

Lecture 7.

- Equilibrium vs steady state
 - processes, paths, cycles
 - Internal energy, thermal energy
 - ↳ special example: ideal gas
 - ↳ here internal = thermal (not in general!)
 - First law, work, heat .
-

Example Questions

- Is a cat at constant temperature & mass best described as approximately at
 - equilibrium OR
 - steady state ?

Why?

- Suppose I smash a priceless sculpture with a hammer & wait for it to settle to its new equilibrium. Is this best described as a
 - (quasi-)equilibrium process OR a
 - non-equilibrium process ?

Why?

1. Briefly define internal energy U .
 2. What is the relationship between internal energy, heat and work (i.e. the first law of thermodynamics)?
 3. For an ideal gas, what does the internal energy represent?
-

25) State the first law of thermodynamics

Answer:

Key

2.2.1 Equilibrium, steady state and quasi-steady-state

At steady state the system properties are not changing in time but the environment properties may be. Interactions may be occurring as long as the system properties are unchanging. Hence a steady-state is a non-equilibrium condition.

since equil requires unchanging env.

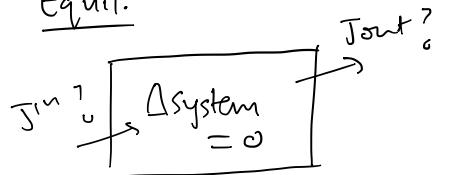
since thermo based on equilibrium.

In order for this definition to make sense we must suppose that we can *measure* system properties at steady state in essentially the same manner as we do at equilibrium. One way of doing this is to introduce the idea of a *measurement device* and use the idea of *equilibrium between the system and the measurement device*, rather than between the system and the environment, to define system properties. Thus we imagine that *a system can be in equilibrium with a measuring device while out of equilibrium with its environment*.

This appears to violate the zeroth law, however! To avoid this we can suppose that the 'inside' of the system is in one state, the environment in another, and that there is a *boundary or transition region* separating the two. The measuring device is imagined to have 'access' to the internal state of the system, while the environment can only interact via the outside of the boundary. Hence the inside of the system and the environment can have two well-defined, but different, temperatures without violating the zeroth law.

Equilibrium vs steady state

Equil.

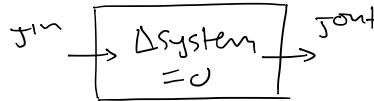


$$\Delta \text{Env} = 0$$

$$\begin{aligned} J^{\text{in}} &= 0 \\ J^{\text{out}} &= 0 \end{aligned} \quad \left. \begin{array}{l} \text{each flux} \\ \text{is zero} \end{array} \right.$$

Boring!

Steady State



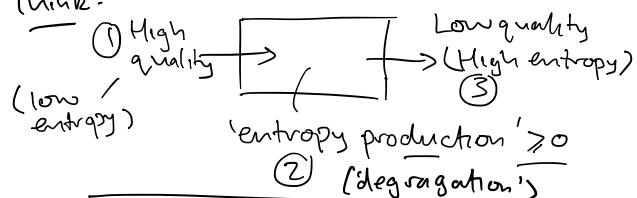
$$\Delta \text{Env} \neq 0$$

usually $J^{\text{in}} = J^{\text{out}} \neq 0$ (e.g. mass, energy)

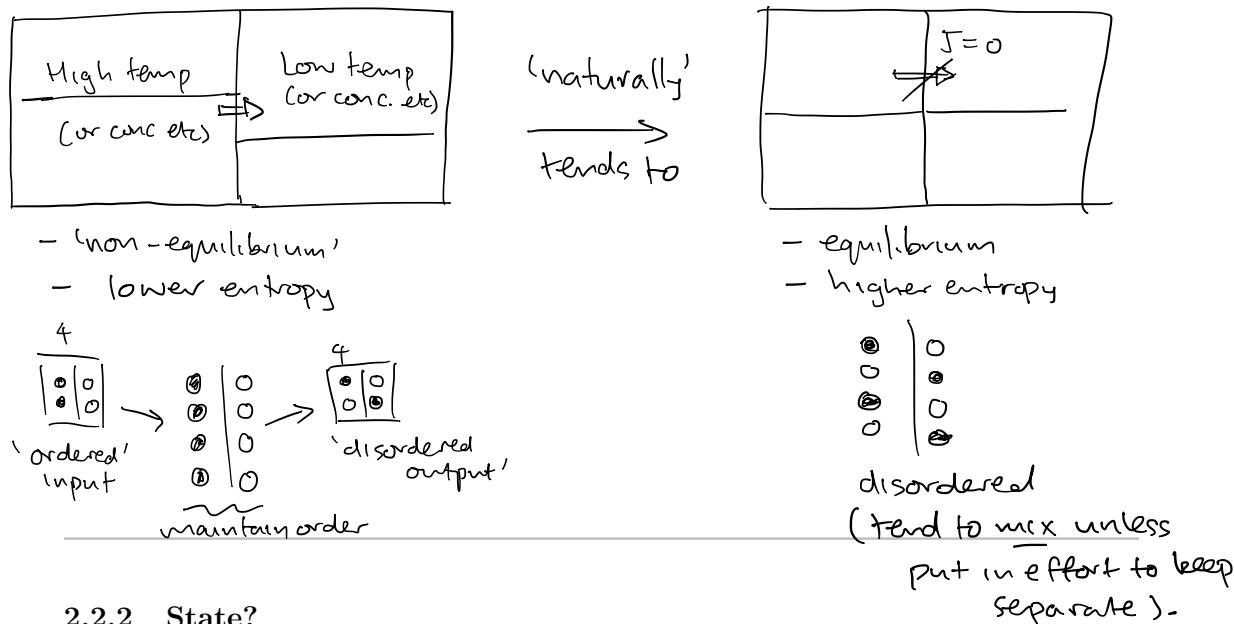
what changes?

| Entropy | !

Think:



$(1) + (2) = (3)$ } need to import more high quality to make up for internal degradation

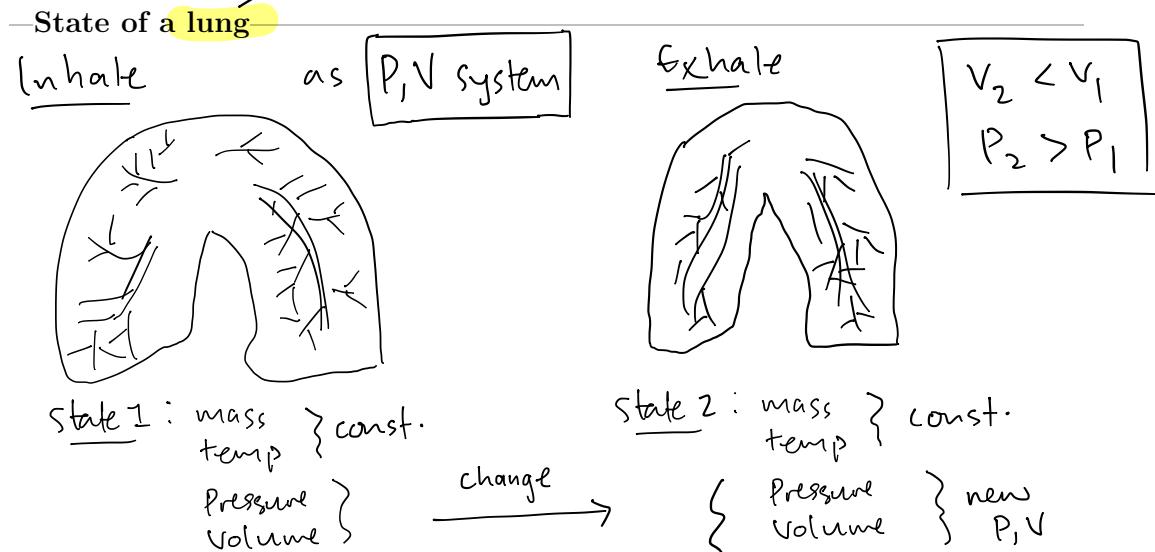


2.2.2 State?

The term **state** refers (roughly) to a **list of properties sufficient to describe our macroscopic system**. This is also relative to our analysis goals: e.g. we do not need to characterise the nuclear state of our system if we are not interested in nuclear processes.

For example a (P, V) system is a system sufficiently described by its pressure and volume.

non-equilibrium system! (not dead....)



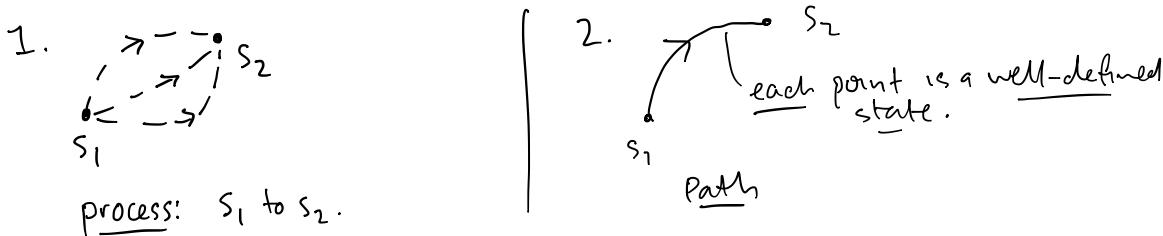
2.3 Processes, paths and cycles

How can we apply thermodynamics under time-varying conditions - everything so far refers essentially to *static* conditions⁶?

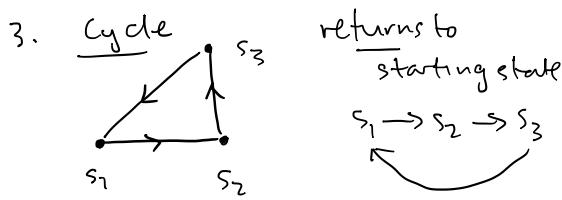
To make these ideas more precise will give some definitions. These are perhaps best understood via pictures, however, so we draw these afterwards.

- Key**
1. A **thermodynamic process** is a change or series of changes from one equilibrium (or steady) state of the system to another. We don't necessarily specify the path between, but always give the start and end states. (We may or may not specify how the environment changes.)
 2. A **process path** is a continuous sequence of equilibrium (or steady) states between two start and end states of the system.
 3. A **(cycle)** is any process path that returns to its initial state, i.e. where the starting state and end state are the same.
 4. A **quasi-equilibrium process** is when a system follows a well-defined process path of equilibrium states during a process. Similarly, a **quasi-steady-state process** is when a system follows a well-defined process path of steady-states.
 5. A **non-equilibrium process** is when the system doesn't have a well-defined process path of equilibrium states during the process. We will assume in general that it does however, start and end in a well-defined equilibrium state. Note: a *quasi-steady-state process is in general a non-equilibrium process.*
 6. A **process diagram** is when we plot a process in state space, i.e. on a diagram with the state variables as the axes.

Illustration of our process definitions



⁶In fact, some argue that thermodynamics would be better named *thermostatics*!



system has well-defined path } (either ss or equil.) } in this course usually assume equil./quasi-equil. processes .

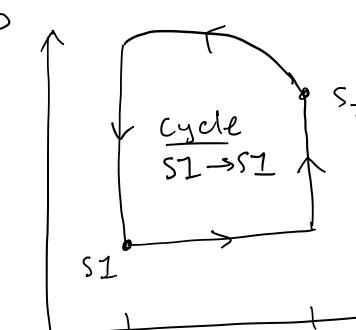
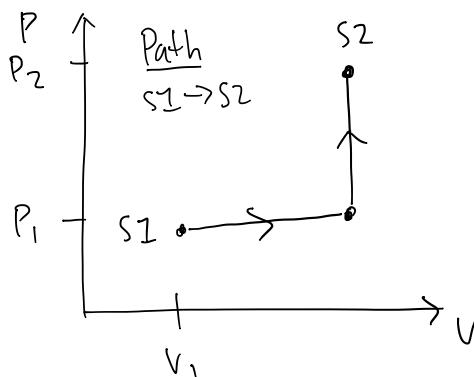


(usually use dotted lines)



Process diagram
 e.g. PV diagram.

Example: a beating heart process diagram.



The cardiac cycle
 → sometimes called a 'PV loop'

Example Problems 2: Basic concepts of thermodynamics

1. Which of the following statements is **false**, regarding properties of a thermodynamic system:
 - A. Extensive properties can be converted to intensive properties by dividing by moles.
 - B. Intensive properties are independent of the quantity of matter.
 - C. Volume is an extensive property.
 - D. Heat is a property of the system.**
 - E. Temperature is a property of the system.

—Answers—

2.4 Internal energy, work and heat

2.4.1 Internal energy

$$\boxed{U}$$

Given a thermodynamic system, we define the **internal energy** as the 'total' energy stored (or 'allocated') *inside* the system. Some key points:

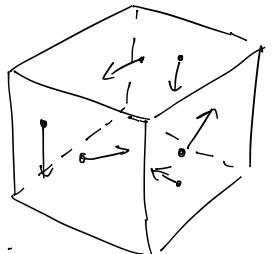
1. By 'inside', we mean we exclude the *bulk* translational and rotational kinetic energy of the system as a whole, relative to the environment or other external frame of reference.
2. We do, however, include the translational, rotational and vibrational energy of the *microscopic* constituents of the system (as measured relative to the bulk system motion).
3. This 'microscopic' kinetic energy is called the **thermal energy**. } Note: not same as internal energy.

4. We also [include in the internal energy] (but [not in the thermal energy]) the chemical energy in bonds, long range interactions between molecules, nuclear energy etc.
5. Since internal energy, like all energies, is only defined up to a reference value/reference state we don't actually need to track all energy sources, just those that will change or those that affect our problem.

—Internal energy of an ideal gas

Assume : molecules don't interact with each other

(do interact with, ie collide with, walls)



Then:

→ Internal energy is just sum of microscopic kinetic energy of molecules
→ This is just the thermal energy!

} only for ideal gas

Can show:

→ thermal energy of an ideal gas is proportional to temperature, so

$$U = \frac{3}{2} n R T \quad \text{ie } U \propto T$$

→ Also, the key constitutive eqⁿ for an ideal gas ie

$$PV = n R T \rightarrow \text{ideal gas law}$$

n = number of moles
 R = ideal gas constant

U : internal energy

[Extra]

Micro: can derive:

$$E_{\text{molecule}} = \frac{3}{2} k_B T$$

↑
number of molecules
↓ Boltzmann's constant

$$U = N \times E_{\text{molecule}}$$

$$= \frac{3}{2} k_B N T \quad] \quad k_B = \frac{n}{N} R$$

links micro & macro

will use a lot!

2.4.2 The first law of thermodynamics

The **first law of thermodynamics** is 'simply': **energy is conserved**. Hidden in this, however, is that **energy can be transferred between systems via both macroscopic mechanical work and heat**. Another more explicit statement is: **the change in internal energy of a system equals the sum of energy transferred**, where energy can be transferred via **both mechanical work and heat**.

Recognition of the existence - and essential equivalence between - heat and work, in terms of both being energy transfers, was a crucial point in the development of thermodynamics. Originally heat and work were measured in different units - James Prescott Joule carried out the original experiments relating heat and work, starting around 1840, and established the conversion between the old unit of heat, the calorie, and the measurement of work. The conversion factor 1 cal = 4.2 joule is called **the mechanical equivalent of heat**.

Key equation and sign conventions

w : work, Q : heat

$$\Delta U = W^{on} + Q^{in}$$



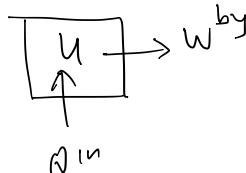
Change in stored
sum of additions

U :
internal
energy.

Note: $Q^{in} = \Delta U - W^{on}$ can be used as def'n of Q !

Engineers often use

$$\Delta U = -W^{by} + Q^{in}$$



where $W^{by} = -W^{on}$

'extract work' from system.

Key

As discussed previously, work can be usefully thought of as a type of energetic interaction or exchange of energy. Similarly, heat can be considered as a form of ‘thermal work’: a new form of macroscopic ‘work’ not fitting under our usual definition of macroscopic mechanical work.

Like mechanical work, heat is an energetic interaction. Ultimately, heat can be thought of as arising from microscopic mechanical work that we do not directly observe. Instead we macroscopically observe the differences in microscopic kinetic energy as ‘temperature’ differences, and observe the resulting macroscopic energy exchange, due to the net microscopic differences and microscopic work, as ‘heat flow’.

In mechanics of course, we express work in terms of a force times a displacement (or integrated over a series of displacements). In the reversible case we will see that ‘thermal work’, i.e. heat flow, can also be imagined as a sort of ‘force times displacement’, where temperature is the force and entropy is the ‘displacement’.

Things are not completely symmetric, however: we will return to how work and heat differ in the irreversible case when we discuss the second law and entropy. This asymmetry prevents thermodynamics from being completely reduced to macroscopic mechanics⁷; instead, thermodynamics can be considered as an extension of macroscopic mechanics to deal with irreversible processes.

—Work from internal energy

convert stored energy to work:

$$\text{Suppose: } Q^{\text{in}} = 0 \Rightarrow W^{\text{by}} = -\Delta U \quad \left. \begin{array}{l} \text{Key here is} \\ \text{always 1st} \\ \text{law 1st!} \end{array} \right\}$$

for example. ‘use up’ to do work.

⁷We assume it *is* potentially reducible to microscopic mechanics; however, doing this fully rigorously is still an incomplete task to date.

Converting heat to work



for example
Suppose $\Delta U = 0$

$$\Rightarrow \Delta U = -W^{\text{by}} + Q^{\text{in}} = 0$$

$$\boxed{W^{\text{by}} = Q^{\text{in}}} \quad \left\{ \begin{array}{l} \text{convert } Q \\ \text{to work.} \end{array} \right.$$

Step 1:
write down law.
Step 2:
apply to special case.

Note: limitations on efficiency of converting heat to work ('heat engines')

→ apparent when considering cycles (see later)

Example Problems 3: Internal energy and the first law

1. Briefly define internal energy U .
2. What is the relationship between internal energy, heat and work (i.e. the first law of thermodynamics)?
3. For an ideal gas, what does the internal energy represent?

Answers

1. 'total' energy stored 'inside' system
→ includes the thermal energy, chemical energy, etc
2. $\Delta U = -W^{\text{by}} + Q^{\text{in}}$
3. Thermal energy. (Microscopic kinetic energy)
⁷⁰

see full
defn.

end L7.