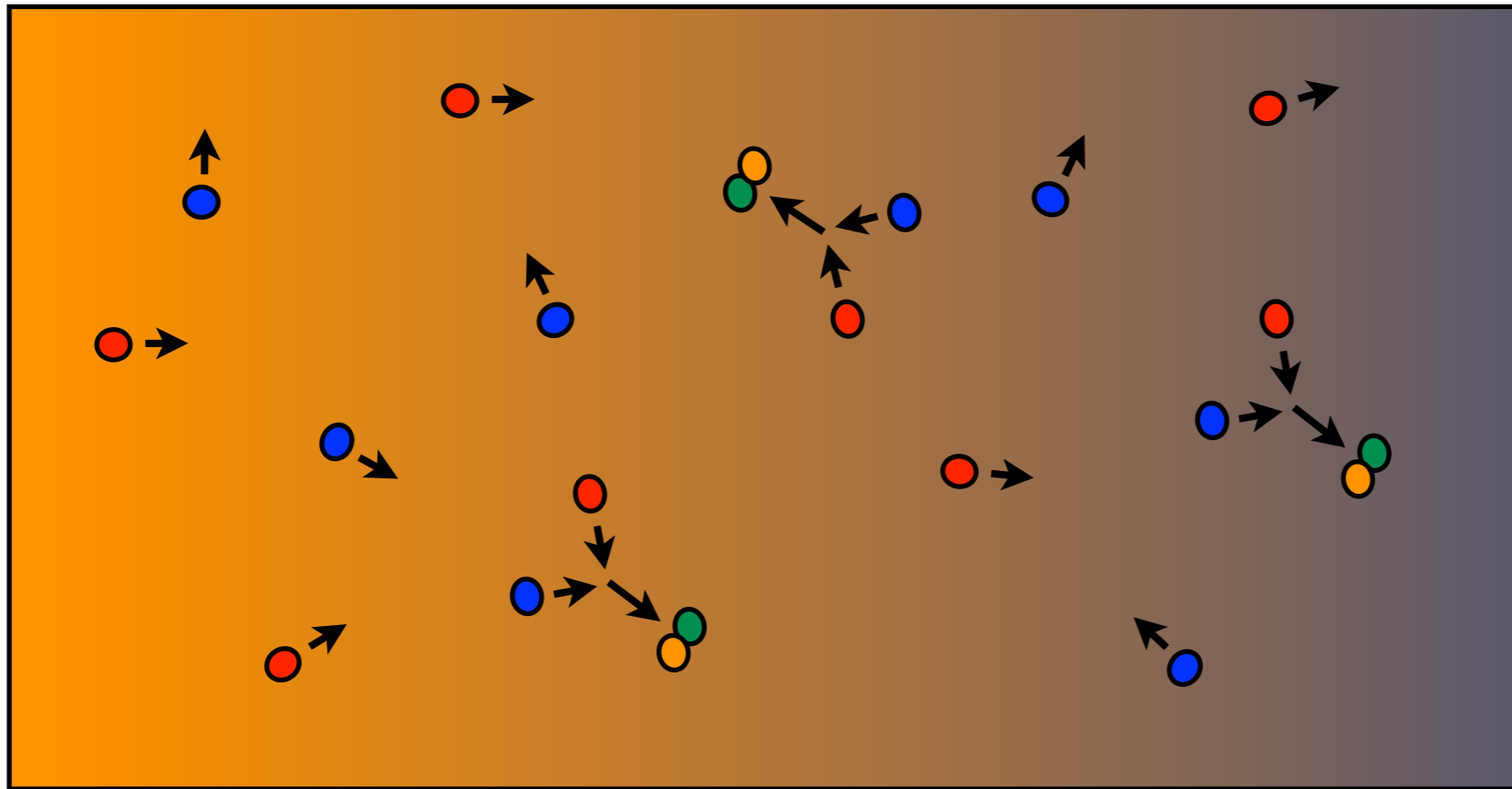# Mathematical Modelling

Lecture 2
Reaction kinetics

Reaction kinetics

- Molecules in a reactive gas mixture. Reaction occurs when two reactants undergo collision, and a new molecule is produced.

- The reaction rate depends on the likelihood of collisions.

- In epidemiology, the reactants may be invected and noninfected individuals, and the collisions are chance meetings.

- In population dynamics, the reactants may be predators and prey.

Aphids and Ladybugs
predator-prey problem

- In the absence of predators, prey population grows exponentially $\dot{A} = \beta A$

- In the absence of prey, predator population decays exponentially $\dot{L} = -\alpha L$

- When predators and prey are well-mixed, the populations of both change at distinct rates

$$\dot{L} = \gamma A L$$
$$\dot{A} = -\delta A L$$

- Full model:
$$\dot{L} = \gamma A L - \alpha L$$
$$\dot{A} = -\delta A L + \beta A$$

Kinetic equations (chemistry)

- Example: two chemical species A and B fill a region. These are supposed to be well mixed and in motion. Upon collision, they form a new compound C. In symbols:

$$A + B \rightarrow C \qquad\qquad \text{(A, B, C are labels)}$$

- Interpretation: one *unit* of A combines with one *unit* of B to produce one *unit* of C. Rates of change:

$$\frac{dA}{dt} = \frac{dB}{dt} = -\frac{dC}{dt} \qquad\qquad \text{(A, B, C denote concentrations)}$$

- Posit the existence of a rate function r(A,B):

$$\frac{dA}{dt} = -r(A, B)$$
$$\frac{dB}{dt} = -r(A, B)$$
$$\frac{dC}{dt} = r(A, B)$$

Kinetic equations (chemistry)

- Supposing the concentrations are small, r can be approximated by a Taylor expansion

$$r(A, B) = r_{00} + r_{10}A + r_{01}B + r_{20}A^2 + r_{11}AB + r_{02}B^2 + \cdots$$

$$r_{00} = r(0,0), \quad r_{10} = \frac{\partial r}{\partial A}(0,0), \quad r_{01} = \frac{\partial r}{\partial B}(0,0), \quad r_{20} = \frac{\partial^2 r}{\partial A^2}(0,0), \quad \text{etc.}$$

- If either A or B is absent, the rate should go to zero identically

$$r(A, 0) = r(0, B) = 0 = \frac{\partial r}{\partial A}(A, 0) = \frac{\partial r}{\partial B}(0, B) = \cdots$$

- Hence the first not-necessarily-vanishing term is

$$r_{11} = \frac{\partial^2 r}{\partial A \partial B}(0, 0)$$

- and we take

$$r = kAB$$

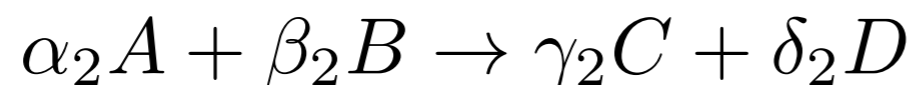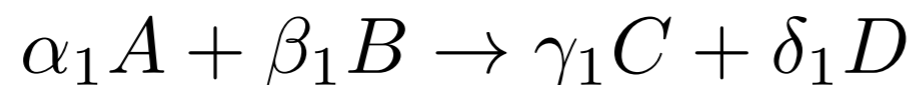$$\frac{dA}{dt} = -kAB$$
$$\frac{dB}{dt} = -kAB$$
$$\frac{dC}{dt} = kAB$$

- Alternative reasoning: *bilinearity, polynomial approximation, ...*

The Law of Mass Action
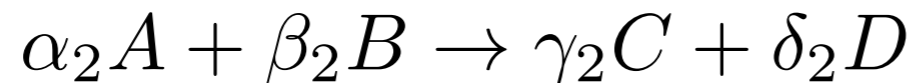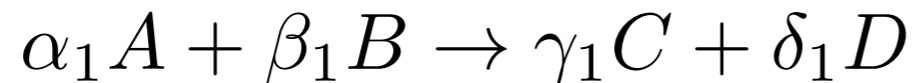
- In general we can have systems of reactions

$$\alpha_1 A + \beta_1 B \rightarrow \gamma_1 C + \delta_1 D$$

$$\alpha_2 A + \beta_2 B \rightarrow \gamma_2 C + \delta_2 D$$

- The coefficients α_i, β_i, γ_i, δ_i are called the stoichiometric coefficients. They are positive and indicate the number of each species involved in the reaction.

- A and B are reactants, C and D are products.

- The *LAW OF MASS ACTION* (Def'n 3.1) states:
  - *The rate, r, of the reaction is proportional to the product of the reactant concentrations, with each concentration raised to the power equal to its respective stoichiometric coefficient.*
  - *The rate of change of the concentration of each species in the reaction is the product of its stoichiometric coefficient with the rate of the reaction, adjusted for sign (+ if product, - if reactant).*
  - *For a system of reactions, the rates add.*

The Law of Mass Action

ITS THE LAW
PLEASE LEASH, CURB AND CLEAN UP AFTER YOUR DOG!

- In general we can have systems of reactions

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  - *For a system of reactions, the rates add.*

- Example. For the above reaction, $r_1 = k_1 A^{\alpha_1} B^{\beta_1}, \quad r_2 = k_2 A^{\alpha_2} B^{\beta_2}$

$$\frac{dA}{dt} = -\alpha_1 r_1 - \alpha_2 r_2, \quad \frac{dC}{dt} = ?$$

Conservation laws

- Consider the single reaction

$$\alpha A + \beta B \rightarrow \gamma C + \delta D$$
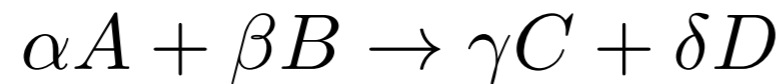
- The rate is $r = kA^\alpha B^\beta$

- Hence, $\dfrac{dA}{dt} = -\alpha k A^\alpha B^\beta,$ $\qquad \dfrac{dB}{dt} = -\beta k A^\alpha B^\beta,$

  $\dfrac{dC}{dt} = \gamma k A^\alpha B^\beta,$ $\qquad \dfrac{dD}{dt} = \delta k A^\alpha B^\beta,$

- But note that $\quad \beta \dfrac{dA}{dt} - \alpha \dfrac{dB}{dt} = \dfrac{d}{dt}(\beta A - \alpha B) = 0$

- For given initial conditions $\beta A(t) - \alpha B(t) = \beta A_0 - \alpha B_0$

- Similar conservation laws

$$\dfrac{d}{dt}(\gamma A + \alpha C) = \dfrac{d}{dt}(\delta A + \alpha D) = 0$$

Conservation laws

- Conservation laws are nifty because they define a submanifold to which the solution is constrained.

- In fact, we can solve for B, C, and D in terms of A:

$$\beta A(t) - \alpha B(t) = \beta A_0 - \alpha B_0$$

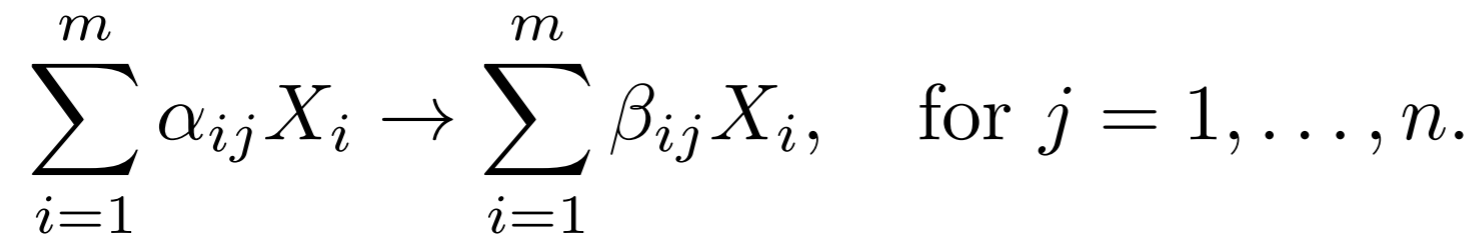$$B(t) = B_0 + \frac{\beta}{\alpha}(A(t) - A_0)$$

- And reduce the system to a single scalar equation for A:

$$\frac{dA}{dt} = -\alpha k A^\alpha (a + bA)^\beta$$

The Law of Mass Action

- General formulation. Consider n reactions in m species:

$$\sum_{i=1}^{m} \alpha_{ij} X_i \rightarrow \sum_{i=1}^{m} \beta_{ij} X_i, \quad \text{for } j = 1, \dots, n.$$

- The reaction rates are $r_j = k_j \prod_{i=1}^{m} X_i^{\alpha_{ij}}$

- The kinetic equations are

$$\frac{d}{dt} X_i = \sum_{j=1}^{n} (\beta_{ij} - \alpha_{ij}) r_j$$

- In matrix form $\quad \frac{d}{dt} X = Sr, \quad S_{ij} = \beta_{ij} - \alpha_{ij}$

- A conservation law satisfies $\quad \frac{d}{dt} a^T X = 0, \quad a^T X(t) = a^T X(0)$

$$a \in K(S^T) \Rightarrow a^T S r = a^T \frac{dX}{dt} = \frac{d}{dt} a^T X = 0$$

Example: enzyme catalyzed reaction

- Consider the reactions (actually 3) $\quad S + E \rightleftharpoons C$

$$C \to P + E$$

- The reaction rates are

$$r_1 = k_1 SE, \quad r_{-1} = k_{-1}C, \quad r_2 = k_2 C$$

- Kinetic equations:

$$\frac{dS}{dt} = -k_1 SE + k_{-1}C$$

$$\frac{dE}{dt} = -k_1 SE + k_{-1}C + k_2 C$$

$$\frac{dC}{dt} = k_1 SE - k_{-1}C - k_2 C$$

$$\frac{dP}{dt} = k_2 C$$

- Two conservation laws: $\quad \dfrac{d}{dt}(E + C) = 0, \quad \dfrac{d}{dt}(S + C + P) = 0$

Equilibria

- For a general system of evolution equations

$$\frac{dy}{dt} = F(y)$$

- The equilibria, or steady states are the points

$$\{y_s : F(y_s) = 0\}$$

- Furthermore, an equilibrium is stable if any solution that originates near enough to the equilibrium stays near it. It is asympototically stable if any solution that originates near the equilibrium eventually tends to it in infinite time.

- A sufficient condition for an equilibrium to be asymptotically stable is if all eigenvalues of the Jacobian matrix $A_{ij} = \dfrac{\partial F_i}{\partial y_j}(y_s)$ have strictly negative real part.

Linear stability

- Consider a solution that is a small perturbation from the equilibrium

  $$y(t) = y_s + \delta y(t)$$

- Taylor expanding the solution

  $$\frac{d}{dt}(y_s + \delta y(t)) = F(y_s) + A(\delta y(t)) + \cdots, \quad A = \frac{\partial F}{\partial y}(y_s)$$

- Suppose A has a basis of eigenvectors

  $$Ax_i = \lambda_i x_i, \quad i = 1, \ldots, n$$

- The perturbation solution can be expanded in the eigenbasis

  $$\delta y(t) = a_1 e^{\lambda_1 t} x_1 + \cdots + a_n e^{\lambda_n t} x_n$$

- The perturbations decay if $\quad \operatorname{Re} \lambda_i < 0, \quad \text{for all } i$

- The perturbations grow unbounded if $\quad \operatorname{Re} \lambda_i > 0, \quad \text{for some } i$

Example: van der Pol equation

- Consider the model

$$\frac{du}{dt} = -v$$

$$\varepsilon \frac{dv}{dt} = u + \mu(v - v^3/3) \qquad \varepsilon \ll 1$$

- Steady state $u_s = 0, v_s = 0$

$$A = \begin{bmatrix} 0 & -1 \\ \frac{1}{\varepsilon} & \frac{\mu}{\varepsilon}(1 - v_s^2) \end{bmatrix} = \begin{bmatrix} 0 & -1 \\ \frac{1}{\varepsilon} & \frac{\mu}{\varepsilon} \end{bmatrix}$$

- Eigenvalues $\quad \lambda = \frac{1}{2\varepsilon}\left(\mu \pm \sqrt{\mu^2 - 4\varepsilon}\right)$

- The steady state is asymptotically stable if $\mu < 0$

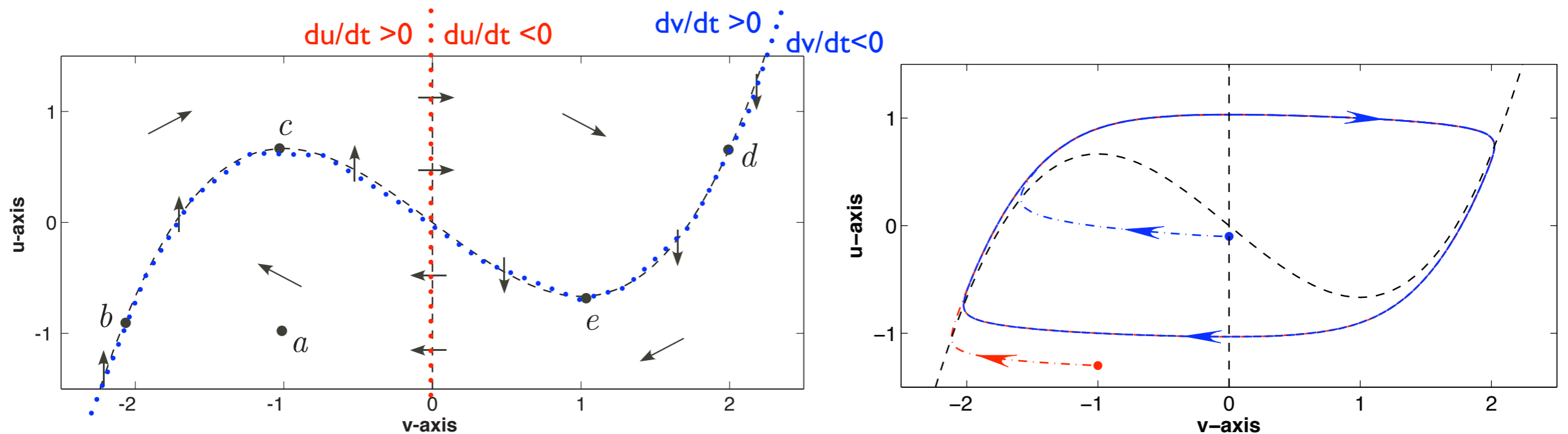- What happens for $\mu > 0$? "Hopf bifurcation"

Example: van der Pol (-like) equation

- The phase plane (v,u)

$$\frac{du}{dt} = -v$$

$$\varepsilon \frac{dv}{dt} = u + \mu(v - v^3/3)$$

$$\frac{du}{dv} = \frac{-v/\varepsilon}{u + \mu(v - v^3/3)}$$

- Nullclines $\{v = 0\}, \quad \{u = -\mu(v - v^3/3)\}$

- For small ε, the second equation is nearly an algebraic relation (more on this next week). The solution rapidly approaches the v-nullcline.