Maxwell Distribution

Have learned that there are fluctuations in large number of particles

Can we use Stat Mech to calculate distribution of velocities. Yes, for a very dilute system.

Consider particle in 3D box

Wave function

$$\phi(x,y,z) = A sin\left(\left(\frac{n_1\pi}{L_x}\right)x\right) sin\left(\left(\frac{n_2\pi}{L_y}\right)y\right) sin\left(\left(\frac{n_3\pi}{L_z}\right)z\right)$$

n_1, n_2, n_3 integers

Energy $E = \frac{\hbar^2\pi^2}{2m}[n_1^2 + n_2^2 + n_3^2]$

Previously found partition function

$$Z = L_x L_y L_z \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}$$

Probability particle in energy state $\mathcal{E}_i$

$$p_i = \frac{e^{-\beta\varepsilon_i}}{Z}$$

For all N particles probability that $\mathcal{E}_i$ occurs is approximately

$$n_i = Np_i = N\frac{e^{-\beta\varepsilon_i}}{Z}$$

Ignoring possibility that two particles in same state. Very dilute.

Maxwell-Boltzmann Distribution

$$n_i = N\frac{e^{-\beta\varepsilon_i}}{Z}$$

To carry out calculations consider k-space

$$sin\left(\left(\frac{n_1\pi}{L_x}\right)x\right) = sin(k_x x) \quad \text{etc.}$$

$$k_x = \frac{n_1\pi}{L_x} \qquad k_y = \frac{n_1\pi}{L_x} \qquad k_z = \frac{n_1\pi}{L_z}$$

Each allowed state can be represented as a point in k-space with volume $\frac{\pi^3}{L_x L_y L_z}$

Density of points in k-space is then $\frac{V}{\pi^3}$

Number of points in small shell defined by polar co-ordinates, k, θ, φ

Is $dN = k^2 dk sin\theta d\theta d\varphi.\frac{V}{\pi^3}$

Integrate over θ, φ for a quadrant

$$dN = k^2\frac{V}{2\pi^2}dk$$

Density of states in 3D

$$D^{3D}(k)dk = k^2\frac{V}{2\pi^2}dk$$

$$D^{2D}(k)dk = k\frac{A}{2\pi}dk$$

$$D^{1D}(k)dk = k\frac{L}{\pi}dk$$

In energy space (where we usually work)

$$D^{3D}(E)dE = k^2\frac{V}{2\pi^2}\frac{dk}{dE}dE$$

For free particle $E = \frac{\hbar^2 k^2}{2m}$ $\quad \frac{\partial E}{\partial k} = \frac{\hbar^2 k}{m}$ $\quad$ Use $k = \left(\frac{2mE}{\hbar^2}\right)^{1/2}$

Find

$$D^{3D}(E)dE = \frac{Vm}{2\pi^2\hbar^3}(2mE)^{1/2}dE$$

Relativistic particle

$E = \hbar ck$ $\quad \frac{\partial E}{\partial k} = \hbar c$

$$D^{rel}(E)dE = \frac{VE^2}{2\pi^2\hbar^3 c^3}dE$$

Can now calculate interesting properties

Particles in classical gas

Probability state $\varepsilon(k)$ $p_k = \frac{e^{-\beta\varepsilon(k)}}{Z}$

For N particles number of particles in state $\varepsilon(k)$ is $n_k = Np_k$

Number of particles with $k < k' < k + dk$

Is $\quad f(k)dk = N\frac{e^{-\beta\varepsilon(k)}}{Z}D(k)dk = \frac{N\lambda_D^3}{2\pi^2}k^2 e^{-\beta\varepsilon(k)}$

Since velocity $u = \frac{\hbar k}{m}$ find

$$n(u)du = \frac{N\lambda_D^3 m^3}{2\pi^2\hbar^3} u^2 e^{-\frac{mu^2}{2k_BT}}$$

This is the Maxwell distribution for speeds

Can also calculate average wave vector

$$\bar{k} = \frac{\int_0^\infty f(k)kdk}{\int_0^\infty f(k)dk} = \frac{\int_0^\infty k^3 e^{-\frac{\hbar^2k^2}{2mk_BT}}dk}{\int_0^\infty k^2 e^{-\frac{\hbar^2k^2}{2mk_BT}}dk}$$

Or $\bar{k} = \sqrt{\frac{2mk_BT}{\hbar^2}} \int_0^\infty x^3 e^{-x^2}dx / \int_0^\infty x^2 e^{-x^2}dx = \sqrt{\frac{8mk_BT}{\pi\hbar^2}}$

Mean speed $\bar{u} = \frac{\hbar\bar{k}}{m} = \sqrt{\frac{8k_BT}{\pi m}}$

Also

$$\overline{k^2} = \frac{\int_0^\infty f(k)k^2dk}{\int_0^\infty f(k)dk} = \frac{\int_0^\infty k^4 e^{-\frac{\hbar^2k^2}{2mk_BT}}dk}{\int_0^\infty k^2 e^{-\frac{\hbar^2k^2}{2mk_BT}}dk}$$

$$\overline{k^2} = \left(\frac{2mk_BT}{\hbar^2}\right)\int_0^\infty x^4 e^{-x^2}dx \Big/ \int_0^\infty x^2 e^{-x^2}dx = \frac{3mk_BT}{\hbar^2}$$

Find $\overline{u^2} = \frac{3k_BT}{m}$ or average kinetic energy

$$E = \frac{3}{2}k_BT$$

Problems

Chap.7

7.6

Relativistic particle

$E^2 = p^2c^2 + m^2c^4$ High p $E \cong pc = \hbar kc$ $\frac{\partial E}{\partial xk} = \hbar c$

Density of states $D(E) = \frac{V}{2\pi^2}\frac{k^2}{\left(\frac{\partial E}{\partial k}\right)} = \frac{V}{2\pi^2}\frac{k^2}{\hbar \mathrm{c}} = \frac{V}{2\pi^2}\frac{E^2}{\hbar \mathrm{c}^3}$

For one particle partition function

$$Z_1 = \int e^{-\beta E} D(E) dE$$

$$Z_1 = \int \frac{V}{2\pi^2}\frac{(\beta E)^2}{\hbar \mathrm{c}^3} e^{-\beta E} d(\beta E)\beta^{-3} = \frac{V}{2\pi^2}\left(\frac{k_B T}{\hbar c}\right)^3 \int_0^\infty e^{-x} x^2 dx$$

Find $Z_1 = \frac{V}{\pi^2}\left(\frac{k_B T}{\hbar c}\right)^3$

For N particles $Z_N = \left[\frac{V}{\pi^2}\left(\frac{k_B T}{\hbar c}\right)^3\right]^N / N!$