Lecture 32

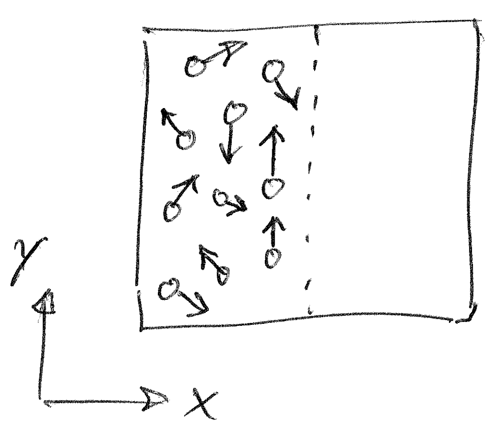
A new kind of equilibrium

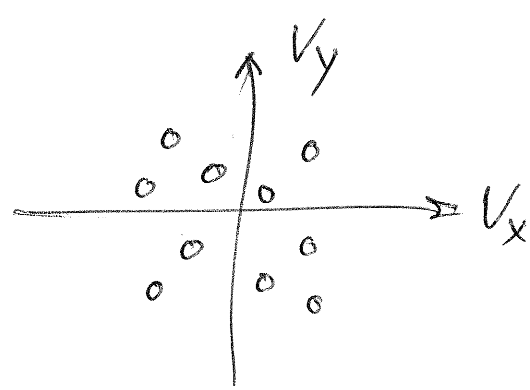
In mechanics, the "state of equilibrium" is usually understood to mean the exact cancellation of forces and torques on a system. A system "in equilibrium" is static because there is no net force or torque that would make it change its state of motion (i.e. accelerate).

In systems comprising many particles it is natural to generalize the notion of equilibrium so that it includes aggregate or "statistical" properties. Normally we are not interested in the motion of each individual particle in a gas or liquid. But we *do* care about such things as the density of particles or their average speed. More generally, we are interested in how microscopic quantities are *distributed* even if we don't care what the individual particles are doing. When these *distributions* are static (not the particles), we say the system is in "thermodynamic equilibrium".

The best way to understand this new kind of equilibrium is to consider examples of systems out-of-equilibrium and the processes that restore equilibrium.

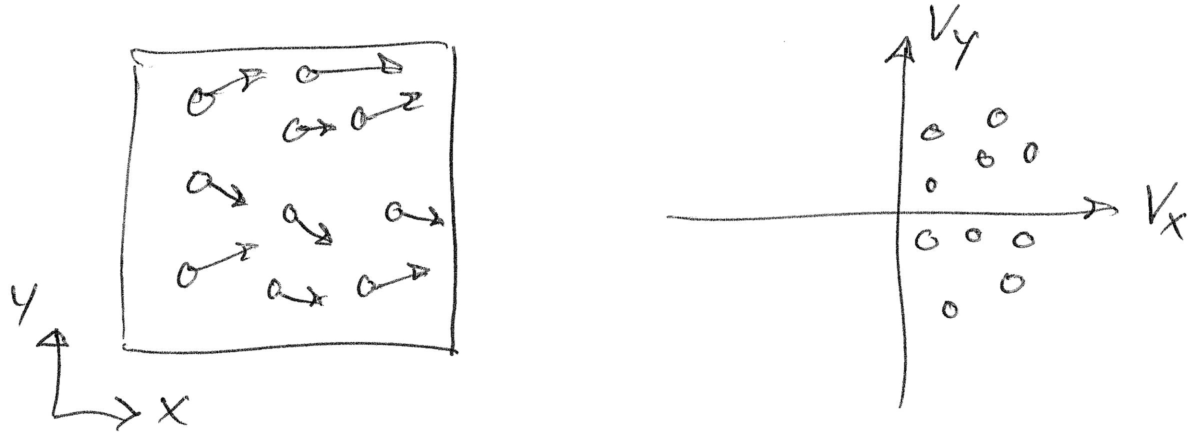
First consider a gas of many particles that starts out with a very non-uniform distribution in positions: all particles are in only one half of the "box" that contains them:





We'll avoid bias in the velocity distribution (arrows left, scatter plot right). After the particles have made several collisions with the walls and each other, we see [demo] that the distribution of positions is now very uniform in the box and the velocity distribution is still isotropic. This new "state" is apparently in thermodynamic equilibrium in that the uniformity does not go away — the distributions are static.

Next consider a gas where the positions start out very uniform but the velocities have a strong bias (drift):

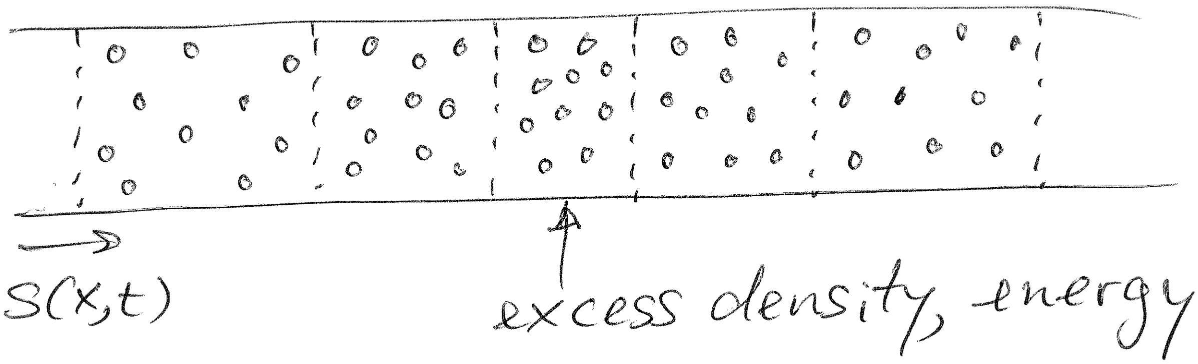


Again, we see [demo] over time that the random collisions restore the isotropic velocity distribution while keeping the positions uniform as well.

Finally, consider a gas in which there is a standing or running sound wave. In this system in thermodynamic equilibrium?

A gas with a sound wave is "near equilibrium", but not quite (we'll assume the sound amplitude is small). This is a good example for showing how equilibrium is restored, and we will estimate how long it takes.

Consider a sound wave in a cylinder of gas as we did previously:

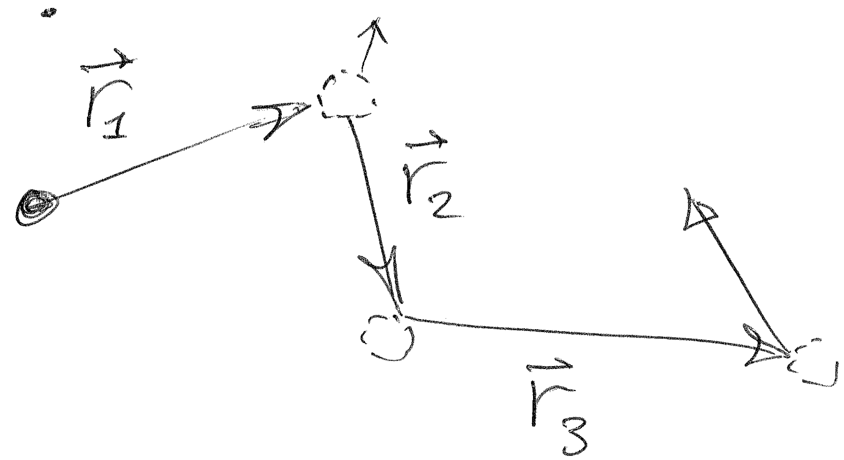


The density is slightly (for $s \ll \lambda$) non uniform, and so are the velocities (since $\dot{s}(x,t) \neq 0$). The non-uniformities evolve in a systematic, oscillatory manner much like a mechanical system. It is in this sense that we originally modeled sound waves.

However, there is a very different way in which the system can evolve which restores thermodynamic equilibrium, the uniform particle distribution with <u>no</u> <u>sound</u>.

This is a very general process that applies to any kind of inhomogeneity in a gas or liquid. The latter may be an excess in particle number or energy, or even concentration inhomogeneities when there is more than one particle type. The process whereby the inhomogeneity disappears is through the "random walk" motion of individual particles.

Consider one particle that has an excess energy. There are many such particles at the compression maximum of a sound wave. This particle will collide with others and either continue to carry some excess energy or transfer some excess energy to the particle it collides with. Either way, we see that excess energy is transported away by a sequence of <u>random</u> steps, each having length on the order of the mean-free-path. How far does the excess energy go after a certain number of steps?



$\vec{r}_i$ = i^{th} step of random walk

N steps:

$$\vec{R} = \vec{r}_1 + \vec{r}_2 + \cdots + \vec{r}_N$$

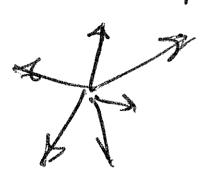
net distance squared:

$$D^2 = \vec{R} \cdot \vec{R} = (\vec{r}_1 + \cdots + \vec{r}_N) \cdot (\vec{r}_1 + \cdots + \vec{r}_N)$$

$$= \vec{r}_1 \cdot \vec{r}_1 + \cdots + \vec{r}_N \cdot \vec{r}_N$$

$$+ \underbrace{2\vec{r}_1 \cdot \vec{r}_2 + \cdots}_{\substack{N(N-1)/2 \\ \text{cross terms}}}$$

In a random walk the steps are

- isotropic 

- independent (uncorrelated)

We can rewrite the sum of the cross terms like this:

$$2\,\vec{r}_1\cdot\vec{r}_2+\cdots=N(N-1)\langle\vec{r}_i\cdot\vec{r}_j\rangle$$

where $\langle\ \rangle$ means "perform an average over different steps". The independence property implies

$$\langle\vec{r}_i\cdot\vec{r}_j\rangle=\langle\vec{r}_i\rangle\cdot\langle\vec{r}_j\rangle$$

and isotropy

$$\langle\vec{r}_i\rangle=0=\langle\vec{r}_j\rangle\ .$$

The squared distance therefore reduces to

$$D^2=N\langle\vec{r}_i\cdot\vec{r}_i\rangle=N\,l^2$$

where

$$l=\sqrt{\langle\vec{r}\cdot\vec{r}\rangle}$$

is the root-mean-square definition of the mean free path (step) distance.

We've thus determined (32.11) that in a gas or liquid the inhomogeneities are spread out a distance

$$D = \sqrt{N}\, l$$

after N steps. Let's put this in the context of a sound wave to understand its implications. As a mechanical system the energy inhomogeneity lasts on the order of one period of the sound wave, T. In this time ~~[illegible]~~ we normally do <u>not</u> want the random walk process to spread out the energy appreciably, since that is what sustains the wave. Clearly the wave is completely smoothed out

if the random walks (32.12)
transport energy over half of one wavelength (from max. to min. amplitude). We are therefore interested in the time required for this and how this compares with the period T :

Q = number of oscillations before "thermalization" (also called "quality factor")

$$= \frac{\left(\text{time for random walk to spread } D = \lambda/2\right)}{T}$$

$$= \frac{N_{therm} \cdot (\ell / v_p)}{T} \qquad v_p = \left(\text{particle speed}\right)$$

$$D = \frac{\lambda}{2} = \sqrt{N_{therm}} \cdot \ell$$

$$\Rightarrow \quad Q = \frac{(\lambda/2\ell)^2 \frac{\ell}{v_p}}{T} = \frac{1}{4} \frac{\lambda^2}{\ell v_p T}$$

Recall that $v_p \simeq v_s$ (sound speed, and $v_s T = \lambda$; hence:

$$Q = \frac{1}{4} \frac{\lambda}{\ell}$$

Echolocation in bats has evolved to a point that is close to a limit implied by this equation. Suppose a bat wants to bounce a sound pulse off a~~n~~ ~~the~~ ~~s~~ small insect 5m away. The pulse had better not damp out before it

has propagated 10 m (32.14)
(round trip). In Q oscillations (periods) the pulse will move a distance

$$d < Q\lambda = \frac{1}{4}\frac{\lambda^2}{l}$$

but not further, since it will have damped out. This puts a lower limit on the wavelength of sound the bat can use:

$$\lambda > 2\sqrt{dl}$$

$$d = 10\,m, \quad l = 10^{-7}\,m \Rightarrow \lambda > 2\,mm$$

A 2mm sound wave has frequency

$$f = \frac{340\ m/s}{2\times 10^{-3}\,m} = 170\ kHz$$

(Bats can hear up to 120 kHz!)