BVP: Finite Differences or Method of Lines

\[ \frac{\partial C}{\partial x} = \text{Forward/Upwind/Central difference formulas} \]

\[ \frac{\partial^2 C}{\partial x^2} = \text{Central difference-like} \]

Understand when to use the different formulas.

Boundary Condition (Flux) \( D \frac{\partial C}{\partial x} \) \_Boundary = Reaction per surface area \( [\text{moles/m}^2 \cdot \text{s}] \)

\[ [\text{m}^2/\text{s}] \text{ Internal Flux } [(\text{mol/m}^3)/\text{m}] \]

The flux is the same for these two arrows can solve even if A and B are not known

Figure 1. The flux is the same for arrows at A and B.

Method of Lines

Initial Condition

Solve a differential equation along line \( i = 2, ..., N-1 \)

\[ \frac{\partial C}{\partial x} \bigg|_2 = \frac{C_3 - C_1}{2x} \]

Figure 2. Example problem good for method of lines.

If this is the B.C.: \( \frac{\partial C}{\partial x} \bigg|_1 = \frac{C_2 - C_1}{\Delta x} \)

Use this additional equation with rest to solve for \( C_1 \) D.A.E.

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Models vs. Data

\[ y = f(x, \theta) \]

\[ y_1 = f(x_1, \theta) \]

\[ y_2 = f(x_2, \theta) \]

\[ \vdots \]

\[ y_n = f(x_n, \theta) \]

Assumption: 1) \( y \) distributed normally around \( \hat{y} \)

2) \( x \) are known exactly

\[ P(y) \propto \exp \left(-\frac{(y_i - f(x_i, \theta))^2}{\sigma^2} \right) \]

\[ P(y) \propto \prod_{i=1}^{N} \exp \left(-\frac{(y_i - f(x_i, \theta))^2}{2\sigma^2} \right) \times \exp \left[-\frac{1}{2\sigma^2} \sum_{i=1}^{N} (y_i - f(x_i, \theta))^2 \right] \]

FIT: Max \( P(y) \) \( \rightarrow \) Min \( \sum_{i=1}^{N} (y_i - f(x_i, \theta))^2 \)

\[ k = A \cdot \exp\left(\frac{E_a}{RT}\right) \]

\[ \ln k = \ln A - \frac{E_a}{R} \left(\frac{1}{T}\right) \]

Linear in parameters \( \ln k, \ln A, \frac{E_a}{R} \)

\[ y = x_n \cdot \theta \rightarrow \theta = [x^T x]^{-1} x^T y \]

\( x_n \): n rows (measurements), m parameters

Figure 3. A normal distribution.
S.V.D.: \( x = U_{mxm} \Sigma_{mxn} V_{n xn} \)

\[ \theta = \sum_{i=1}^{N} \left( \frac{v_i \cdot y}{\sigma_i} \right) v_i \]

Sample variance guess for \( \sigma: \)

\[ s^2 = \frac{\sum_{i=1}^{N} (y_i - \bar{y})^2}{N - \text{dim}(\theta)} \]

\( \bar{y} \) is mean \( y, f(x, \theta) \)

If non-linear, use optimization methods.

For correctness, compare \( s \) to \( \sigma \). Quantitatively, use \( \chi^2 \) (chi squared)

\[ \chi^2 = \sum_{i=1}^{N} \frac{(y_i - f(x_i, \theta))^2}{\sigma^2} \]

Transform to \( z \)

\( P(y) \to y \to \hat{y} \to 0 \to z \)

mean of 0, \( \sigma = 1 \)

\[ \text{Goodness of fit: area under curve } \chi^2_{\text{min}} \text{ to } \infty \]

Figure 4. Usually we will accept a model with the integral greater than 5%, but we would like it higher. If 99% chance it is wrong, reject.

**Error Bars – Difficult**

If linear in parameters and \( \sigma \) is known, covariance(\( \theta \)) = \( \sigma^2 [x^T x]^{-1} \) (diagonal \( m \times m \) matrix)

\[ \theta_i = \theta_{\text{min},i} \pm z_{2.5} \sigma [x^T x]_i^{-1/2} \]

\( m = \# \text{ parameters} \)

Figure 5. Chi-squared distribution.

Non-linear: \( \sigma [x^T x]_i \)

\[ x_{i,j} = \frac{\partial f(x_i, \theta)}{\partial \theta_j} \]

Find \( x_{i,j} \)
In MATLAB, use \texttt{nlinfit}, \texttt{nlparci}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{chi2_conf_interval.png}
\caption{Location of chi-squared and 95\% confidence interval in \(\theta_1-\theta_2\) space. \(\Delta \chi^2 = [\chi^2_1 - \chi^2_{\text{min}}]\) \(\nu = 2\) additional degrees of freedom: let \(\theta_1, \theta_2\) vary}
\end{figure}

If \(\sigma\) unknown, use student t distribution based on \(s\).

\[\Delta \chi^2 \equiv \left[ \chi^2_1 - \chi^2_{\text{min}} \right] \nu = 2\] additional degrees of freedom: let \(\theta_1, \theta_2\) vary.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{normal_vs_student_t.png}
\caption{Comparison of normal and Student-t distributions.}
\end{figure}

\(\gamma_i = \theta\ (\leftarrow\ you\ want\ to\ calculate\ \theta)\)

\(\sigma\) is known, \(\gamma_i\) is to be measured.

Average value of parameter: \(\theta_m = (\sum \gamma_i)/N\)

\[
\begin{bmatrix}
\theta_1, \theta_2
\end{bmatrix} = N
\begin{bmatrix}
\frac{1}{N}
\end{bmatrix}
\begin{bmatrix}
\theta_1
\theta_2
\end{bmatrix} \Rightarrow \sigma/\sqrt{N}
\]

\section*{Global Optimization}

Convex function \(- \mathbf{H} \geq 0\) (Hessian Matrix is positive definite)

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{convex_function.png}
\caption{Example of a convex function. Only 1 minimum}
\end{figure}

Non-convex:
Branch and bound

Professor Barton – Non convex function guarantees global minimum

Figure 9. An example of a non-convex function.

Figure 10. An illustration of the branch and bound algorithm.
If new upper bound is lower than the lower bound, use other region; can stop considering that section.

Multistart:
Take a bunch of initial guesses and then run local minimization.
No guarantee.
100 points, 6 variables – $100^6$ calculations.
Simulated annealing

\[ E \]

\[ 0 \quad 2\pi \quad \phi \quad \text{Dihedral angle} \]

**Figure 11.** The energy varies with dihedral angle. Start at high temperature, decrease T eventually can sample wells once the point is caught in a minimum.

**Genetic Algorithms**

Hybrid system: integer variables and continuous variables
Sample space by allowing function values to live, die, replicate, switch values, etc.

Monte Carlo: Metropolis Monte Carlo
Gillespie Kinetics Monte Carlo

**Stochastics**

Look at homework solutions to 10 and 11.

**Additional Topics**

Fourier Transforms and operator splitting may make a showing.