Lecture 6: Intro to Thermodynamics } difficult subject. easy (?) questions?

- Waffly big picture stuff
  - L what is thermodynamics about?
- Thermodynamic systems
  - L key features as 'macroscopic' objects

definitions

- Types of system
  - L open
  - L closed
  - L isolated
- Thermodynamic Properties
  - L extensive & intensive
- Interactions
  - L mechanical
  - L thermal.
- zeroth law
  - L thermal equilibrium
  - L temperature.

Example Questions

o **11)** Which of the following are NOT properties of a thermodynamic system:

(1 mark)

A. Temperature
B. Pressure
C. Volume
D. Heat
E. Entropy

Answer: ____________

o **29)** Which are the following statements is FALSE, regarding properties of a thermodynamic system:

(1 mark)

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

Answer: ____________

o **1)** Which of the following properties is an extensive physical property? **(1 mark)**

A. Density
B. Concentration
C. Volume
D. Pressure

Answer: __________

o What type of thermodynamic system is an unopened bottle of water?

o What condition ensures two systems don't exchange heat when placed in thermal contact?

↳ which law of thermodynamics is this most directly related to?

2 Thermodynamics

Learning Objectives

- Understand the scope and limitations of thermodynamics. State and apply the zeroth, first and second laws of thermodynamics.
- Understand the concept and types of thermodynamic 'system'. Identify state properties and distinguish them from process variables. Understand the concepts of equilibrium, process, path and cycle.
- Understand the concepts of heat, thermal energy and internal energy. Understand and do basic calculations involving heat capacity and latent heat.
- Recognise various types of thermodynamic process, including isothermal, adiabatic and isobaric. Calculate work done/heat transferred during different process types and sketch associated process diagrams.
- Understand heat engines and do basic efficiency calculations. Understand the connection between the second law, limits on work extraction and the definition of 'reversible' processes.
- Understand the concept of a spontaneous process, identify which processes are spontaneous in different types of system and know which energy function - internal energy, Helmholtz free energy, Gibbs free energy or enthalpy - governs spontaneous processes in which type of system. Calculate changes in Gibbs free energy and/or enthalpy.
- Carry out basic calorimetry (energy measurement) calculations, e.g. know how to determine the heat capacity of an unknown substance.

2.1 Overview and basic concepts of thermodynamics

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2.1.1 The scope of thermodynamics

Thermodynamics is a *general science of macroscopic 'systems' and energy transfer between systems.* A key characteristic of it is that it doesn't require detailed knowledge of the internal structure of the system, nor the specific process carried out.

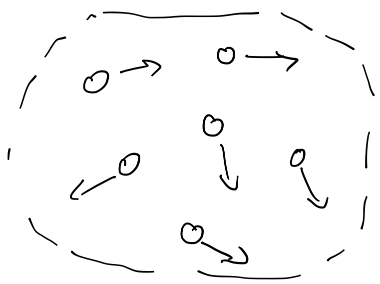
This may remind you of our discussion of energy conservation and its independence from specific, detailed mechanisms - if so, you are on the right track! For example, Pierre Duhem (1861–1916), a prominent French physicist and philosopher of science in the nineteenth and early twentieth centuries, promoted ‘energetics’, essentially thermodynamics, as the foundation of all physical theory including mechanics, chemistry, physics etc[3]. Towards the end of the nineteenth century, before the existence of atoms was definitively established, Duhem famously argued against atomism; more precisely, he argued that the chemistry of the time was *independent of*, and consequently offered no support for, atomism! In a sense he wasn't wrong - much of thermodynamics and its associated application *is* independent of the particular constitution of matter.

This generality continues to be a key feature of modern thermodynamics: it applies to all systems, regardless of their details. This is just like conservation of energy - actually, conservation of energy is the first law of thermodynamics! The generality of thermodynamics can clearly be considered both a strength and a weakness: while it can often tell us a lot about what's possible/impossible, it often isn't enough to tell us precisely what actually happens, nor the rate at which it happens. As we discussed previously, conservation of energy is not sufficient to (macroscopically) explain e.g. the differences in the material properties of wood and metal. To answer these sorts of more detailed questions we need to supplement thermodynamics with constitutive equations and/or kinetic/statistical theories. It helps to know, after all, that atoms really do exist!

[3]He is also well-known in philosophy of science for his contributions to what is now called the Quine-Duhem thesis: in essence the idea that any given body of empirical data is equally consistent with multiple theories.

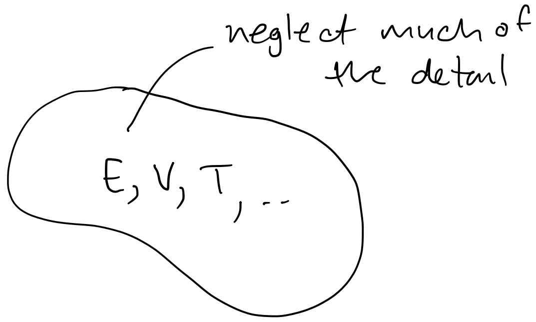
Thermodynamics, mechanics and partial descriptions

Full details:



vs

Thermodynamic System



- mechanics of each particle etc

  Need position, momentum of each particle

  → eg 6×10^{23} Avogadro's number

- thermodynamics

  small number of 'overall', 'macroscopic' variables

  eg 3: energy, volume, temperature

2.1.2 The laws of thermodynamics: a preview

Here we give a brief overview of the content of the laws of thermodynamics. In the next few subsections we will get a feel for what these 'really' mean by using them!

1. **Zeroth Law:** Establishes the concept of thermal equilibrium and the existence of empirical temperature. temp
2. **First Law:** Energy is conserved. energy
3. **Second Law:** Entropy in an isolated system is non-decreasing (stays the same or increases). entropy

One of the key themes of thermodynamics is the *interplay between the first and second laws.* We will see that the upshot of this interplay is: ie energy & entropy.

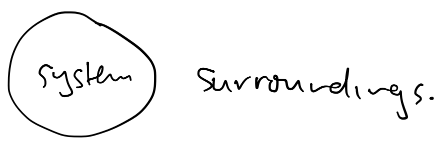
1. Energy is conserved and can be transferred to macroscopic systems via both 'work' and 'heat'.
2. There are limitations on how efficiently energy can be transferred between macroscopic systems, and this is intimately related to entropy increase.

Now we develop the key thermodynamic concepts in more detail.

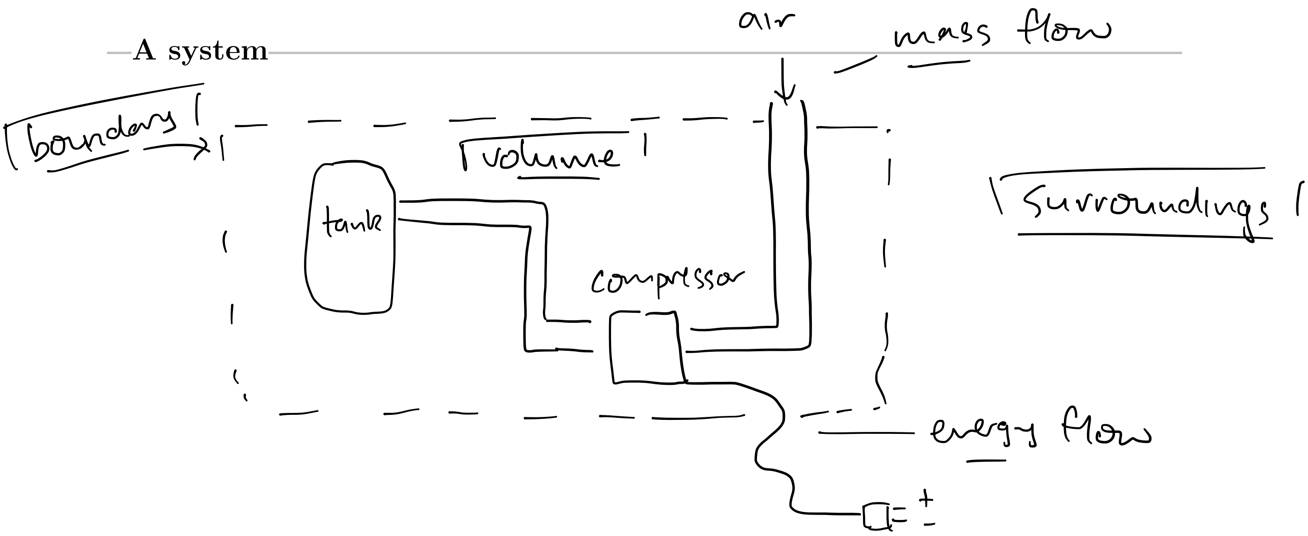
2.1.3 Thermodynamic systems

A thermodynamic **system** is a *macroscopic* object, collection of objects or region that an analysis is performed on. 'Macroscopic' means that our region or object has

1. A boundary
2. A volume
3. A surroundings



A system



The distinction between macroscopic/macroscale and microscopic/microscale is not precise and is often relative.

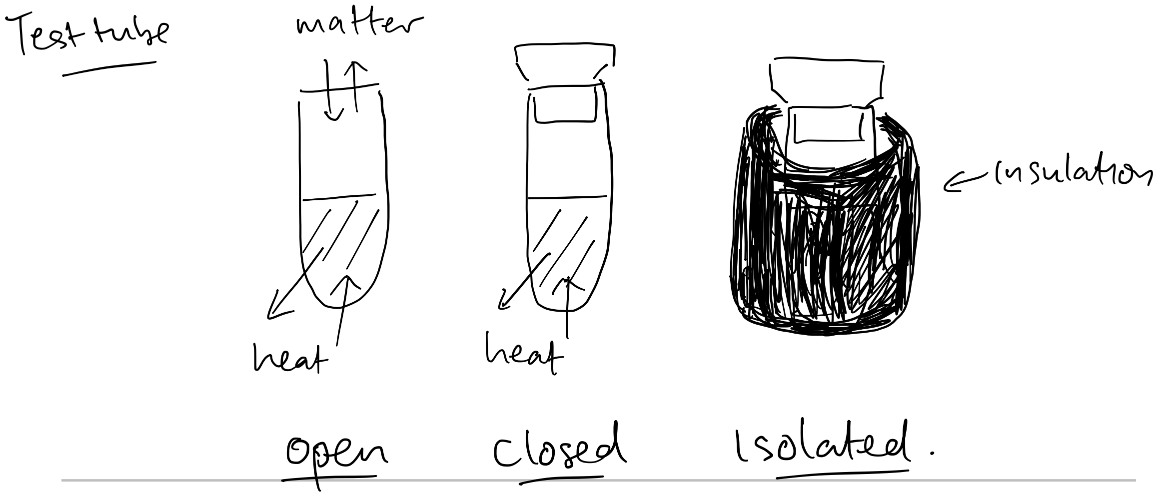
In practice, one can imagine 'macroscopic' to mean the scale at which we treat a collection of entities as 'a whole', while microscopic as the scale at which we consider the individual entities making up that whole. For example one might consider a planet to be a 'microscopic' - or more appropriately a microscale - entity when considered as part of a galaxy[4]!

Choosing a system also requires us to define what *interactions* are possible between the system and its surroundings. In particular, this leads us to distinguish between the following types of system:

1. **Open:** both matter and energy can cross the boundary
2. **Closed:** energy can cross the boundary, but matter cannot
3. **Isolated:** neither matter nor energy can cross the boundary

[4]There is no reason, however, why we can't consider a 'continuum' of scales from the smallest particle (or perhaps string!) to the largest collection of entities. In practice it is also common to explicitly introduce a 'mesoscopic', intermediate scale, lying in-between our smallest and largest scales.

Open, closed and isolated systems



The key is to ask yourself what types of interactions or *transfers* are possible: mass and/or energy.

Example Problems 1: Classification of systems

Classify the following systems as open, closed or isolated:

1. A river. open
2. The interior of a closed can of L&P. closed
3. The interior of a closed freezer that is turned off. isolated
4. Interior of a closed freezer that is turned on. closed
5. A cat. open.

2.1.4 Properties

A **thermodynamic property** is any measurable characteristic of a macroscopic system 'at equilibrium', e.g. volume, pressure, temperature etc. The concept of *equilibrium* is discussed further below, but is roughly 'nothing is happening' on the macroscopic measurement scale of interest. In order to apply our ideas to the real world, however - which is never fully at equilibrium - we really need to be able to measure and define quantities 'outside of equilibrium'. This is a somewhat controversial topic; we discuss it a little later on.

Note: atoms are continually 'jiggling' at the *microscopic* level, even at thermodynamic - i.e. macroscopic - equilibrium!

Properties can be classified as either

1. **Intensive:** independent of the size (mass, volume etc) of the system.
2. **Extensive:** depends on the size (mass, volume etc) of the system.

We can *convert* extensive properties to intensive properties by dividing by the size of the system (e.g. mass, volume etc), or by taking the *ratio* of two extensive quantities.

Examples of extensive and intensive properties

Extensive

volume, mass, energy, amount (moles) entropy, heat capacity

Intensive

temperature, density, pressure, concentration, specific heat capacity.

2.1.5 Interactions

What do we mean by 'interactions' and what types are possible? Roughly, an interaction is an exchange of mass or energy[5].

[5] In fact, mass can be considered as a special type of energy transfer, that of mass-energy.

We assume here that the basic ideas of **mechanics** are known and given, e.g. we take *mechanical work* and *mechanical energy* as known concepts. For example, we assume that the idea of mechanical work as given by *force times distance* (or integrated over a series of displacements) is familiar. Furthermore, we usually classify e.g. electrical current etc interactions as 'mechanical' processes here. The increments in work of these processes can also be expressed in the form 'force times displacement'.

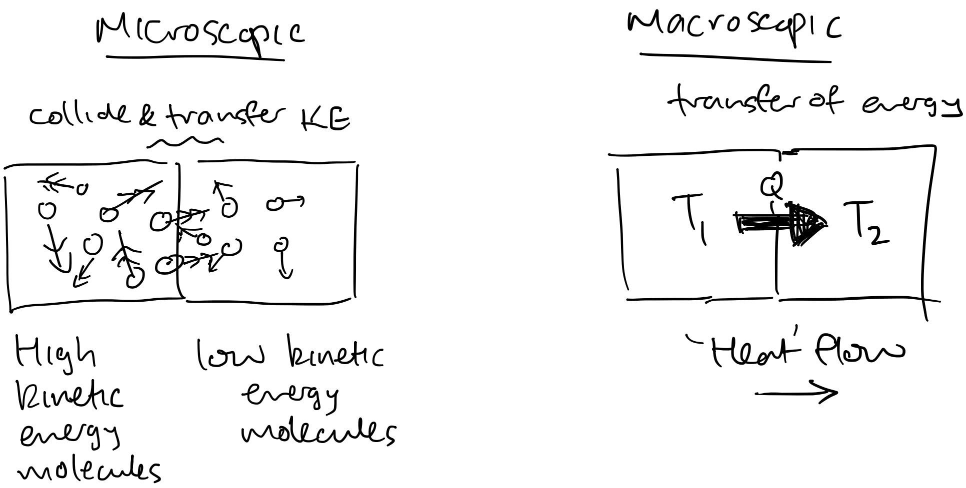
essence

Thermodynamics introduces the idea of a *new type of macroscopic interaction*, not given by 'ordinary' (conservative/reversible) macroscopic mechanics: **thermal interactions**. A thermal interaction is roughly defined as a type of interaction that is...'*not macroscopic mechanical work nor mass transfer*'!

This arises because we *know from experience* that we can place two closed (no mass transfer) systems into 'contact' and have them *exchange energy without either doing macroscopic mechanical work on the other.*

This form of 'thermal energy transfer' or 'thermal interaction' will be called **heat** and is discussed in detail later.

Thermal interactions: macroscopic and microscopic pictures



It is important to remember that **interactions are not properties of the system**, they are *exchanges* of quantities between systems. Think: *bank transfer* (interaction) between systems) vs *bank balance* (property of a system).

heat, work

energy, temperature etc.

2.2 Equilibrium and the zeroth law

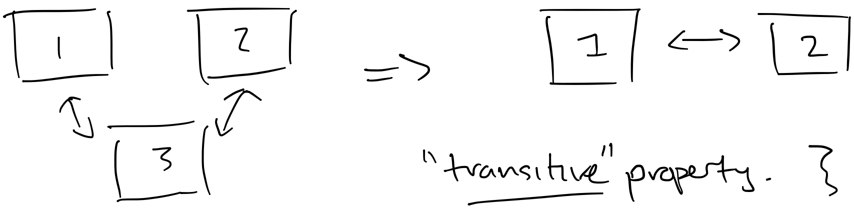
As mentioned above, **macroscopic equilibrium** is essentially the idea that *nothing is happening* on the macroscopic scale of interest.

This includes **both the system and the environment** – *neither* is changing (in time or space) at equilibrium. No macroscopic 'interactions' or processes are occurring at equilibrium (though microscopic interactions continue in general). } don't 'add up' to anything

Thermal equilibrium is a special type of equilibrium: two systems are in thermal equilibrium when they are placed in thermal contact and no thermal interaction (i.e. heat flow) takes place between them. This leads to the idea of the zeroth law, which allows us to define a *property*, called **temperature** to *compare systems thermally*. In particular, we can now say that *systems at the same temperature do not thermally interact (exchange heat)*.

interaction

Zeroth law and temperature



"transitive" property. } need for number

zeroth law ["Two systems in thermal equil. with a third are in thermal equil. with each other"

$\Rightarrow$ can use a number T to compare systems thermally: $T_1 = T_3$ & $T_2 = T_3 \Rightarrow T_1 = T_2$ }

defines temp.

That *heat flows from higher to lower temperatures* is an empirical fact that, when generalised, becomes a form of *the second law of thermodynamics*, which is discussed later.

L6 end.