Lecture 13 - Thermal distributions

What's Important:
- phase space of non-interacting particles
- Maxwell-Boltzmann distribution

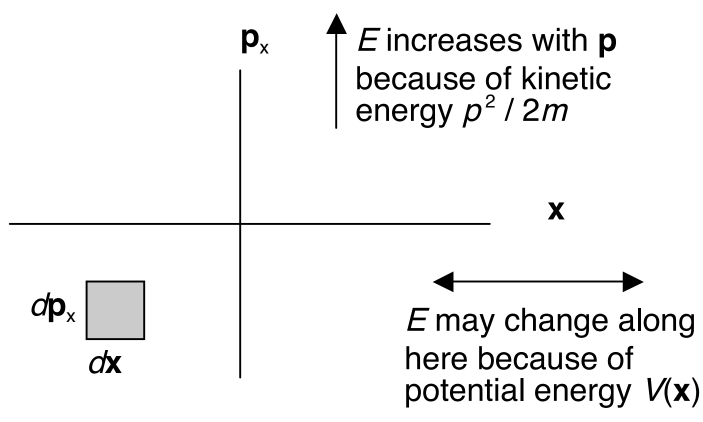
Text: Reif

Phase space of non-interacting particles

As particles interact with one another, even if only through hard core collisions, they exchange energy with each other and their environment. At any given time, there will be a distribution of energies, with few particles having either a very low or very high energy with respect to the energy scale $k_B T$ set by the temperature. In this lecture, we determine this distribution for a fixed number of particles N occupying an overall volume V, in contact with a heat reservoir at a temperature T (called the canonical ensemble). We ignore the spin of the particles (*i.e.* whether they are fermions or bosons) and take their speeds to be non-relativistic.

Now, the probability that a particle can be found within a specific range of position $d^3\mathbf{r}$ and momentum $d^3\mathbf{p}$ centered on specific values **r** and **p** depends on
(i) the size of the range $d^3\mathbf{r}\ d^3\mathbf{p}$
(ii) the energy (both kinetic and potential) at this value of **r** and **p**.

As established in statistical physics (see notes for PHYS 445), the likelihood that a specific state with a given energy $E(\mathbf{r},\mathbf{p})$ will be occupied is proportional to the Boltzmann factor $\exp(-E / k_B T)$. In one dimension, for potentials that do NOT depend on position, this means



Let's apply this idea to the translational motion of an ensemble of point-like particles of equal mass m in the absence of a potential energy bias $V(\mathbf{r})$. Rotational or vibrational motion is ignored. Including the Boltzmann factor, the distribution would look like

$$[\textit{probability of } \mathbf{r},\mathbf{p}]\ d^3r\, d^3p \propto \exp(-\beta E)\ d^3r\, d^3p, \tag{13.1}$$

where $\beta = 1/k_B T$.

Because **p** = *m***v** for non-relativistic particles, the distribution in velocity is proportional to the distribution in momentum, so that

$$[\textit{probability of } \mathbf{r},\mathbf{v}]\ d^3r\, d^3v \ \propto\ \exp(-\beta E)\ d^3r\, d^3v, \qquad (13.2)$$

To go from a probability density to a number density, one just multiplies by the total number of particles in the ensemble. Let's start our formal development by introducing the number density $f(\mathbf{r},\mathbf{v})$ as

$$f(\mathbf{r},\mathbf{v})\ d^3r\, d^3v = [\textit{mean number of particles in the range } \mathbf{r} \textit{ to } \mathbf{r}+d\mathbf{r} \text{ and } \mathbf{v} \textit{ to } \mathbf{v}+d\mathbf{v}],$$

where $f(\mathbf{r},\mathbf{v})$ is a number density in both position and velocity space - it has units of $[\textit{length}]^{-3} \cdot [\textit{velocity}]^{-3}$. From Eq. (13.2), $f(\mathbf{r},\mathbf{v})$ must be proportional to $\exp(-\beta mv^2/2)$, so we expect

$$f(\mathbf{r},\mathbf{v})\ d^3r\, d^3v = C\exp(-\beta mv^2/2)\ d^3r\, d^3v. \qquad (13.3)$$

The normalizing constant C can be obtained by integrating out $d^3r\, d^3v$

$$N = \iint..\int f(\mathbf{r},\mathbf{v})\ d^3r\, d^3v\,.$$

Replacing $f(\mathbf{r},\mathbf{v})$ by Eq. (13.3), the normalization condition reads

$$N = C\int d^3r \int \exp(-\beta mv^2/2) d^3v$$

$$= C\,V\left(\frac{2}{\beta m}\right)^{3/2} \int e^{-(a^2+b^2+c^2)} da\, db dc$$

Each of the $da\ db\ dc$ integrals has the form

$$\int_{-\infty}^{\infty} e^{-a^2} da = \sqrt{\pi}$$

(proof uses the square of the integral and changes variables to 2D polar coordinates) so that

$$N = C\,V\left(\frac{2\pi}{\beta m}\right)^{3/2}$$

or

$$C = \frac{N}{V}\left(\frac{\beta m}{2\pi}\right)^{3/2}, \qquad (13.4)$$

where the particle number density n is

$$n = N/V.$$

Substituting back into Eq. (13.3) we finally obtain

$$f(\mathbf{r},\mathbf{v})\, d^3r\, d^3v = n\left(\frac{\beta m}{2\pi}\right)^{3/2} \exp(-\beta mv^2/2)\, d^3r\, d^3v \qquad (13.5)$$

Note that βm has units of $[\textit{velocity}]^{-2}$ as required. There is no spatial dependence in the exponential on the right-hand side, so it is appropriate to divide out d^3r from the equation, leaving

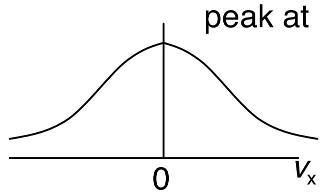
$$f(\mathbf{v})d^3v = n\left(\frac{\beta m}{2\pi}\right)^{3/2} \exp(-\beta m v^2 / 2)\, d^3v \qquad (13.6)$$

which is the *Maxwell-Boltzmann* distribution of velocities:

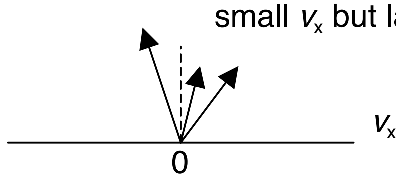
$f(\mathbf{v})\, d^3v$ = [*mean number of particles per unit volume between* **v** *and* **v**+*d***v**]

where $f(\mathbf{v})$ still has units of [*length*]$^{-3}$ • [*velocity*]$^{-3}$.

For a given component, the Gaussian function implies



This tells us that the most likely value of $\mathbf{v} = (v_x, v_y, v_z)$ is (0,0,0). However, just because a given component is peaked at $v_i = 0$ does not mean that the distribution in speeds |**v**| is peaked at $v = 0$. In a picture



To obtain the speed distribution, the volume element d^3v in velocity space must be transformed to polar coordinates:

$$dv_x\, dv_y\, dv_z = \sin\theta\, d\theta\, d\phi\, v^2 dv.$$

As $\exp(-\beta m v^2/2)$ has no angular dependence, we can obtain the distribution in speeds $F(v)$ by integrating over the angular components of the velocity:

$$F(v)\, dv = \iint f(\mathbf{v}) \sin\theta\, d\theta\, d\phi\, v^2 dv$$
$$= f(\mathbf{v})\, v^2\, dv \iint \sin\theta\, d\theta\, d\phi$$

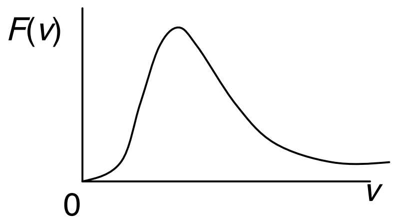
Now, the angular variables just yield 4π, as expected for the area of a sphere:

$$\int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi = \int_{-1}^{1} d\cos\theta \int_0^{2\pi} d\phi = 2 \bullet 2\pi = 4\pi$$

Thus

$$F(v)\, dv = 4\pi f(\mathbf{v})\, v^2\, dv.$$

The presence of the v^2 term indicates that the distribution in v is **NOT** centered at the origin, but rather looks like:



Mean speeds

Several quantities can be used to characterize this distribution, such as the mean, mean square, or most likely speed. We just work through the mean kinetic energy as an example of the mean square speed:

$$< K > = \frac{m}{2} < v^2 > = \frac{m}{2}\frac{1}{n}\int F(v) v^2 dv .$$

Substituting for $F(v)$

$$< K > = \frac{m}{2n} \bullet 4\pi n \left(\frac{\beta m}{2\pi}\right)^{3/2} \int \exp(-\beta m v^2 / 2) v^4 dv$$
$$= 2\pi m \left(\frac{\beta m}{2\pi}\right)^{3/2} \left(\frac{2}{\beta m}\right)^{5/2} \int \exp(-z^2) z^4 dz$$
$$= \frac{2^2}{\sqrt{\pi}} \frac{1}{\beta} \int \exp(-z^2) z^4 dz$$

The integral is given by

$$\int_0^\infty \exp(-z^2) z^4 dz = \frac{3}{8}\sqrt{\pi}$$

so the mean kinetic energy is

$$< K > = \frac{4}{\sqrt{\pi}} k_B T \frac{3}{8}\sqrt{\pi} = \frac{3}{2} k_B T .$$

This last result is an example of the *equipartition theorem*, which states that each mode of motion has an average energy of $k_B T/2$.