

Lecture 35 (2-18), Apr 10, 2023

Maxwell-Boltzmann Speed Distribution

- We will consider as our “system” one of the particles and the rest of the particles as the “thermostat”; for our “system”, what is $P(v)$, i.e. the probability density function of the speed?
- Applying the Boltzmann distribution gives us $P(v) dv = ce^{-\frac{E}{kT}} v^2 dv = ce^{-\frac{mv^2}{2kT}} v^2 dv$
 - $v^2 dv$ is the number of microstates that have speed in $[v, v + dv]$; this is proportional to the surface area of a sphere with radius v
 - The exponential term is the probability of each microstate with energy v
- After applying normalization, in 3D we get $P(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}}$
 - In 2D, the number of microstates with speed in $[v, v + dv]$ would be proportional to $v dv$, since it is now proportional to the circumference of a circle with radius v
 - * In 2D the function is linear near $v = 0$ and the peak is closer to 0
 - Note this distribution is for a classical gas, which breaks down as $v \rightarrow 0$
- $P(v)$ is maximum at $v^* = \sqrt{\frac{2kT}{m}}$
 - $\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{m}{2} \int_0^\infty P(v)v^2 dv$ works out to be $\frac{3}{2}kT$, which once again verifies equipartition

Intuition for the Partition Function

- Let the ground state have energy $E_0 = 0$, then $Z = \sum e^{-\frac{E}{kT}} = 1 + e^{-\frac{E_1}{kT}} + e^{-\frac{E_2}{kT}} + \dots$
- The partition function tells us roughly which states are important and which ones are not important at a given temperature; it “partitions” the microstates into significant ones and insignificant ones
- If $E \gg kT$, its contribution to Z will be very small, making them insignificant; they are *decoupled* from thermodynamics at the given temperature
 - Because Z determines F , the thermodynamic potential, which determines macroscopic properties, this means these states are unimportant to the macroscopic behaviour
- e.g. at room temperature $kT \approx 0.02\text{eV}$, which allows us to ignore excitations in the electronic and nuclear states, because they have energies that are significantly larger
 - This is why we only need to consider translational, rotational and vibrational energies and not electronic and nuclear structures

Equivalence of T, V, N and E, V, N Systems

- The Boltzmann distribution was derived with a different set-up, yet it still gives the same results in the case of the Einstein solid in the thermodynamic limit, if we use the average energy $\bar{E} = \langle E \rangle$
- We can show that in the TD limit, the two formulations will arrive at the same results
- The main difference is that for the Boltzmann distribution E varies, but E is constant for the multiplicity function approach
- We can find $\langle E \rangle$ as shown in the previous lecture and similarly $\langle E^2 \rangle$ and using this we can find $\frac{\sigma_E^2}{N}$;
this turns out to scale as $\frac{1}{\sqrt{N}}$
- In the thermodynamic limit with very large N , the variance of E becomes negligible compared to N , so the spread of energies is minimal and the average energy becomes functionally the same as the energy itself