Today

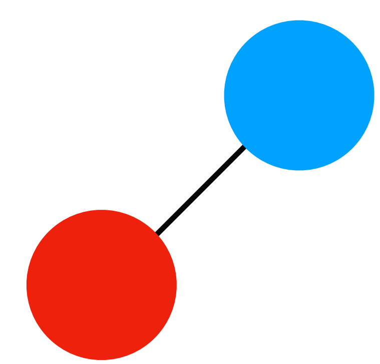
I. Last Time
II. Rotation of Diatomic Molecules and the Equipartition Theorem
III. The Maxwell-Boltzmann Speed Distribution

I. Last time we discussed a couple of examples of the canonical distribution. We found the partition functions for paramagnetism and for the rotational spectrum of a diatomic molecule.

The spectrum $E(j) = j(j+1)\epsilon$, which gave us a partition function

$$Z = \sum_s e^{-\beta j(j+1)\epsilon} = \sum_j (2j+1)e^{-\beta j(j+1)\epsilon} \approx \int_0^\infty (2j+1)e^{-\beta j(j+1)\epsilon} dj = \frac{kT}{\epsilon} \text{ when } kT \gg \epsilon \, .$$

$$\overline{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -(\beta\epsilon)\frac{-1}{\beta^2\epsilon} = kT. \ \ (\text{when } kT \gg \epsilon)$$



I. In the identical particle case there is the symmetry of interchanging the two molecules and the partition function is half as much:

$$Z \approx \frac{1}{2}\frac{kT}{\epsilon} \quad \text{(identical atoms in the } kT \gg \epsilon\text{).}$$

II. We're in good stead to prove the equipartition result. I'll do the proof for a single degree of freedom, but it's not hard to generalize to N degrees of freedom.

$$H(q,p) = E(q,p) = cq^2, \text{ where } c \text{ is constant.}$$

Let's imagine that the allowed q's are a discrete set, each separated by a spacing Δq. Then, the partition function is

$$Z = \sum_q e^{-\beta E(q)} = \sum_q e^{-c\beta q^2} = \frac{1}{\Delta q}\sum_q e^{-c\beta q^2}\Delta q \approx \frac{1}{\Delta q}\int_{-\infty}^{\infty} e^{-c\beta q^2} dq$$

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This is a gaussian integral

$$Z = \frac{1}{\Delta q} \sqrt{\frac{\pi}{c\beta}} = C\beta^{-1/2}.$$

The average contribution to the energy is then

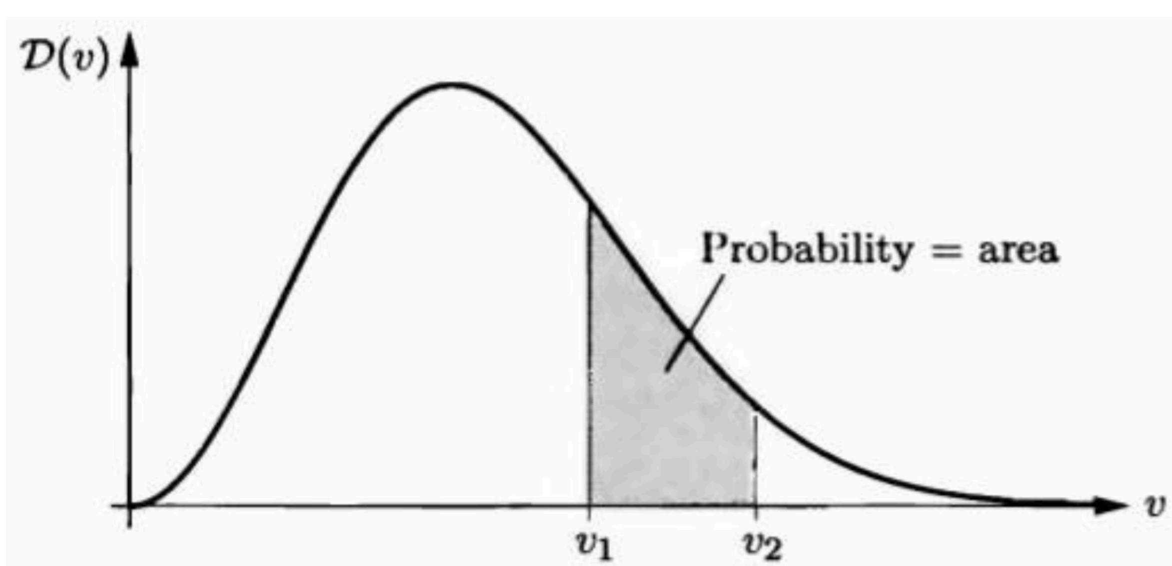
$$\overline{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{1}{C\beta^{-1/2}} \left(-\frac{1}{2} C\beta^{-3/2} \right) = \frac{1}{2}\beta^{1/2}\beta^{-3/2} = \frac{1}{2}kT.$$

Just as above, this holds in the limit where the states or closely spaced compared to kT (i.e. $kT \gg \epsilon$).

II. The Maxwell-Boltzmann speed distribution.

If you think about the gas in the room you are in, the various molecules have a huge variety of speeds. At this point we shift to asking probabilistic questions, for example, what's the probability of finding a molecule with a particular speed. To do this properly we need intervals of speeds and the notion of a probability distribution, and probability densities.

$\mathscr{D}(v)dv$=the probability of finding a molecule with speed between v and $v + dv$



II.$\mathscr{D}(v)dv$=the probability of finding a molecule with speed between v and $v + dv$. Let's try to find $\mathscr{D}(v)$: this is a bit tricky because velocity is a vector,

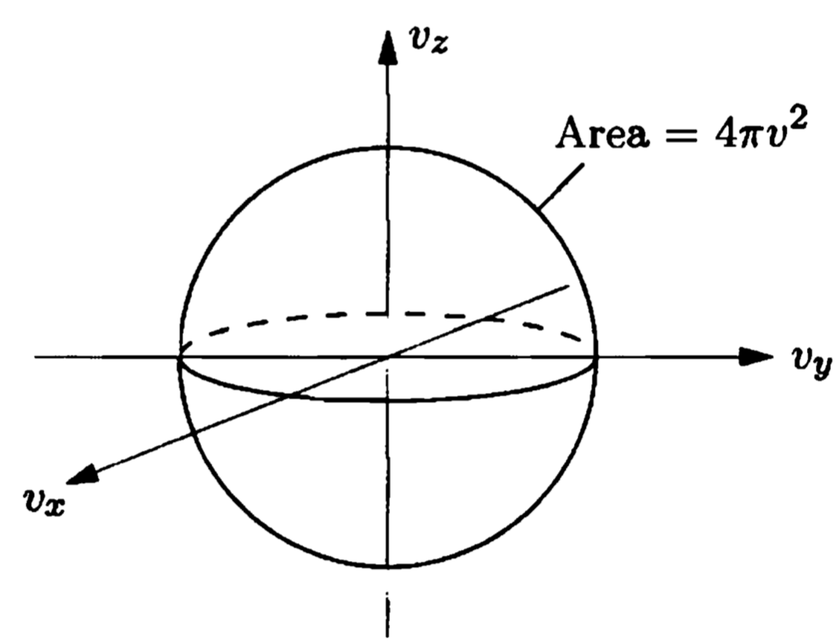
$$\mathscr{D}(v) \propto (prob.of vel.\overrightarrow{v}) \times (\#of vecs.\overrightarrow{v} giving v).$$

We know how to compute the first factor, the relative probability of a state is given by its Boltzmann factor:

$$\propto e^{-\beta(\frac{1}{2}mv^2)}.$$

To get the other factor we need to think about how many different velocities correspond to the same speed (and hence the same energy) The relative number of these is given by the area of the velocity space sphere with radius v, namely $4\pi v^2$. Then,

$\mathscr{D}(v) = C \cdot 4\pi v^2 e^{-mv^2/2kT}$



II. Then, $\mathscr{D}(v) = C \cdot 4\pi v^2 e^{-mv^2/2kT}$. We can normalized this distribution:

$$\int_0^\infty \mathscr{D}(v)dv = 4\pi C \int_0^\infty v^2 e^{-mv^2/2kT} dv = \frac{1}{2} 4\pi C \int_{-\infty}^\infty v^2 e^{-mv^2/2kT} dv = 1,$$

Carrying this out using the derivative of a gaussian trick gives

$$\boxed{\mathscr{D}(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 e^{-mv^2/2kT}.}$$