# Contents of Today

Review (Units,math)

$0^{th}$ law

System and surroundings

Intensive and extensive properties

Energy

Work, heat transfer

Notation

etc.

Page 1 to Page 16

# 课程补充说明

- 互动knowledge / idea 课堂 / office hours

Email, website, Bolg, MSN et al

- 双语
- 考试
- 专业词汇 thermodynamics of materials
- 网站

# Purpose

Thermodynamics is about developing a rigorous understanding of natural processes.

Much of what you will learn about materials science will rely on your comprehension of thermodynamics.

The basis of your future major courses

# Purpose

The science of thermodynamics is concerned with heat and work, and transformations between the two. It is based on two laws of nature, the first and second laws of thermodynamics. By logical reasoning and skillful manipulation of these laws, it is possible to correlate many of the properties of materials and to gain insight into the many chemical and physical changes that materials undergo.

# Contents of the course

热力学研究热功转换的方向、限度以及能量的衡算。

- 0, 1, 2, 3th law
- Property Relationships
- Equilibrium
- Chemical Equilibrium
- Electrochemistry
- Solution
- Phase rule
- Phase diagrams
- Statistical Thermodynamics
- Surfaces and Interfaces

# How to learn?

- Reading
- Discussion
- Exercise

God helps those who help themselves!

# Units

- Temperature
  - 1 Kelvin
  - F=32+1.8C
- Composition
  - 18K: 18/24
  - Measurement

# Math

- Total differential

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x = -1$$

$$\left(\frac{\partial y}{\partial x}\right)_z = -\frac{\left(\frac{\partial z}{\partial x}\right)_y}{\left(\frac{\partial z}{\partial y}\right)_x}$$ Euler

- Stiring approximately equation

$$\ln N! \approx N \ln N - N$$

# Index of nomenclature

- System / surroundings系统、环境
- Open / close / isolated systems敞开、封闭、孤立
- Thermal equilibrium / steady state平衡、稳态
- Heat / work热、功
- Internal energy内能热力学能
- State function状态函数
- Intensive / extensive properties强度、容量性质
- Enthalpy焓
- Heat capacity热容

# $0^{th}$ law

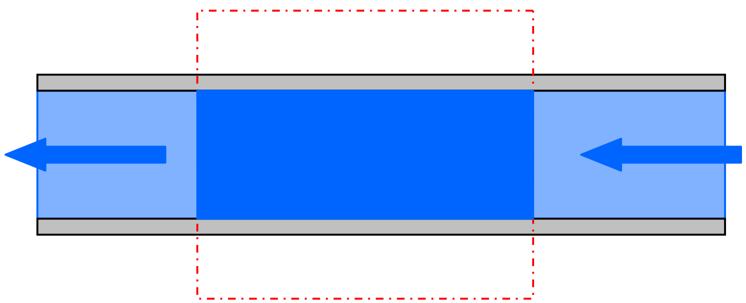
- Two systems in thermal equilibrium with a third system are also in thermal equilibrium with each other.

Principle of measuring Temperature!

Thermometer -> the third system

# 1.1 Systems and Surroundings

- A system: any portion of space or matter set aside for study < How the system is defined
  – Open system: matter is allowed to enter or leave
  – Close system: no matter enters or leaves



A bottle of water?

- Surroundings: everything else

# 1.2 Energy Transfer (1)

- Energy transfer between system and surroundings is divided into heat and work
  - Heat: energy transferred between the system and surroundings because of temperature difference
  - Work: all other forms of energy transferred between the system and its surroundings

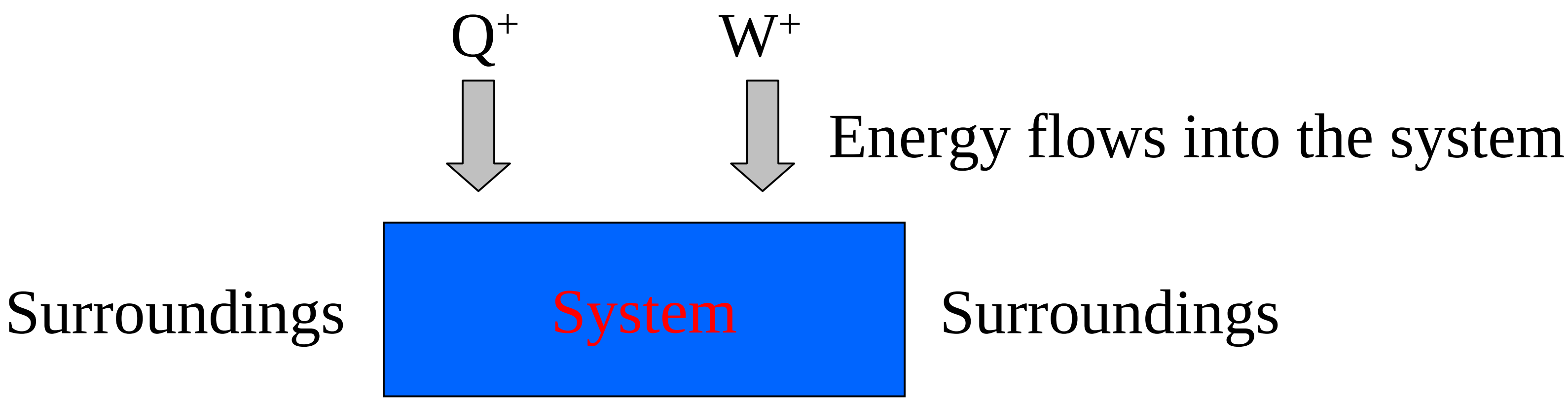
# 1.2 Energy Transfer (1)

– Heat: because of temperature difference

Q: positive from surroundings to the system

– Work: all other forms of energy transferred

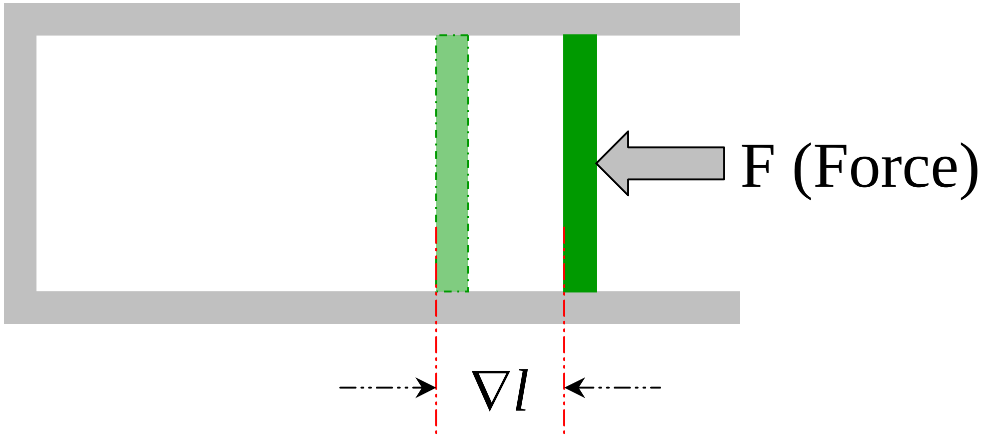
W: positive work done on a system by surroundings



# 1.2 Energy Transfer (2)

## Mechanical work

$$W = F\nabla l = \frac{F}{A}A\nabla l = P\nabla V$$




Resisting pressure multiplied by the change in volume

**Reversible:** the initial state of the system can be restored with no observable effects in the system or the surroundings

# 1.3 Energy of a System

Energy of system:

- Internal energy
- Potential energy: gravitational; centrifugal; electrical; and magnetic potential energies
- Kinetic energy: overall motion
  - » Translational
  - » Rotational

*Have absolute value*

Internal energy: inherent qualities or properties

Composition; physical form; environmental variables

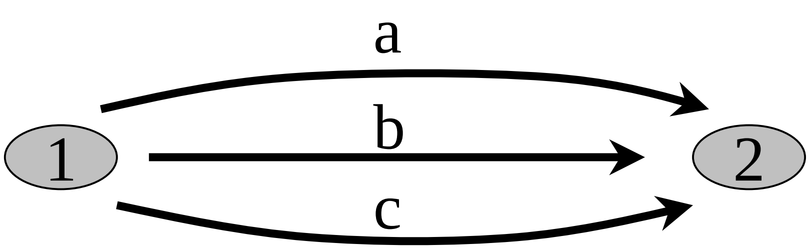
Temperature, pressure, electric and magnetic field, etc.

Mechanical (spring), chemical ($H_2O$), thermal energy (possessed)

# 1.4 Energy as a State Function

Equilibrium state and not depend on the thermodynamic path

Determined by the parameters that specify the system in its final state and in its initial state.




$$\nabla U = U_2 - U_1$$

Equilibrium: its temperature, pressure, density, and other physical properties are uniform throughout.

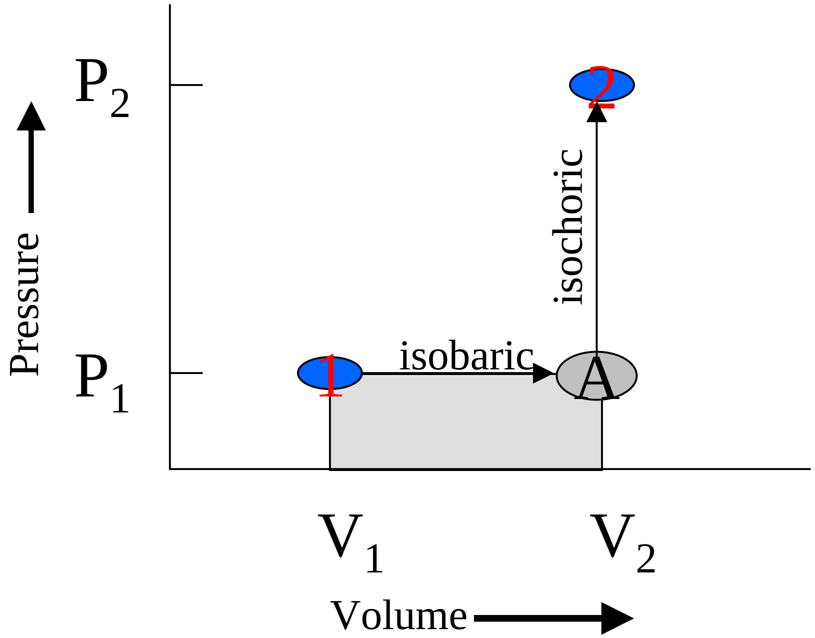
Steady: the system does not change with time.

# 1.5 Work

Work a function of the path taken

Case I: A

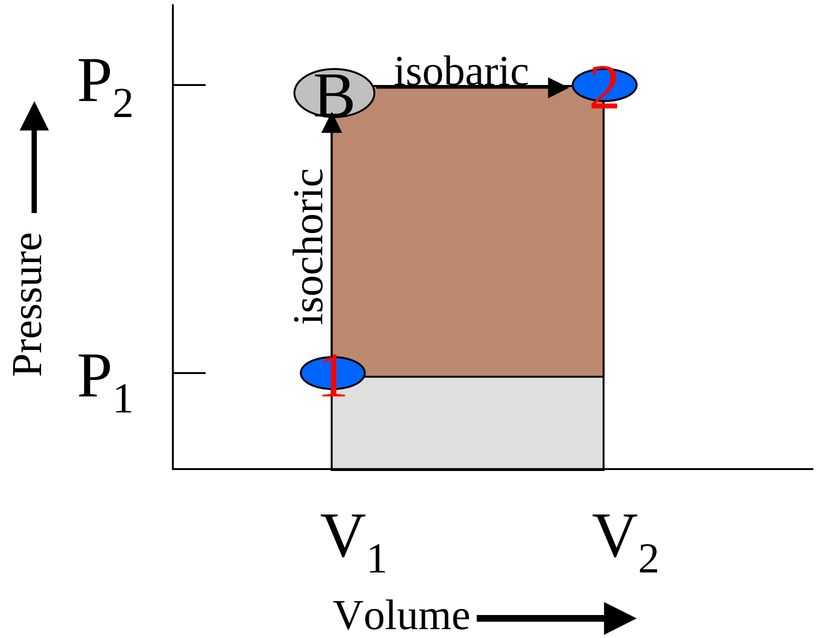
$$W = -P_1(V_2 - V_1)$$




Case II: B

$$W = -P_2(V_2 - V_1)$$

$$W = \oint PdV = (P_2 - P_1)(V_2 - V_1)$$



# 1.6 The Closed System

1st Law: for a closed system

Conservation of energy

$$\delta Q + \delta W = dU$$

*Nuclear reaction?*

Q and W are not state functions

U is a point or state function

$$\delta Q + \delta W = dU + d(PE) + d(KE)$$

PE: potential energy

KE: kinetic energy

Usefulness: one of the terms is unknown

# 1.7 Notation

Specific properties: properties per unit mass

$$\underline{U} \equiv \frac{U}{m}$$

Specific internal energy

$$\underline{V} \equiv \frac{V}{m} = \frac{1}{\rho}$$

Specific volume

$$\underline{V} \equiv \frac{molecular\ weight}{density}$$

Molar volume

# 1.8 Intensive and Extensive Properties

Extensive properties: depending on mass of the system

Intensive properties: not depending on mass of the system
Pressure, temperature, specific volume and density

Imagining another identical system created alongside the system under consideration, if the property or quantity in question has doubled, then that property is extensive

# 1.9 The Open System

Flow work: the internal energy of the materials entering and leaving that system, *plus* the work done on the system.

$$W_i = \int_0^V P dV_i = \int_0^m P d\underline{V_i} m_i = P\underline{V_i} m_i$$

Differential form

$$\delta W_i = P\underline{V_i}\delta m_i$$

# 1.9 The Open System (2)

## First Law for an open system

$$(\underline{U}_i + P_i\underline{V}_i)\delta m_i - (\underline{U}_o + P_o\underline{V}_o)\delta m_o + \delta Q + \delta W = dU$$

Flow work

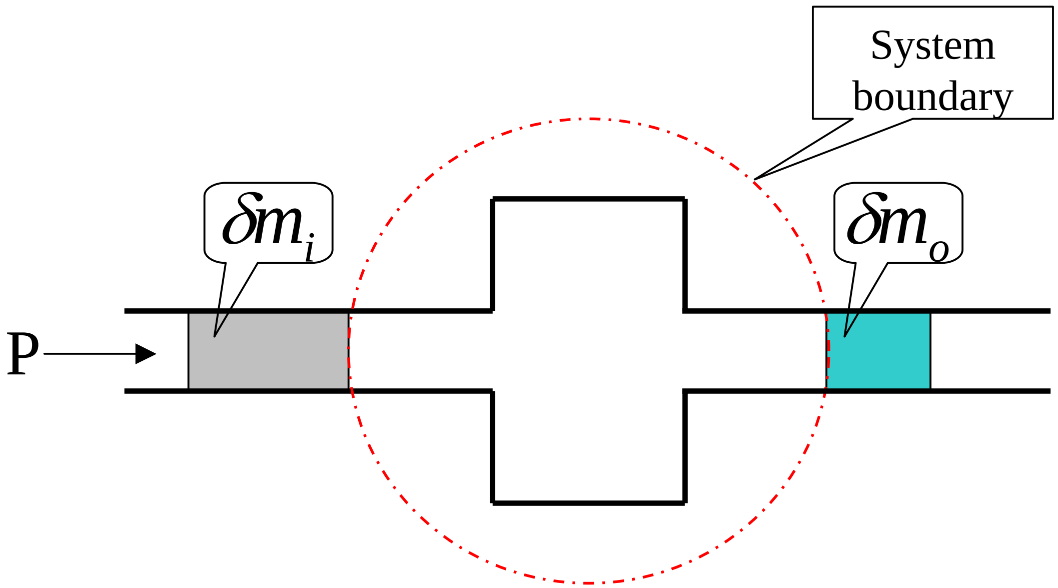


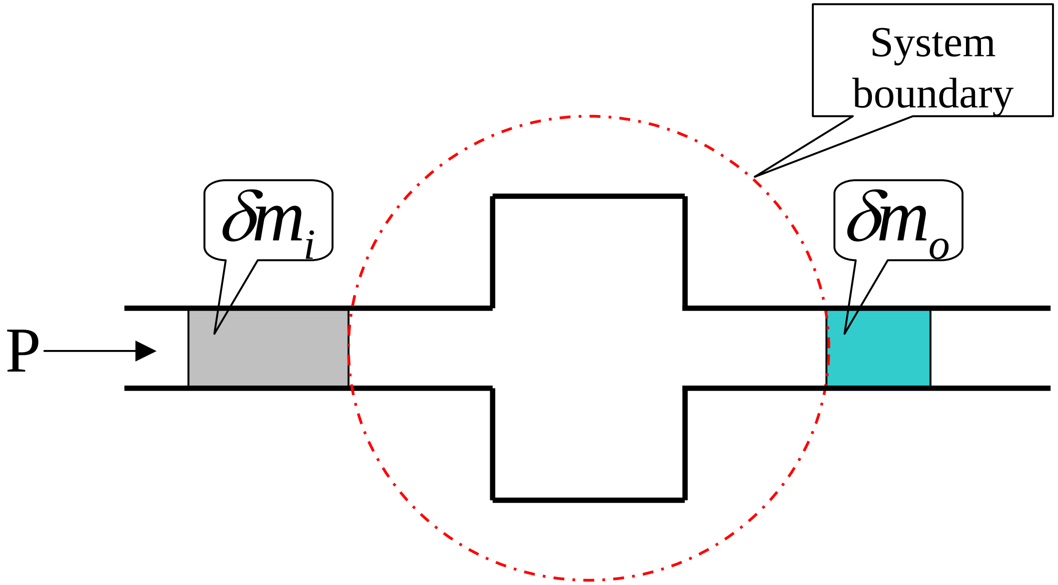

Fig. 1.5
Flow work in an open system

# 1.10 Enthalpy

Enthalpy: defined as U + PV

*Relative value!*

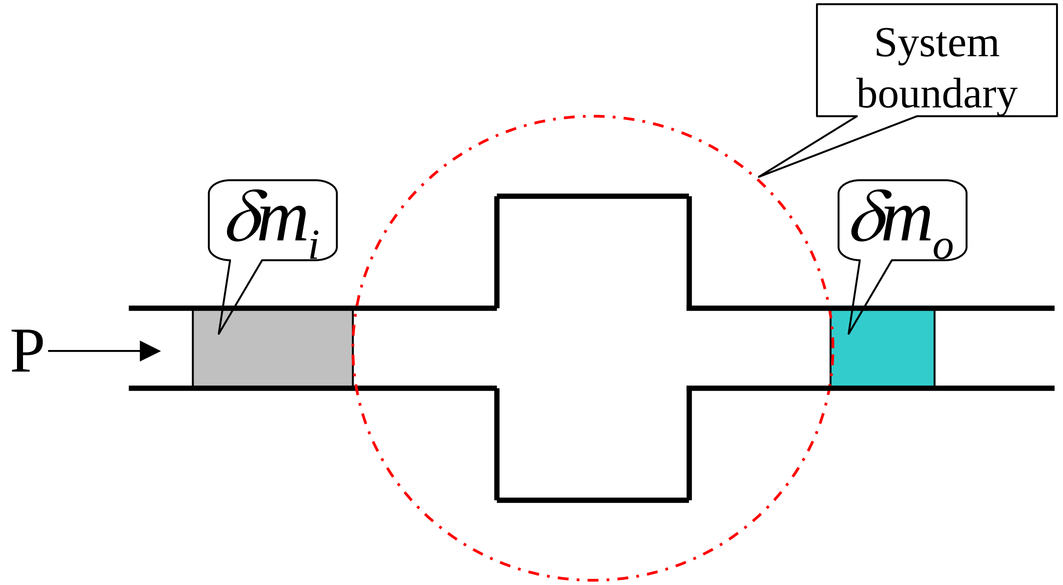
$$(H_i)\delta m_i - (H_o)\delta m_o + \delta Q + \delta W = dU$$



# 1.11 Steady state

Steady state: defined as the system does not change with time.

$$\sum(H_i\delta m_i)-\sum(H_o\delta m_o)+\delta Q+\delta W=dU=0$$




Equilibrium
Steady

Engineering thermodynamics

# 1.12 Heat Capacity at Constant Volume

Heat (energy) capacity: defined as the amount of thermal energy required to change the temperature of a material.

$$\delta Q = dU = mCdT$$

$$CdT = \frac{dU}{m} = d\underline{U}$$

$$C_V \equiv \left(\frac{\partial \underline{U}}{\partial T}\right)_V$$

No other forms of *work* involved

$$dU = mC_V dT$$

Need to specify Path / Condition

A function of temperature and specific volume of the material to which it applies.

# 1.13 Heat Capacity at Constant Pressure

Heat (energy) capacity: defined as the amount of thermal energy required to change the temperature of a material.

$$\delta Q = dU - \delta W = dU + PdV = dH = mCdT$$

$$CdT = \frac{dH}{m} = d\underline{H}$$

$$C_P \equiv \left(\frac{\partial \underline{H}}{\partial T}\right)_P$$

No other forms of work (except volume work) involved

$$dH = mC_P dT$$

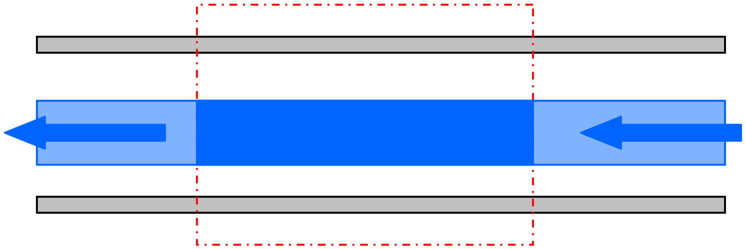
Need to specify
Path / Condition

A function of both temperature and presure

# Example

Calculate the energy required and the cost of heating a slab of aluminum of mass one metric ton (1000kg) from 300 K to 800 K, a temperature that might be used to reduce the thickness of the aluminum through rolling.

The aluminum will be heated by passing it through a furnace that uses electricity as its source of energy. The cost of electrical energy is assumed to be 5 cents per kilowatt-hour. Assume all the electrical energy entering the furnace is used to heat the aluminum.



# Example

Select the furnace as the system

It is an open system. Assume it is at steady state.

$$\sum(H_i \delta m_i) - \sum(H_o \delta m_o) + \delta Q + \delta W = dU = 0$$

0

Energy entered the system as work because of an electrical potential difference (non volume work)

$$W = m_{Al}(\underline{H}_0 - \underline{H}_i)$$

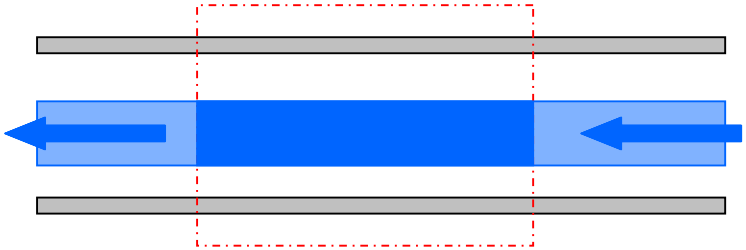
$$\underline{H}_0 - \underline{H}_i = \int_{300}^{800} C_P \, dT$$

# Example

Select an aluminum slab as the system, It is a closed system. The first law equation in integrated form.

$$Q + W = U_2 - U_1$$

$$Q = U_2 - U_1 - W = U_2 - U_1 + P(V_2 - V_1)$$
$$= U_2 + PV_2 - (U_1 + PV_1)$$
$$= H_2 - H_1 = \left(\underline{H}_2 - \underline{H}_1\right)m$$



This is essentially the same as the result obtained using the open system. The energy supplied to the slab is treated as heat in this case. Because there are no extraneous heat losses from the furnace, the energy transferred as heat is identical to that supplied as electrical energy to the furnace. The approaches, thus, yield the same answer, as they should.

# Review / Key points

- System / surroundings系统环境
- Open / close / isolated systems敞开封闭孤立
- Thermal equilibrium / steady state平衡稳态
- Heat / work热功
- Internal energy内能热力学能
- State function状态函数
- Intensive / extensive properties强度容量性质
- Enthalpy焓
- Heat capacity热容

# Review / Key points

- Systems can be classified as open, close and isolated systems
- 0th law
- 1st law / energy conservation
- Heat / work
- Internal energy / enthalpy / heat capacity
- State function

# Review / Key points

- The first law of thermodynamics is simply the principle of conservation of energy: that is, energy can be neither created or destroyed. To derive the practical benefits of knowing this principle, we must construct an accounting system for energy, sometimes called an energy balance. This system must handle flows of energy, such as heat and work, as well as the various forms of energy that matter possesses. To operate this accounting system, we will need to understand a series of basic notions and definitions.

# Homework

Any comments, suggestion and questions

- Exercises in Chap 1

  P 38, 1.2, 1.3