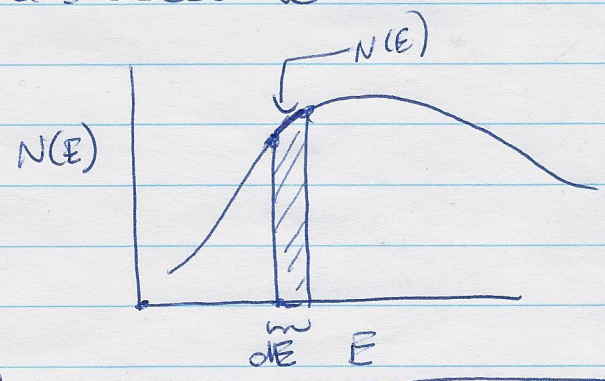


The Dist'n fun of an Ideal Gas

assume $f=3$, i.e. a monatomic gas so that only translational motions are relevant.

want: $N(E)$

a small element is $dN(E) = N(E) dE$



The total # of particles would be $N = \int dN(E) = \int N(E) dE$

$dN(E) = \# \text{ of particles with energies between } E \text{ and } E+dE$
$\frac{g_E}{z} e^{-E/kT}$

for a discrete case, we had $\frac{N_i}{N} = \frac{g_i}{z} e^{-E_i/kT}$ where i refers to the energy level and g_i is the degeneracy of that level.

For a continuous distribution, then (statistical wt)

$$\frac{N(E)}{N} = \frac{g_E}{z} e^{-E/kT} \quad (\text{the statistical wt can change with } E)$$

so $dN(E) = \frac{dg_E}{z} e^{-E/kT}$ ① for a fixed T , there is a range of E .

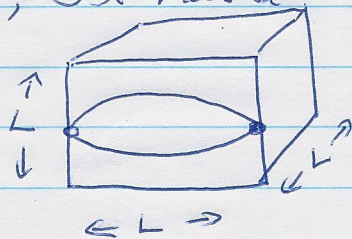
The next goal is to find expressions for dg_E and z in terms of E

Let's start with dg_E

dg_E we want to know how many states are available for a given E (between E & $E+dE$)

Consider a particle inside a box, It has a de Broglie wavelength, λ , \exists

$$p = \frac{h}{\lambda}$$



what is the smallest box

size, L , that can contain a particle? $L = n \frac{\lambda}{2}$
 (Recall our early development of Kinetic Theory. we considered a box size \exists a particle hit a wall and made it back to the other side again)

In 1-Dimension;

$$p = \frac{nh}{2L}$$

n an integer, i.e. a "quantum #" for free space

In 3-D:

SEE FIGURE

$$p^2 = p_x^2 + p_y^2 + p_z^2 = (n_x^2 + n_y^2 + n_z^2) \left(\frac{h}{2L}\right)^2$$

For translational motion only:

$$E = \frac{1}{2} m v^2 = \frac{1}{2} \frac{p^2}{m} = \frac{1}{2} \frac{(n_x^2 + n_y^2 + n_z^2)}{m} \left(\frac{h}{2L}\right)^2 = \frac{n^2 h^2}{8m L^2}$$

where $n^2 = n_x^2 + n_y^2 + n_z^2$

$$\therefore n = \frac{L}{h} (8mE)^{1/2} \quad \text{and} \quad dr = \frac{L}{h} (8m)^{1/2} \frac{1}{2} E^{-1/2} dE$$

what is the volume in "state space"?

$$dg_E = \frac{1}{8} (4\pi r^2) dr = \frac{1}{8} (4\pi) \left[\frac{L^2}{h^2} (8mE) \right] \left[\frac{L}{h} (8m)^{1/2} \frac{1}{2} E^{-1/2} dE \right]$$

$n_x, n_y, n_z \geq 0$ so looking at one octant only

$$= \frac{2\pi V}{h^3} (2m)^{3/2} E^{1/2} dE \quad V = L^3$$

3

Now let's consider the partition for Z

I will write Z_{tr} to indicate that I am considering the partition function for translational states only. For discrete energy states, i ,

$Z_{tr} = \sum_i e^{-E_i/kT}$ but from Eqn (2), $E = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$

So $Z_{tr} = \left[\int e^{-\frac{h^2 n_x^2}{8mkTL^2}} dn_x \right] \left[\int e^{-\frac{h^2 n_y^2}{8mkTL^2}} dn_y \right] \left[\int e^{-\frac{h^2 n_z^2}{8mkTL^2}} dn_z \right]$

Now carry out the integration, noting that $\int_0^\infty e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}}$

to find $Z_{tr} = V \left(\frac{2\pi mkT}{h^2} \right)^{3/2}$ (4) let $v_q = \left(\frac{h^2}{2\pi mkT} \right)^{3/2}$ be the "quantum volume"

then $Z_{tr} = V/v_q$ see also eq'n 6.82, 6.83 text For a given T, v_q is the smallest volume that can contain a particle

We now have both dg_E (eqn 3) and Z (eqn 4), so can return to Eqn (1)

$dN(E) = \frac{N dg_E}{Z} e^{-E/kT} = N \frac{2}{\pi^{1/2} (kT)^{3/2}} E^{1/2} e^{-E/kT} dE$ Dist'n fun in KE
particles between E and E+dE

noting that $E = \frac{1}{2} m v^2$ we can change to v

$dN(v) = N \left(\frac{m}{2\pi kT} \right)^{3/2} 4\pi v^2 e^{-\frac{1}{2} m v^2 / kT} dv$ Maxwell-Boltzmann vel. dist'n

of particles between v and v+dv

where $\int dN(v) = N$

cf. eq'n 6.50, Fig 6.13 text