Lecture 17 - Ideal gas in detail

What's Important:

- phase space of non-interacting particles
- Maxwell-Boltzmann distribution

Text: Reif

Phase space of non-interacting particles

An ideal gas is one in which particles are essentially non-interacting because their number density is sufficiently low. Because of the energy scales involved, the rotational and vibrational motion of the gas particles can be separated from their translational motion, allowing the particles to be treated as point objects for the time being.

As introduced in an earlier lecture, the number of states Ω available for translational motion is proportional to the phase space volume

$$\Omega(E) \propto d^3r\, d^3p$$

for a single particle. In the canonical ensemble, each state E is weighted by $\exp(-\beta E)$, so the probability of a particle being in the phase space volume element $d^3r\, d^3p$ is just

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

or

$$P(\mathbf{r},\mathbf{p})\, d^3r\, d^3p \propto \exp(-\beta p^2/ 2m)\, d^3r\, d^3p \qquad (17.1)$$

the last relationship following because the energy is not position-dependent.

Letting the total number of particles in the system be N, the mean number of particles in phase space volume $d^3r\, d^3p$ is

$$NP(\mathbf{r},\mathbf{p})\, d^3r\, d^3p \propto N \exp(-\beta p^2/ 2m)\, d^3r\, d^3p. \qquad (17.2)$$

In many situations, the quantity of interest is not so much the momentum as the velocity, so we want to find

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

Clearly, $f(\mathbf{r},\mathbf{v})$ must be proportional to $\exp(-\beta mv^2/2)$, and we expect

$$f(\mathbf{r},\mathbf{v})\, d^3r\, d^3v = C \exp(-\beta mv^2/2)\, d^3r\, d^3v. \qquad (17.3)$$

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

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

Thus

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

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

Each of the *da db dc* integrals has the form

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

so that

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

or

$$C = \frac{N}{V}\left(\frac{\beta m}{2\pi}\right)^{3/2}, \qquad (17.4)$$

where the particle number density *n* is

$n = N/V$.

Substituting back into Eq. (17.3) we finally obtain

$$f(\mathbf{r},\mathbf{v})\, d^3r\, d^3v = n\left(\frac{\beta m}{2\pi}\right)^{3/2} \exp(-\beta m v^2/2)\, d^3r\, d^3v \qquad (17.5)$$

Clearly, 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

$$f(\mathbf{v})\, d^3v = n\left(\frac{\beta m}{2\pi}\right)^{3/2} \exp(-\beta m v^2/2)\, d^3v \qquad (17.6)$$

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

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

The distribution of the velocity components in a particular direction can be obtained from Eq. (17.6) by integration; for example

$g(v_x)\, dv_x$ = [*mean number of particles per unit volume between* v_x *and* v_x+dv_x]

$= dv_x \iint f(\mathbf{v})\, dv_y\, dv_z$.

Evaluating the integrals:

$$g(v_x)dv_x = n\left(\frac{\beta m}{2\pi}\right)^{3/2} \int \exp(-\beta m[v_x^2 + v_y^2 + v_z^2]/2)\, dv_y dv_z dv_x$$

$$= n\left(\frac{\beta m}{2\pi}\right)^{3/2} \exp(-\beta m v_x^2/2)\, dv_x \left[\int \exp(-\beta m x^2/2)\right]^2$$

The integral in the braces is

$$\int \exp(-\beta m x^2/2)dx = \left(\frac{2}{\beta m}\right)^{1/2} \int_{-\infty}^{\infty} \exp(-y^2)dy = \left(\frac{2\pi}{\beta m}\right)^{1/2}$$

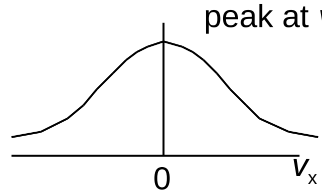
so that

$$g(v_x)dv_x = n\left(\frac{\beta m}{2\pi}\right)^{3/2}\left(\frac{2\pi}{\beta m}\right)^{\frac{1}{2}\cdot 2}\exp(-\beta m v_x^2/2)dv_x$$
$$= n\left(\frac{\beta m}{2\pi}\right)^{1/2}\exp(-\beta m v_x^2/2)dv_x \quad . \qquad (17.7)$$

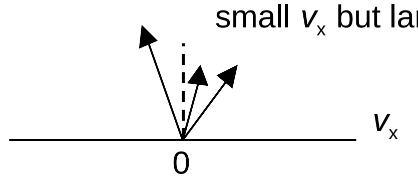
Comparing with Eq. (17.6), f/n is seen to factor into three equivalent distributions

$$\frac{f(\mathbf{v})}{n} = \left[\frac{g(v_x)}{n}\right]\left[\frac{g(v_y)}{n}\right]\left[\frac{g(v_z)}{n}\right] \qquad (17.8)$$

For a given component, the gaussian function implies



However, just because a given component is peaked at $v_i = 0$ does not mean that the distribution in speeds is peaked at $v = 0$.



To obtain the speed distribution, d^3v 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 write

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

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

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

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:


F(v)
0
v