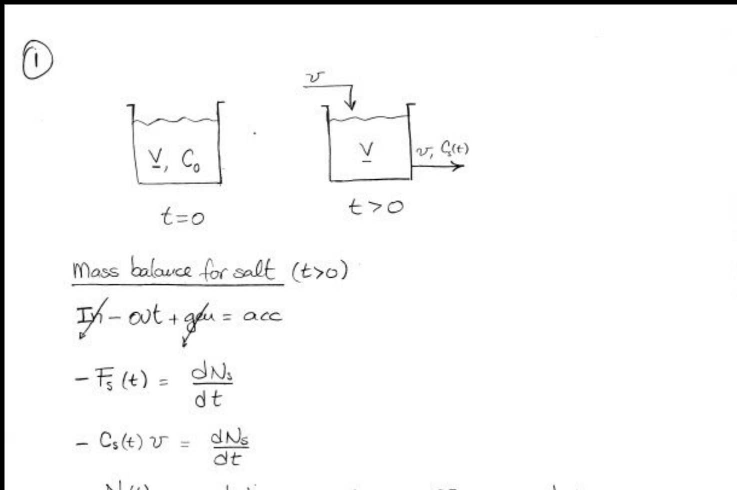
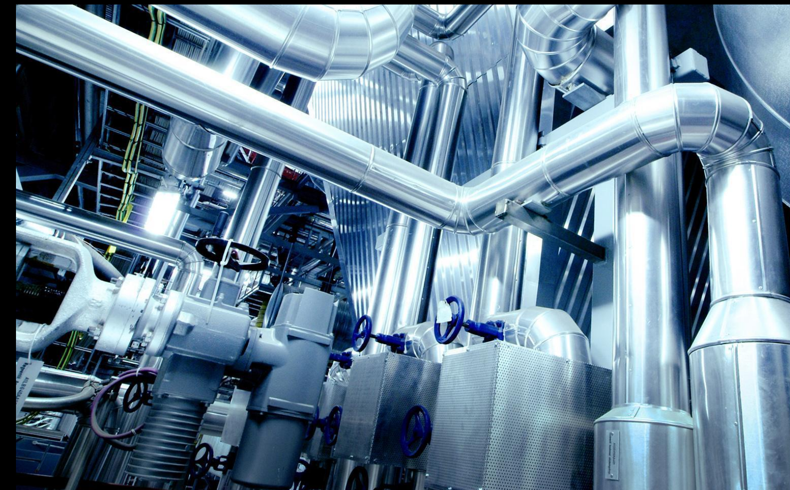
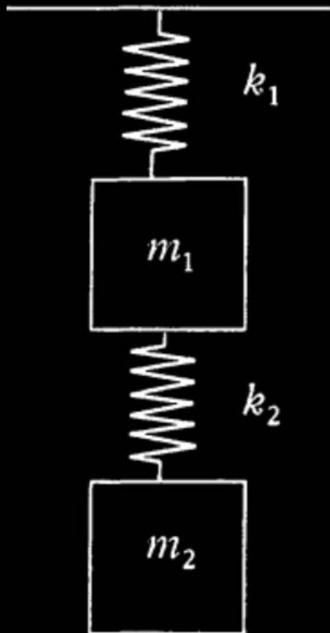




ChE352
Numerical Techniques for Chemical Engineers
Professor Stevenson

Lecture 12

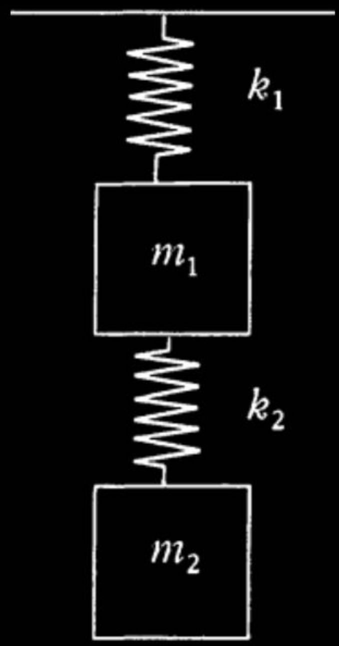
IVPs for springs



$k_2 > k_1$

$$m_1 x_1'' = -k_1 x_1 + k_2(x_2 - x_1)$$
$$m_2 x_2'' = -k_2(x_2 - x_1)$$

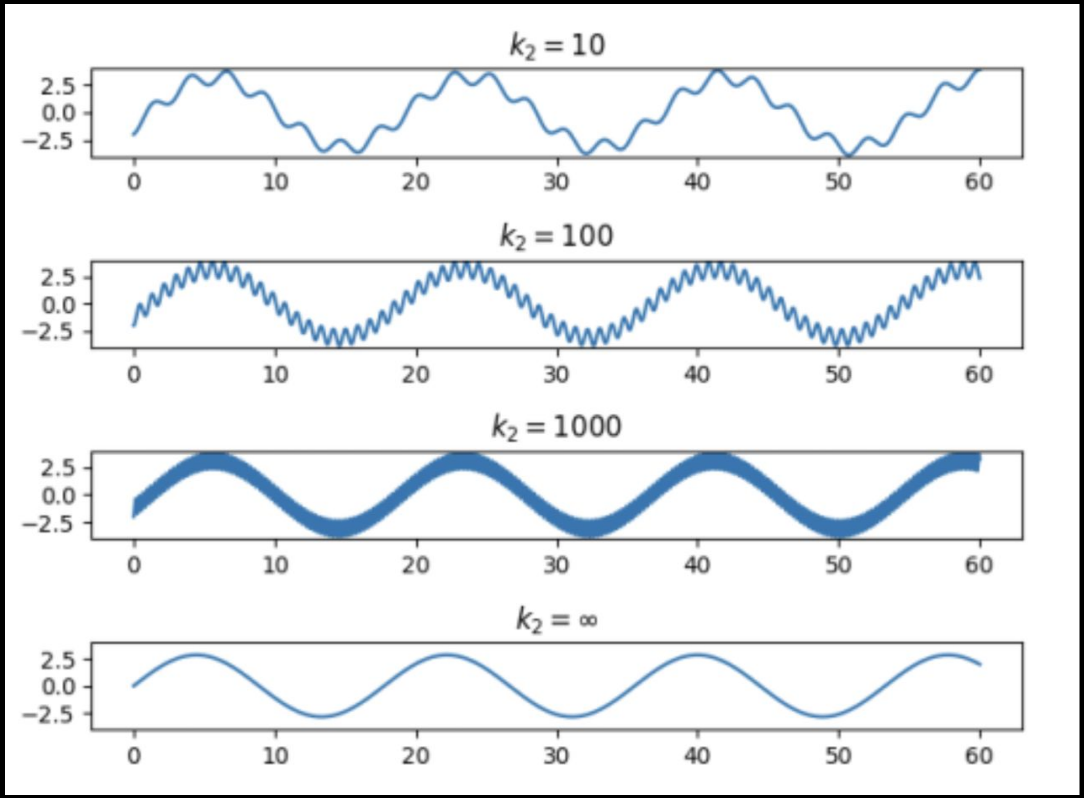
IVPs for springs



$$m_1 x_1'' = -k_1 x_1 + k_2(x_2 - x_1)$$
$$m_2 x_2'' = -k_2(x_2 - x_1)$$

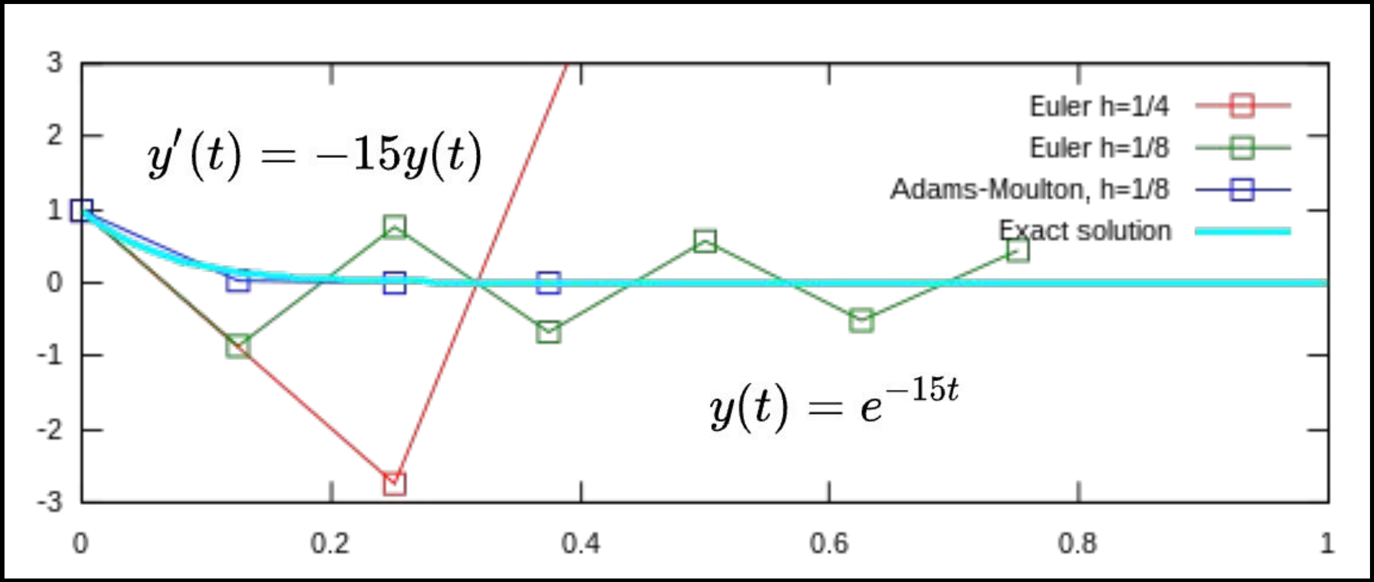
$k_2 > k_1$

When k_1 and k_2 are very different, this IVP becomes numerically difficult



Stiff IVPs

What happens when f(t, y) is very sensitive to y, so small errors in w_i have a big effect?



Common for chemical reactions, especially when a system has both fast & slow reactions.

Where does exp() appear in chemistry?

Stiff IVPs

- When the derivatives of f grow rapidly, higher order methods can have INCREASING error. These IVPs are called <u>stiff</u> (after stiff springs, which have equations with this property).

$$f(t,y) = e^{-ct} \quad \rightarrow \quad f^{(n)}(t,y) = (-1)^n c^n e^{-ct}$$

- Problems with e^{-ct} in their solutions, for large c, are often stiff (How is this like a spring?)
- How do we know if our IVP is stiff?
- Stiff IVPs require tiny steps or stable methods

Runge-Kutta-Fehlberg, RK45

- Error bound (ε) is <u>chosen by the user</u>
- Uses Runge-Kutta order 5 to estimate the error in a Runge-Kutta order 4 step
  - Shares some ks for efficiency
  - Only <u>six different evaluations of f per step</u>
  - Why not just use RK6?
- Fast, versatile, and returns correct answers if it returns at all: great algorithm
- Could RK45 still be dangerous in an engineering situation? How?

RK45 Step Size

- An <u>adaptive method</u> uses “big” steps when f is well-behaved and “small” ones when it isn’t
- For RKF45, the step size $t_{i+1} - t_i$ is qh, where:

0. $\textit{Set } h \textit{ to default, e.g.} \quad h = 0.1$

1. $\textit{Find} \quad k_1, k_2, k_3, k_4, k_5, \quad \textit{and} \quad k_6$

2. $\textit{Find} \quad \tilde{w}_{i+1}, w_{i+1}, \quad \textit{and} \quad q \textit{ where:}$

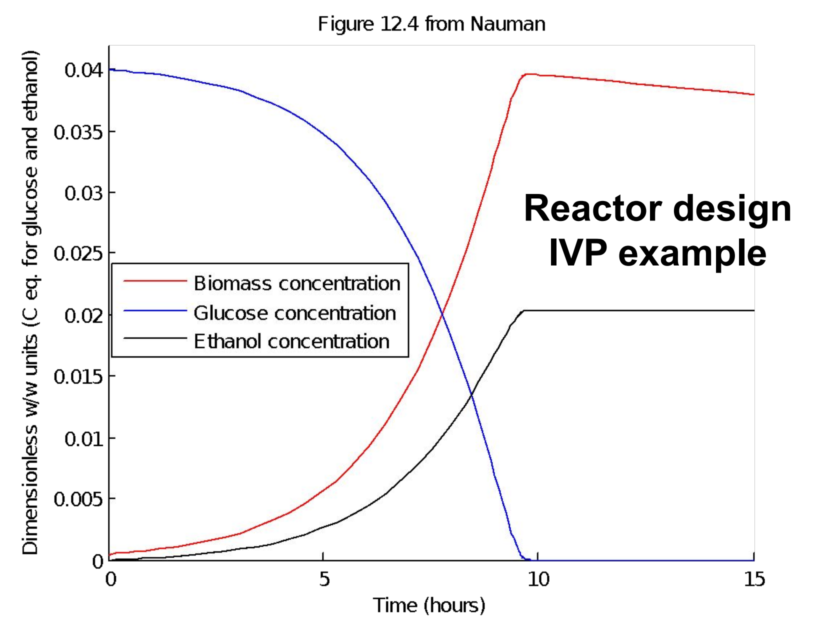
$$q = \sqrt[4]{\frac{h\varepsilon}{2\left|\tilde{w}_{i+1} - w_{i+1}\right|}}$$

What’s ε?

3. If $q > 1$: Keep w_{i+1}. Else: let $h = qh$ and go to 1.

RK45 in practice

- Error for a given h is $O(h^5)$, but since the method is adaptive, it will shrink h to get local error below your user-set tolerance ε
- RK45 uses qh to find k_1 through k_5, uses those to get order 4 approx. (w_{i+1}), calculates order 5 step ($\hat{w}_{i+1}$), then calculates q from h and ($\hat{w}_{i+1}$ - w_{i+1})



- If the steps get too small, RK45 may suffer from numerical errors. It may also simply run out of time.

One-step & explicit IVP methods

- All methods we've seen so far (Euler, RK2, RK4) are explicit, one-step methods
- A one-step method gives the next step y_{i+1} using only the previous step y_i (not y_{i-1} etc)
- An explicit method is a formula for $y_{i+1} = \ldots$

...How can we use a method that is not an explicit formula for y_{i+1}?

Implicit & multistep IVP methods

- All methods we've seen so far (Euler, RK2, RK4) are explicit, one-step methods
- A one-step method gives the next step y_{i+1} using only the previous step y_i (not y_{i-1} etc)
- An explicit method is a formula for $y_{i+1} = \ldots$
- Implicit methods require solving a system of algebraic equations **within** each step, in terms of $f(t_{i+1}, y_{i+1})$ & y_{i+1} - slow, but very **reliable**
- Multistep methods increase accuracy using more old steps y_{i-1}, y_{i-2}, etc (example: BDF)

For Stiff IVPs, higher RK = Bad

- Stiff equations often have less error with low order methods - Why?
- But they will still be sensitive to step size – needs to be "small enough"
- For Euler, $h < 2 / |c|$ will be stable, where c comes from the solution form e^{-ct}
- <u>Implicit methods</u> are the most reliable
- Try sensitivity analysis (e.g. RK45 vs BDF)

Solving Stiff IVPs in Python

- Use scipy.integrate.solve_ivp
  - `sol = solve_ivp(fun, (t0, tmax), [y0])`
- If default (RK45) doesn’t work (slow, blows up, or has unusual oscillations), IVP is likely stiff. Try method='Radau' or 'BDF'.
  - `sol = solve_ivp(fun, (t0, tmax), [y0], method='BDF')`
  - Implicit multistep methods, good for stiff IVPs

Higher-Order IVPs

Let's say we have an m^{th} order problem instead of a first order problem: we want y(t), y'(t), etc:

You want each of these

$$t_0 \leq t \leq t_{max}$$

$$y^{(m)}(t) = \frac{d^m y}{dt^m} = f\left(t, y(t), y'(t), \ldots, y^{(m-1)}(t)\right)$$

- How many initial conditions do we need?
- What is a physical example of this?
- How could we solve this IVP?

Higher-Order IVPs

Let's say we have an m^{th} order problem instead of a first order problem: we want y(t), y'(t), etc:

You want each of these

$$t_0 \le t \le t_{\max}$$

$$y^{(m)}(t) = \frac{d^m y}{dt^m} = f\left(t, y(t), y^{'}(t), \ldots, y^{(m-1)}(t)\right)$$

Take advantage of the fact that each $y^{(i)}(t)$ is the derivative of the one below it $y^{(i-1)}(t)$, so you can treat this as an IVP system instead

m^{th} Order IVP Example

$$0 \le t \le 1, \quad \boxed{y_0 = -0.4, \quad y_0' = -0.6}$$ ⟵ Initial conditions

$$y'' - 2y' + 2y = e^{2t}\sin(t)$$ ⟵ We can calculate y'' if we have the rest, so use that as our f(t, u)

$$\Rightarrow \quad m = 2:$$ ⟵ Two dependent variables

$$\boxed{y''(t) = \frac{d^2y}{dt^2} = f\left(t, y(t), y'(t)\right) = 2y' - 2y + e^{2t}\sin(t)}$$

$$\Rightarrow \quad u_1 \equiv y, \quad u_2 \equiv y':$$

$$\boxed{\begin{aligned} u_1'(t) &= u_2 = f_1(t, u_1, u_2), \quad u_1(0) = y_0 = -0.4 \\ u_2'(t) &= 2u_2 - 2u_1 + e^{2t}\sin(t) = f_2(t, u_1, u_2), \quad u_2(0) = y_0' = -0.6 \end{aligned}}$$

Now we can solve for u_1 & u_2

Activity: Higher Order IVPs
5 min to do, 5 min discuss

Set up the IVP system for the following third order ODE:

$$1 \le t \le 2, \quad y(1) = 2, \quad y'(1) = 8, \quad y''(1) = 6$$

$$t^3 y''' + t^2 y'' - 2ty' + 2y = 8t^3 - 2$$

State the components of u and f:

$u_1, u_2, \ldots u_m$

$f_1, f_2, \ldots f_m$

Answer: Higher Order IVPs

$$u_1 \equiv y, \quad u_2 \equiv y' = u_1', \quad u_3 \equiv y'' = u_2' \quad \rightarrow$$

$$u_1' = u_2, \quad u_2' = u_3,$$

$$t^3 u_3' + t^2 u_3 - 2tu_2 + 2u_1 = 8t^3 - 2 \quad \rightarrow$$

$$\boxed{\begin{aligned} u_1'(t) &= u_2 = f_1(t, u_1, u_2, u_3) \\ u_2'(t) &= u_3 = f_2(t, u_1, u_2, u_3) \\ u_3'(t) &= t^{-3}\left(8t^3 - 2 - t^2 u_3 + 2tu_2 - 2u_1\right) = f_3(t, u_1, u_2, u_3) \end{aligned}}$$

$$u_1(1) = 2, \quad u_2(1) = 8, \quad u_3(1) = 6$$

Differential-Algebraic Systems

- What if we have an IVP system containing an *unknown*, and a *constraint* on the unknown?

$$y^{(m)}(t) = \frac{d^m y}{dt^m} = f\left(t, v, y, y', \ldots, y^{(m-1)}\right)$$

$$\boxed{C(t, v, y) = 0, \qquad C : \mathbb{R}^p \to \mathbb{R}^p, \quad v \in \mathbb{R}^p}$$

Green v here is new

- How many initial conditions do we need?
- How do we solve this IVP system?

Higher Order IVP example: F = ma

- Dynamics (F = ma) is a second-order IVP
- We want to know x(t) & v(t)
- We have a(t) = F/m = v'(t) = x''(t)
- If F is constant (example?), this is an integral
- But usually F = f(x) or f(x, v) - examples?
- We can solve this if we know initial position x and initial velocity v
- You might see intuitively why we need initial conditions for both position & velocity

Where do we get F?

To calculate forces on a system of molecules, you either use quantum mechanics, or this:

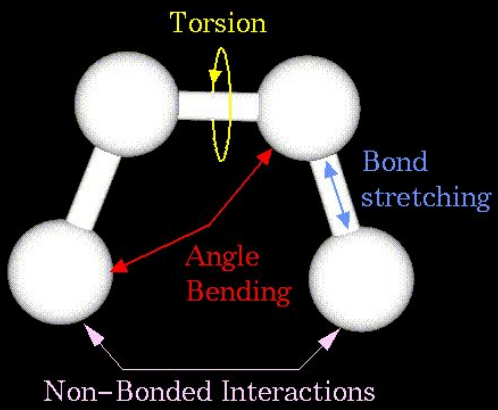
$$E(\widehat{r}) = \sum (E_{bonds}, E_{angles}, E_{torsions}, E_{pairs})$$

$$E_{bonds} = \sum_{bonds} k_r (r - r_0)^2$$

$$E_{angles} = \sum_{angles} k_\theta (\theta - \theta_0)^2$$

$$E_{torsions} = \sum_{torsions} \sum_{n} k_{\phi,n} \cos(n\phi)$$

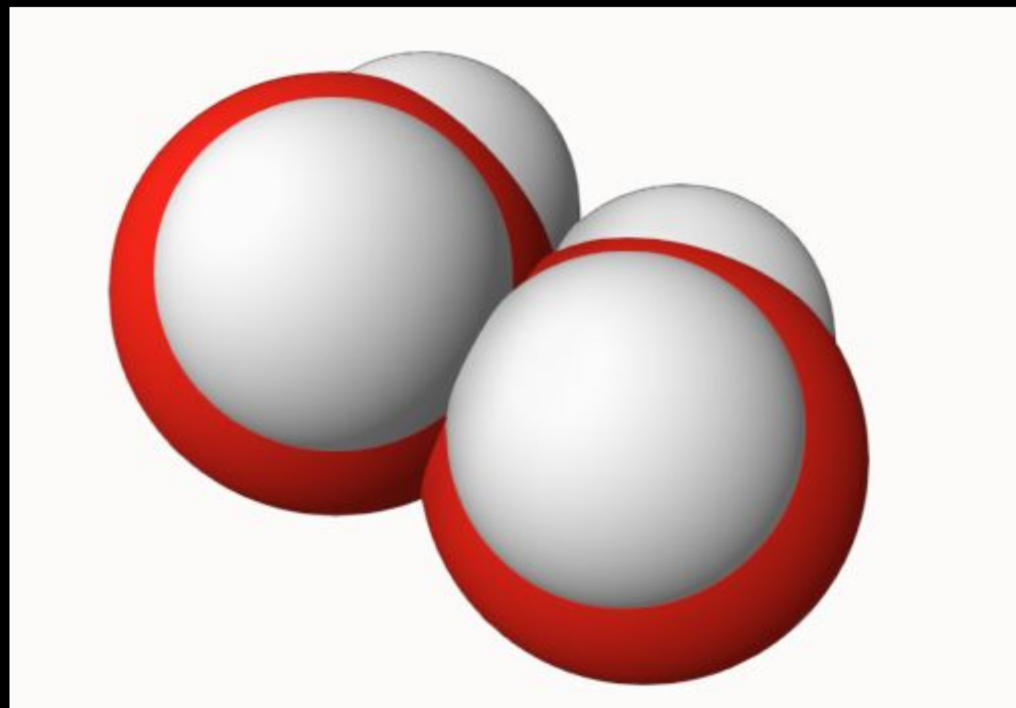
$$E_{pairs} = \sum_{i>j} \left(\frac{A_{ij}}{r_{ij}^{1}2} - \frac{B_{ij}}{r_{ij}^{6}} + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right)$$



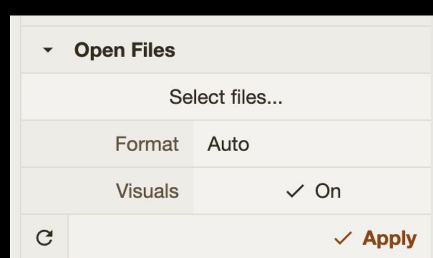
This kind of approximation is called a "force field"

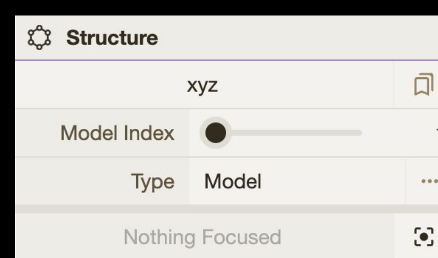
Where do we get F?

https://www.kaggle.com/allaboutchemistry/xtb-water-ivp



To view, download the xyz file and open it using: https://molstar.org/viewer/





Next week: numerical linear algebra

Pre-reading for next week:
Matrix solvers, eigenvectors, & norms:
PNM 14.1-7, 15.1 & 15.4

More math:
F&B 7.1-7.3, 6.2, 6.4-6.6.