Thermal Physics - PH441 **John Waczak**
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Ideal Gas

Start with a big box with 1 atom in it. What are the possible eigenvalues of energy?

$$E = \frac{\hbar^2 k^2}{2m}$$

Our wavefunction only has kinetic energy and there are three degrees of freedom i.e. p_x, p_y, p_z. You get a choice of boundary conditions — if we stick this in a box we now have:

$$E_{n_x,n_y,n_z} = \frac{\hbar^2\pi^2(n_x^2+n_y^2+n_z^2)}{2mL^2}$$

Now we want to work out the partition function:

$$Z = \sum_{n_x}^{\infty}\sum_{n_y}^{\infty}\sum_{n_z}^{\infty} e^{-\beta\frac{\hbar^2\pi^2(n_x^2+n_y^2+n_z^2)}{2mL^2}}$$

This sucks... So lets take a statistical approximation for a REALLY big box. First though let's simplify... We got this by separation of variables in quantum mechanics. Let's try and do that again.

$$\begin{aligned}
\frac{\hbar^2\pi^2(n_x^2+n_y^2+n_z^2)}{2mL^2} &= \sum_{n_x}^{\infty} e^{-\beta\frac{\hbar^2\pi^2 n_x^2}{2mL^2}} \sum_{n_y}^{\infty} e^{-\beta\frac{\hbar^2\pi^2 n_y^2}{2mL^2}} \sum_{n_z}^{\infty} e^{-\beta\frac{\hbar^2\pi^2 n_z^2}{2mL^2}} \\
&= \Big(\sum_{n}^{\infty} e^{-\beta\frac{\hbar^2\pi^2 n^2}{2mL^2}}\Big)^3 \quad \text{same in each dimension} \\
\text{take:} \quad & \frac{\beta\pi^2}{2mL^2} << 1 \quad \text{as classical approximation}
\end{aligned}$$

So in this limit we expect that we can happily turn this sum into an integral for the limit given.

$$\begin{aligned}
&\approx \int_0^{\infty} e^{-\frac{\beta\hbar^2\pi^2}{2mL^2}n^2}\,dn \\
&\xi = \sqrt{\frac{\beta\hbar^2\pi^2}{2mL^2}}n \\
&\Rightarrow = \Big(\frac{2mL^2}{\beta\hbar^2\pi^2}\Big)^3\Big(\int_0^{\infty} e^{-\xi^2}d\xi\Big)^{3/2} = \Big(\frac{mL^2}{\beta\hbar^2 2\pi}\Big)^{3/2} \quad \text{handy integration trick for Gaussians}
\end{aligned}$$

Thus we conclude that:

$$Z = \Big(\frac{mkT}{2\hbar^2\pi}\Big)^{3/2}V = n_Q V \quad \text{quantum density}$$

Question: What are S, U, p?

$$
\begin{aligned}
F &= -kT\ln Z = -kT\ln\left(\left(\frac{mkT}{2\hbar^2\pi}\right)^{3/2}V\right)\\
p &= -\frac{\partial F}{\partial V} = \frac{kT}{V}\\
S &= -\frac{\partial F}{\partial T} = k\ln(n_Q V) + \frac{3}{2}k\\
U &= F + TS = \frac{3}{2}kT
\end{aligned}
$$