

LECTURE 2 :

QUANTITATIVE FORMULATION

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Balance equations :

- ▶ Evolution laws describing how the relevant variables change in the course of time.
- ▶ Microscopic level.
- ▶ Focus on macroscopic level, in which we encounter self-organization in its most familiar forms.

Microscopic level

Systems of interacting particles

State variables :

- ▶ positions $\{\vec{r}_i\}$ and velocities $\{\vec{v}_i\}$, ($i = 1, \dots, N$) or
- ▶ generalized coordinates $\{\vec{q}_i\}$ and moments $\{\vec{p}_i\}$

Evolution in space and time :

Newton's equations

$$\begin{aligned}
 m_i \frac{d^2 \vec{r}_i}{dt^2} &= F_i \{r_j\} && \text{or} \\
 \frac{d \vec{r}_i}{dt} &= \vec{v}_i \\
 m_i \frac{d \vec{v}_i}{dt} &= F_i \{r_j\}
 \end{aligned}$$

Hamilton's equations

$$\begin{aligned}
 \frac{d \vec{q}_i}{dt} &= \partial H / \partial \vec{p}_i \\
 \frac{d \vec{p}_i}{dt} &= -\partial H / \partial \vec{q}_i
 \end{aligned}$$

Hamiltonian H is the sum of the kinetic and potential energies, known function of q 's and p 's

Microscopic level

⇒ **Set of $6N$ coupled ordinary differential equations.** (in 3D)

The concept of integrability :

Possibility to cast these equations, by means of appropriate transformations which preserve the Hamiltonian structure (*canonical transformations*) to as set of $3N$ uncoupled equations.

⇒ regular (typically multi-periodic) and stable motions : pendulum, 2-body problem (planetary motion),

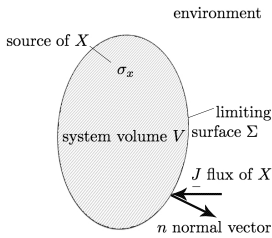
The Kolmogorov revolution (mid 1950's) :

Most of the naturally occurring systems are non-integrable

Way open to unstable and irregular evolutions :

Hamiltonian chaos : 3-body problems, molecular collisions within a fluid, ...

Balance equation of a macroscopic observable



$$\frac{dX}{dt} = \underbrace{\frac{d_e X}{dt}}_{\text{variation due to exchanges with surroundings}} + \underbrace{\frac{d_i X}{dt}}_{\text{variation due to spontaneous processes within the system}}$$

$$= - \int d\Sigma \vec{J}_x \vec{n} + \int_V d\vec{r} \sigma_x$$

or, for a fixed volume and using Gauss' divergence theorem,

Extensive variable

$$X(t) = \int_V d\vec{r} \underbrace{x(\vec{r}, t)}_{\text{intensive (local) variable}}$$

$$\int_V d\vec{r} \frac{\partial x}{\partial t} = - \int_V d\vec{r} \text{div } \vec{J}_x + \int_V d\vec{r} \sigma_x$$

Local form :

$$\frac{\partial x}{\partial t} = -\operatorname{div} \vec{J}_x + \sigma_x$$

Non-closed equation ! Need to relate \vec{J}_x , σ_x to the variables X_1, \dots, X_n describing the state of the system

$$\Rightarrow \frac{\partial x_i}{\partial t} = F_i \left(\underbrace{x_1 \dots x_j}_{\substack{\text{accounting for couplings} \\ \text{between variables}}}, \underbrace{\vec{\nabla}^k x_1, \dots, \vec{\nabla}^k x_j}_{\substack{\text{arises from } J_x \text{ and} \\ \text{accounts for spatial} \\ \text{inhomogeneities}}}, \dots, \underbrace{\lambda}_{\substack{\text{accounts for the} \\ \text{presence of constraints}}} \right)$$

In a natural system the F_i 's are typically nonlinear functions of the x 's

Examples

A. Fluid dynamics

Basic variables :

Mass density ρ

Momentum density $\rho\vec{v}$, (\vec{v} = bulk velocity)

Energy density ρe

	Mass density ρ	Momentum density $\rho\vec{v}$	Energy density ρe
x	ρ	$\rho\vec{v}$	ρe
\vec{J}_x	$\rho\vec{v}$ (mass entrained by bulk velocity)	$\rho\vec{v}\vec{v}$ (momentum entrained by bulk velocity)+ pressure tensor	$\rho e\vec{v}$ (energy entrained by bulk velocity) + heat transfer + work done by pressure forces
σ_x	0 (mass conservation)	ρf (f external force)	0 (energy conservation)

\vec{J}_x : nonlinear terms at the origin of hydrodynamic instabilities and of phenomenon of turbulence !

Examples

A. Fluid dynamics

Closure problem consists in expressing the pressure and heat flux in terms of the Temperature and bulk velocity

To a good approximation ...

- ▶ pressure tensor \rightarrow hydrostatic pressure p +dissipative part (linear in velocity gradient)
- ▶ heat flux \rightarrow linear in temperature gradient
- ▶ Energy e and hydrostatic pressure $p \rightarrow$ known functions of the variables x_i (ρ , etc.)(local equilibrium assumption)

Evolution equations in the form of (nonlinear) partial differential equations for \vec{v} , T , etc ...

- ▶ e.g., Navier-Stokes equation

$$\rho \left[\frac{\partial \vec{v}}{\partial t} + (\vec{v} \cdot \vec{\nabla}) \vec{v} \right] = -\vec{\nabla} p + \eta \nabla^2 \vec{v}$$

(η , shear viscosity coefficient)

Examples

B. Chemical reactions in well-stirred open reactor

$\{X_i\}$: Composition variables (mass densities, molar densities, mole fractions, ...)

$$\begin{aligned}\frac{dX_i}{dt} &= \text{reaction term} + \text{transport term} \\ &= \sigma_i + \frac{1}{\tau_i} (X_i^0 - X_i)\end{aligned}$$

where

- ▶ τ_i is the residence time
- ▶ X_i^0 the inflow concentration (fixed)
- ▶ Transport term is the difference between the initial concentration of the product i which is fed to the system (and assumed to be constant, i.e., in excess) and the actual concentration of i in the reactor times the inverse of the residence time.

Examples

B. Chemical reactions in well-stirred open reactor

Reaction term σ_i is the sum over the reactions of the product between a stoichiometric coefficient and the velocity of the reaction

$$\sigma_i = \sum_{\substack{\text{over reactions} \\ \rho = 1}}^r \nu_{i\rho} \omega_\rho$$

where

- ▶ $\nu_{i\rho}$ represents the gain or the loss of the product i in the reaction ρ (**stoichiometric coefficient**)
- ▶ ω_ρ is the velocity of the reaction ρ .

According to the law of mass action in an ideal system, the rate of an elementary reaction is proportional to the product of the concentrations of the reactants.

$$\omega_\rho = k_\rho(T) \prod_{\substack{\text{over reactants} \\ j}} X_j^{\alpha_{j\rho}}$$

where

- ▶ k_ρ is the rate constant
- ▶ $\alpha_{j\rho}$ is the number of moles of j involved in the reaction ρ .

Examples

B. Chemical reactions in well-stirred open reactor

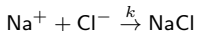
Main features :

- ▶ Evolution equations in the form of (nonlinear) ordinary differential equations (ODE's)
- ▶ Polynomial nonlinearities.
- ▶ Complexity can arise even in absence of spatial degrees of freedom.

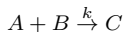
Examples

B. Chemical reactions in well-stirred open reactor

Some practice, ...



can be written as



We have

- ▶ the number of reaction $r = 1$
- ▶ gain of product $\nu_C = 1$
- ▶ loss of reactants $\nu_A = \nu_B = -1$
- ▶ and the number of moles :
 $\alpha_A = \alpha_B = 1$

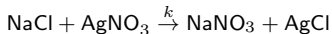
We can then write (using for simplicity the same symbols for the chemicals and their concentrations) $\omega_1 = kAB$. And the corresponding evolution equations :

$$\begin{aligned} \frac{dA}{dt} &= \frac{dB}{dt} = -kAB \\ \frac{dC}{dt} &= kAB \end{aligned}$$

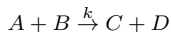
Examples

B. Chemical reactions in well-stirred open reactor

Some practice, ...



can be written as



We have

- ▶ the number of reaction $r = 1$
- ▶ gain of product $\nu_C = \nu_D = 1$
- ▶ loss of reactants $\nu_A = \nu_B = -1$
- ▶ and the number of moles :
 $\alpha_A = \alpha_B = 1$

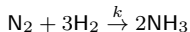
We can then write (using for simplicity the same symbols for the chemicals and their concentrations) $\omega_1 = kAB$. And the corresponding evolution equations :

$$\begin{aligned} \frac{dA}{dt} &= \frac{dB}{dt} = -kAB \\ \frac{dC}{dt} &= \frac{dD}{dt} = kAB \end{aligned}$$

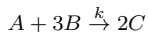
Examples

B. Chemical reactions in well-stirred open reactor

Some practice, ...



can be written as



We have

- ▶ the number of reaction $r = 1$
- ▶ gain of product $\nu_C = 2$
- ▶ loss of reactants $\nu_A = -1, \nu_B = -3$
- ▶ and the number of moles : $\alpha_A = 1, \alpha_B = 3, \alpha_C = 2$

We can then write (using for simplicity the same symbols for the chemicals and their concentrations) $\omega_1 = kAB$. And the corresponding evolution equations :

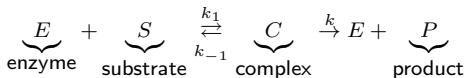
$$\begin{aligned} \frac{dA}{dt} &= -kAB^3 & \frac{dB}{dt} &= -3kAB^3 \\ \frac{dC}{dt} &= 2kAB^3 \end{aligned}$$

Examples

B. Chemical reactions in well-stirred open reactor

Some practice, ...

Michaelis-Menten kinetics



We have

- ▶ the number of reaction $r = 3$

1 Reaction 1

$$\begin{aligned} \nu_E &= \nu_S = -1 & \nu_C &= 1 & \alpha_E &= \alpha_S = 1 & \frac{dS}{dt} &= \nu_{S,1}w_1 + \nu_{S,2}w_2 \\ w_1 &= k_1ES & & & & & &= -k_1ES + k_{-1}C \end{aligned}$$

2 Reaction 2

$$\begin{aligned} \nu_E &= \nu_S = 1 & \nu_C &= -1 & \alpha_C &= 1 & \frac{dE}{dt} &= -\frac{dC}{dt} \\ w_2 &= k_{-1}C & & & & & &= -k_1ES + k_{-1}C + kC \end{aligned}$$

3 Reaction 3

$$\begin{aligned} \nu_C &= -1 & \nu_E &= \nu_P = 1 \\ w_3 &= kC & & & & & & \end{aligned}$$

Examples

C. Chemical reactions in unstirred open reactors

$$\frac{\partial X_i}{\partial t} = -\text{div} J_i^{\text{diff}} + \sigma_i$$

To a good approximation ...

diffusion flux $J_i^{\text{diff}} \Rightarrow$ linear in concentration gradient

Substitution into the balance equation and use of the same expression for σ_x as in well-stirred systems leads to the **reaction-diffusion equations**

$$\frac{\partial X_i}{\partial t} = \underbrace{\sum_{\rho=1}^r \nu_{i\rho} w_{\rho}}_{\text{reaction term}} + \underbrace{D_i \nabla^2 X_i}_{\text{transport through diffusion}}$$

(D_i assumed to be X – independent)

Nonlinear partial differential equations of the parabolic type.

Nonlinear source term, linear transport term contrary to fluid mechanics where nonlinearity comes primarily from transport.

Examples

D. Biology

Kinetics of biological processes is in many cases isomorphic to the kinetics of chemical reactions.

Example from population biology :

X population density

$$\frac{dX}{dt} = \text{birth} - \text{death}$$

Malthusian view : birth = $k_1 X$, death = $k_2 X$

Verhulst view : birth = $(k_1 - bX) X$ (regulation), death = $k_2 X$

Examples

D. Biology

Verhulst equation

$$\frac{dX}{dt} = kX - bX^2 \quad (k = k_1 - k_2)$$

or,

$$\frac{dX}{dt} = kX \left(1 - \frac{X}{N}\right) \quad \left(N = \frac{k}{b}\right)$$

Fisher equation

(in presence of migration)

$$\frac{\partial X}{\partial t} = kX \left(1 - \frac{X}{N}\right) + D\nabla^2 X$$

Also applies to population genetics (propagation of a neutral mutation)