longrightarrow$ By uniqueness, the <u>only</u> soln

Returning to example:

$$\underline{\underline{A}} = \begin{bmatrix} -2 & -1 \\ -2 & -3 \end{bmatrix} \quad \text{eigenvalues:} \quad \begin{aligned} \lambda_1 &= -4 \\ \lambda_2 &= -1 \end{aligned}$$

$$\text{eigenvectors:} \quad \bar{v}_1 = \begin{bmatrix} 1 \\ 2 \end{bmatrix} \quad \bar{v}_2 = \begin{bmatrix} -1 \\ 1 \end{bmatrix}$$

(since $\lambda_1 < 0$, $\lambda_2 < 0$, exponential decay to zero along these eigenvectors)

<u>general soln:</u>

$$\bar{x}(t) = c_1 \exp(-4t)\begin{bmatrix} 1 \\ 2 \end{bmatrix} + c_2 \exp(-t)\begin{bmatrix} -1 \\ 1 \end{bmatrix}$$

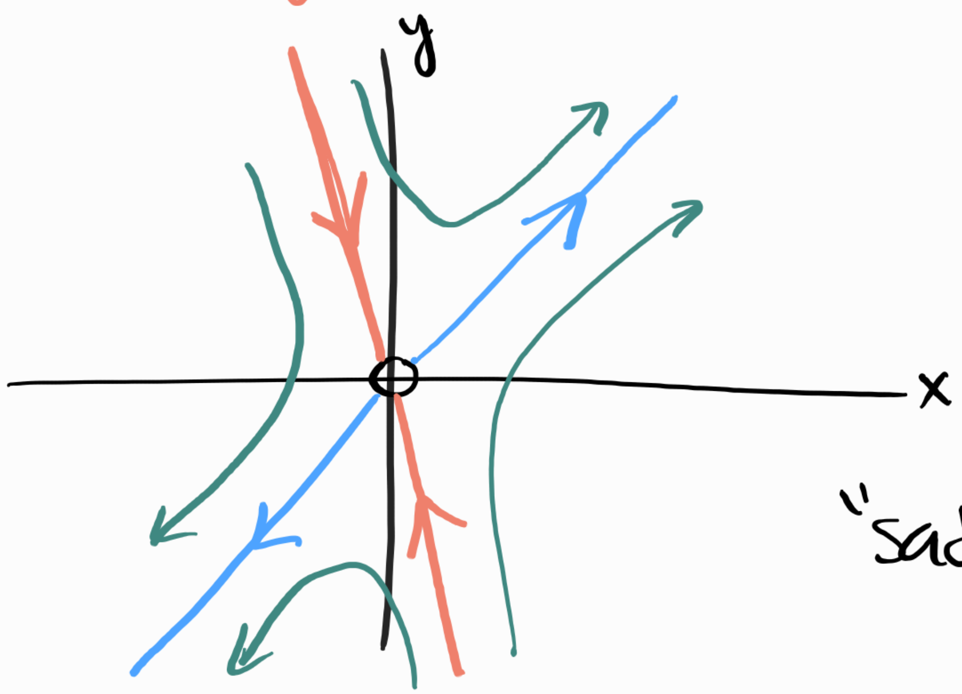
Example: (Linear) (Saddle point)

$$\begin{cases} \frac{dx}{dt} = x + y \\ \frac{dy}{dt} = 4x - 2y \end{cases} \Rightarrow \underline{\underline{A}} = \begin{bmatrix} 1 & 1 \\ 4 & -2 \end{bmatrix}$$

$\Rightarrow$ eigenvalue-eigenvector pairs:

$$\left(\lambda_1 = 2, \ \bar{v}_1 = \begin{bmatrix} 1 \\ 1 \end{bmatrix}\right) \quad \left(\lambda_2 = -3, \ \bar{v}_2 = \begin{bmatrix} 1 \\ -4 \end{bmatrix}\right)$$

$\uparrow$ growing $\qquad\qquad$ $\uparrow$ decaying



$v_1 = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$

$v_2 = \begin{pmatrix} 1 \\ -4 \end{pmatrix}$

"saddle point"

Example: (Linear) (spiral)

$$\begin{cases} \frac{dx}{dt} = x + y \\ \frac{dy}{dt} = -x \end{cases} \Rightarrow \underline{\underline{A}} = \begin{bmatrix} 1 & 1 \\ -1 & 0 \end{bmatrix}$$

eigenvalues

$$\lambda_1 = \frac{1}{2} + i\frac{\sqrt{3}}{2}$$

$$\lambda_2 = \frac{1}{2} - i\frac{\sqrt{3}}{2}$$

complex!

Suppose $\lambda = \alpha + i\beta$:

$$\exp(\lambda t) = \exp(\alpha)\exp(i\beta t)$$

$$= \underbrace{\exp(\alpha)}_{\text{exponential magnitude}} [\underbrace{\cos(\beta t)}_{\text{oscillatory}} + i\sin(\beta t)]$$

$\rightsquigarrow$ if $Re(\lambda) < 0 \Rightarrow$ stable spiral

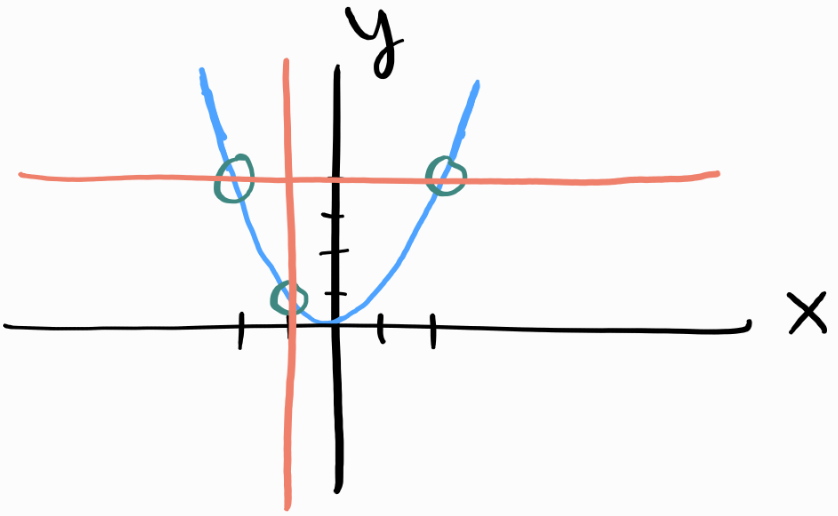
$Re(\lambda) > 0 \Rightarrow$ unstable spiral

$Re(\lambda) = 0 \Rightarrow$ center

note: neither stable nor unstable!

Example:

$$\begin{cases} \frac{dx}{dt} = (x+1)(y-4) \\ \frac{dy}{dt} = y - x^2 \end{cases}$$



$(x^*, y^*) = (2, 4)$

$(x^*, y^*) = (-2, +4)$

$(x^*, y^*) = (-1, 1)$

$\Rightarrow$ how to assess stability?

↳ in 1D, we look at $f'(y)$ because of linear stability analysis

↳ equivalent in 2D is linearization, which uses the Jacobian:

$$\mathbb{J} = \begin{bmatrix} \frac{\partial f}{\partial x} & \frac{\partial f}{\partial y} \\ \frac{\partial g}{\partial x} & \frac{\partial g}{\partial y} \end{bmatrix}$$

Let $u = x - x^*$ and $v = y - y^*$
small small

$$\Rightarrow \frac{du}{dt} = \frac{dx}{dt} = f(u + x^*, v + y^*)$$

↓ Taylor series

$$\approx \cancel{f(x^*,y^*)} + u \left.\frac{\partial f}{\partial x}\right|_{x^*,y^*} + v \left.\frac{\partial f}{\partial y}\right|_{x^*,y^*}$$

$$\Rightarrow \frac{du}{dt} = u \left.\frac{\partial f}{\partial x}\right|_{x^*,y^*} + v \left.\frac{\partial f}{\partial y}\right|_{x^*,y^*}$$

similarly,

$$\Rightarrow \frac{dv}{dt} = u \left.\frac{\partial g}{\partial x}\right|_{x^*,y^*} + v \left.\frac{\partial g}{\partial y}\right|_{x^*,y^*}$$

$$\Rightarrow \begin{bmatrix} \dot{u} \\ \dot{v} \end{bmatrix} = \left.\begin{bmatrix} \frac{\partial f}{\partial x} & \partial f/\partial y \\ \frac{\partial g}{\partial x} & \frac{\partial g}{\partial y} \end{bmatrix}\right|_{x^*,y^*} \begin{bmatrix} u \\ v \end{bmatrix}$$

$\Rightarrow$ a linear system we can analyze like before!

Returning to example:

$$f(x,y) = (x+1)(y-4)$$

$$g(x,y) = y - x^2$$

$$J(x,y) = \begin{bmatrix} y-4 & x+1 \\ -2x & 1 \end{bmatrix}$$

$(x^*, y^*) = (2,4)$: $J = \begin{bmatrix} 0 & 3 \\ -4 & 1 \end{bmatrix}$

$\lambda_{1,2} = \frac{1}{2}\left(1 \pm i\sqrt{47}\right) \Rightarrow$ unstable spiral

$(x^*, y^*) = (-2,4)$: $J = \begin{bmatrix} 0 & -1 \\ -4 & 1 \end{bmatrix}$

$\lambda_{1,2} = \frac{1}{2}\left(1 \pm i\sqrt{15}\right) \Rightarrow$ unstable spiral

$(x^*, y^*) = (-1,1)$: $J = \begin{bmatrix} -5 & 0 \\ +2 & 1 \end{bmatrix}$

$\lambda_1 = -5$

$\lambda_2 = 1$ $\Longrightarrow$ saddle point

If you get one eigenvalue λ with 2 independent eigenvectors:

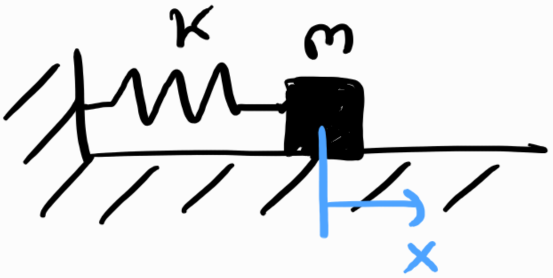
star node

if there is only one eigenvector:

degenerate node

Quiz:

Consider a mass on a spring. Let x be the deviation in position from rest.



Newton's Law tell us that

$$m\ddot{x} + kx = 0$$

You may rewrite this as

$$\begin{cases} \dot{x} = v & \text{(velocity)} \\ \dot{v} = -\omega^2 x & \text{(acceleration)} \end{cases}$$

where $\omega^2 = k/m$.

a) What are the fixed points?

b) What do they represent physically?

c) Classify the fixed points by looking at the eigenvalues

d) Sketch solutions in the phase plane for $(x_0, v_0) = (1, 0), (-2, 0), (0, -3)$ [initial condition]