Lecture 7 - Ensembles and averages

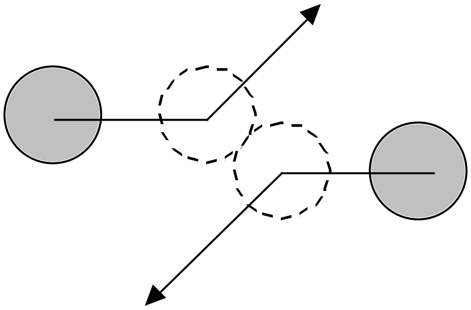
What's Important:

- ensembles and averages
- heat, work, energy

Text: Reif
Demo: mechanical equivalent of heat
Further reading: Secs. 2-10, 2-11.

Ensembles and averages

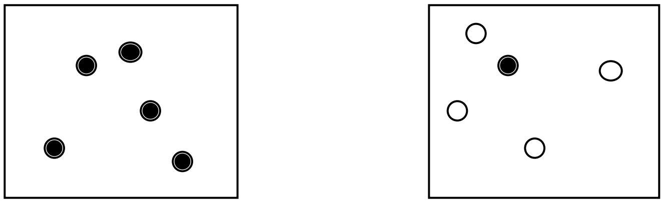
Suppose we have a group of hard spheres confined to a container. The spheres have no other interaction with each other beyond their hard-core potential: when they collide, they exchange energy and momentum according the usual conservation laws.



Suppose that we now want to find the probability of a sphere having a given speed *s*. Few spheres are moving either very slowly or very fast. The probability density distribution might look like:

where $P(s)\,ds$ is the probability of finding a sphere with speed between s and $s + ds$.

We can imagine two ways of measuring this distribution:



measure all spheres at once

make repeated measurements on a single sphere

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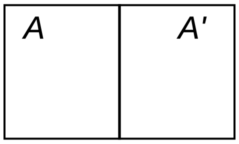
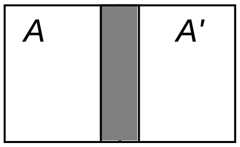
The **ergodic assumption** states that the results of these two measurements will be the same.

Now we generalize beyond particles to consider systems in interaction. The systems are labelled *A* and *A′*, and they interact at their point of contact.

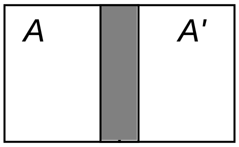
Thermal contact: the energy of a system can change, but not volume or particle number



Mechanical contact: volume can change but not energy (insulating piston)

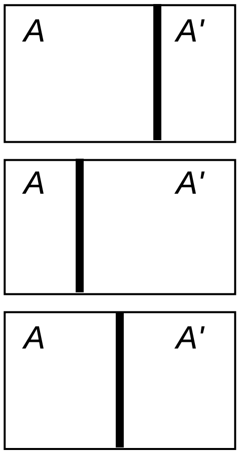


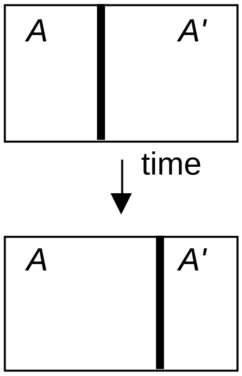
Mechanical plus thermal contact (conducting piston)



Suppose that we wish to measure the energies and volumes of systems in contact. As with the particle collision problem, we could

measure an ensemble of identically prepared systems once	measure one system many times





What can these systems do?

- *thermal contact*: exchange energy (*i.e.* heat); systems may have same *T*, but varying *E*
- *mechanical contact*: exchange volume (*i.e.* do work); systems may have same *P*, but varying *V*

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Work, heat, energy

The change in the mean energy of a system is governed by the heat and work is exchanges with other systems (we have to use the *mean* because the energy fluctuates)

$$\Delta\bar{E} = Q - W \tag{7.1}$$

where

Q = heat absorbed **BY** the system
W = work performed **BY** the system.

For systems in thermal contact only:

$Q_A = -Q_{A'}$ $\quad$ $W = 0$

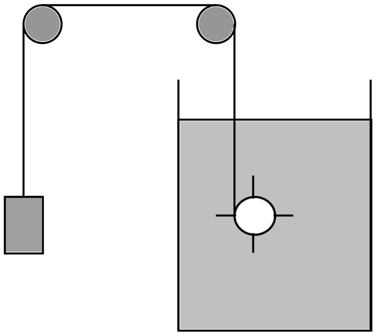
For systems in mechanical contact only

$W_A = -W_{A''}$ $\quad$ $Q = 0$

That is, the heat absorbed by one system is the negative of the heat absorbed by the other. The real definition of heat is

$$Q = \Delta\bar{E} + W$$

Note that work need not be of the *PV* type. A falling weight does work *mgh* on the fluid in the diagram by increasing its kinetic energy by means of the paddle:



For infinitesimal changes, we rewrite $\Delta\bar{E} = Q - W$ as

$$dE = \text{đ}Q - \text{đ}W$$

Note

- The slash through the *d* (should just be through the upright line as in $\hbar$) represents only an infinitesimal quantity, not a "change in" quantity. The system itself does not possess a characteristic value of heat or work which can be changed; Q and W are associated only with the process itself.
- đ rather than d is used because work and heat are *path dependent*: the amount of heat or work depends on the path because the system may be in contact with other systems. đ is an **in**exact differential.

  adiabatic: $\quad Q = 0$ and $\Delta\bar{E} = -W$

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no change in volume or other mechanical characteristics

$$dE = \text{đ}Q$$

Quasi-static processes

Suppose that there are a group of parameters h_1, h_2,...h_n which describe the mechanical features of a system (*e.g.*, volume...). When work is done by the system, some of these characteristics change. If the change occurs sufficiently slowly, so that the system is always close to equilibrium (where *equilibrium* is defined as equal occupancy of accessible states), the process is called **quasi-static**. The timescale for the process to be called "slow" is set by the relaxation time of the process.

If the process is quasi-static, we can talk about continuous changes in the energy as a function of the external parameters h_i. Thus, for a given microstate E_r

$$dE_r = \sum_{\alpha=1}^{n} \frac{\partial E_r}{\partial h_\alpha} dh_\alpha \tag{7.2}$$

For example, the microstate might be characterized by the spin *etc*. of the particles.

If the process keeps the system in a given microstate, even though the energy of the microstate changes as a function of h_α, then we can write

$$\text{đ}W = -dE_r = \sum_\alpha \phi_{\alpha,r} dh_\alpha \,, \tag{7.3}$$

where the ϕs are generalized forces

$$\phi_{\alpha,r} = -\frac{dE_r}{dh_\alpha} \tag{7.4}$$

These quantities look like $f = -\partial V / \partial x$ in classical mechanics.

Eq. (7.3) can be further generalized to include systems in contact, where there are fluctuations around the mean energy:

$$\text{đ}W = \sum_\alpha \left(-\frac{\overline{\partial E}}{\partial h_\alpha} \right) dh_\alpha \tag{7.5}$$

For example, suppose that the volume changes during a process. Eq. (7.5) reads

$$\text{đ}W = \left(-\frac{\overline{\partial E}}{\partial V} \right) dV$$

so that the pressure must be

$$P = \left(-\frac{\overline{\partial E}}{\partial V} \right)$$

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