Lecture 28 (2-11), Mar 23, 2023

Ideal Gas (Sackur-Tetrode Formula)

- For a given U, how many microstates are there?
- $U = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} \implies \sum_{i=1}^{N} \vec{p}_i^2 = \sum_{i=1}^{N} p_{xi}^2 + p_{yi}^2 + p_{zi}^2 = 2mU$
  - How many ways can be distribute this momentum to get the same U?
  - We want the sum of the squares of $3N$ numbers to equal $2mU$
  - This is a sphere that lives in $3N$-dimensional space, or S^{3N-1} in $\mathbb{R}^{3N}$, with radius $r^2 = 2mU \implies r = \sqrt{2mU}$
- p_x, p_y, p_z are all quantized in units of $\frac{\pi\hbar}{L}$ (where $L^3 = V$), like in the case of the infinite square well; these points form a grid in space, the sphere will hit some of these grid points, and each hit is a microstate
  - We only need the sphere to be close to these grid points
  - We expect that the number of hits is proportional to the area of the sphere, proportional to r^{3N-1}, with r defined by the energy
- The area of a $3N-1$-dimensional sphere in $3N$ dimensions can be shown to be $\frac{2\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)} R^{3N-1}$
  - If $\frac{3N}{2}$ is an integer this is $\frac{2\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}-1\right)!}$
  - Therefore $\Omega(N,U) \sim \frac{2\pi^{\frac{3}{2}N}}{\left(\frac{3}{2}N-1\right)!}\left(\sqrt{2mU}\right)^{3N-1}$, but we have to fix it first:
    * The dimensions aren't consistent: to fix it, we divide $\sqrt{2mU}$ by a factor of $\frac{\pi\hbar}{L}$ first to make it unitless and make the units match
      - This basically converts the p_i to n_i
    * The n_i are always positive, so the p_i must all be positive; this means we have to reduce the surface area by a factor of 2 for every axis
      - e.g. for a circle, if we restrict it to $x, y > 0$, we have to divide by a factor of 4; for a sphere, restricting it to the first quadrant divides by a factor of 8
    * The particles should be indistinguishable according to quantum mechanics, which means that if we swap the momenta of two particles, it stays in the same microstate
      - There are $N!$ ways to permute the momenta, which all lead to identical microstates, so we have to reduce Ω by a factor of $N!$
      - This is called the Gibbs factor, which he derived before QM
  - $\Omega(N,U) = \frac{2\pi^{\frac{3}{2}N}}{N!\left(\frac{3}{2}N-1\right)!2^{3N}}\left(\frac{\sqrt{2mU}L}{\pi\hbar}\right)^{3N-1}$
- Now to find the entropy $S = k\ln\Omega$
  - First use Stirling's approximation, $N! = \left(\frac{N}{e}\right)^N$ and ignore the -1
  - Substitute $L = V^{\frac{1}{3}}$
  - $\Omega(N,U) = \frac{e^N}{N^N}\frac{2}{(2^3)^N}\frac{2(\pi^{\frac{3}{2}})^N(e^{\frac{3}{2}})^N}{(3^{\frac{3}{2}})^N(N^{\frac{3}{2}})^N}\frac{V^N}{(\pi\hbar)^{3N}}\left((2mU)^{\frac{3}{2}}\right)^N$

    $= \ldots$ I gave up ...
  - $S = k\ln\Omega$

    $$= k\ln 2 + kN\ln\left(\left(\left(\frac{4\pi mU}{N}\right)^{\frac{3}{2}}\frac{1}{(2\pi\hbar)^3}\frac{V}{N}\right) + \frac{5}{2}\right)$$

    $$= kN\ln\left(\left(\left(\frac{4\pi mU}{N}\right)^{\frac{3}{2}}\frac{1}{(2\pi\hbar)^3}\frac{V}{N}\right) + \frac{5}{2}\right)$$

    * This is known as the Sackur-Tetrode formula for the entropy of an ideal gas
  - Taking $\frac{1}{T} = \frac{\partial S}{\partial U} = Nk\frac{3}{2}\frac{1}{U} \implies U = \frac{3}{2}kNT$ which is the same as the one we got from equipartition
- What can we learn from this formula?
  - S is on the same order as kN
  - For all the extensive quantities, e.g. N, U, V, if we double them, the entropy also doubles
  - S increases with U, and levels off – this is a normal system, the temperature increases with energy and we have a positive heat capacity
  - If we lower U enough, then eventually the stuff inside the log will become less than 1, and we'll get a negative entropy, which is impossible – therefore this formula does not work for gases with very low energy