

$\Omega(E, V, N) \equiv$  Volume of available phase space.

The micro-state  $\mu = \{\vec{r}_i, \vec{p}_i\}$  of an  $N$ -particle gas is just a single point in  $6N$ -dimensional phase space.

If interactions are absent, we can write the Hamiltonian as

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i=1}^N U(\vec{q}_i)$$

'Kinetic energy'

'Box potential due to field'

The joint PDF in this micro-canonical ensemble is:

$$p(\mu) = \frac{1}{\Omega(E, V, N)}, \quad E - \Delta E \leq \sum_{i=1}^N \frac{p_i^2}{2m} \leq E + \Delta E \text{ \& } \vec{q}_i \in \text{box}$$

$= 0$ , otherwise.

While particle positions could be anywhere inside the box, the allowed momenta must be within the hyper-spherical shell of thickness  $\Delta_R$ .

$$\text{where } \Delta_R = (2m)^{1/2} \left\{ (E + \Delta E)^{1/2} - (E - \Delta E)^{1/2} \right\}$$

$$\approx (2m/E)^{1/2} \Delta E$$

, Taylor expanding  $f(E) = \sqrt{E}$  to 1<sup>st</sup> order.

$$\text{--- (1) } \left[ \begin{aligned} f(E + \Delta E) &= \sqrt{E + \Delta E} \\ &= (E)^{1/2} + \frac{\Delta E}{2\sqrt{E}} + O(\Delta E^2) \end{aligned} \right]$$

The allowed phase space is thus

$$\Omega(E, V, N) = \int \dots \int d^3\vec{q}_1 \dots d^3\vec{q}_N d^3\vec{p}_1 \dots d^3\vec{p}_N = V^N \Omega_p \quad \text{--- (2)}$$

where  $\Omega_p = \int \dots \int d^3\vec{p}_1 \dots d^3\vec{p}_N$

Now  $\Omega_p$  is the volume in momentum space of a hyper-spherical shell of thickness  $\Delta_R = \sqrt{2m/E} \Delta E$ .

We can thus write  $\Omega_p$  as :

$$\Omega_p = A_{3N} \Delta_R \quad \text{--- (3)}$$

where  $A_{3N} \equiv$  Area of the  $3N$ -dimensional hyper sphere of radius  $R = \sqrt{2mE}$

We write for  $A_{3N} = S_{3N} R^{3N-1}$  --- (4)

where  $S_{3N}$  is the  $3N$ -dimensional solid angle.

{ for eg. if  $N=1$ , the 3-dimensional surface area becomes :  $A_3 = S_3 R^2$  with  $S_3 = 4\pi$  }

We will now calculate  $S_{3N}$  :

Consider the product of  $3N$  Gaussian integrals.

$$I_{3N} = \left( \int_{-\infty}^{+\infty} dx e^{-x^2} \right)^{3N} = \pi^{3N/2} \quad \text{--- (5)} \quad \because \int_{-\infty}^{+\infty} dx e^{-x^2} = \sqrt{\pi}$$

Alternatively, we may write

$$I_{3N} = \int_{i=1}^{3N} \prod dx_i e^{-x_i^2} = \int_{i=1}^{3N} \prod dx_i e^{-\sum_{j=1}^{3N} x_j^2}$$

Substituting for  $\sum_{j=1}^{3N} x_j^2 = R^2$

and the volume element  $\prod_{i=1}^{3N} dx_i = \underbrace{A_{3N}}_{\text{Area}} \underbrace{dR}_{\text{thickness}}$

$$\therefore I_{3N} = \int_0^{\infty} dR A_{3N} e^{-R^2} = \int_0^{\infty} dR S_{3N} R^{3N-1} e^{-R^2} \dots \text{from (4)}$$

change of variables:  $R^2 = y \Rightarrow 2R dR = dy$

$$\therefore I_{3N} = \frac{S_{3N}}{2} \int_0^{\infty} dy y^{(3N/2-1)} e^{-y} = \frac{S_{3N}}{2} \left(\frac{3N}{2}-1\right)! \quad \text{--- (5)}$$

Comparing (5) & (6), we get:

$$S_{3N} = \frac{2 \pi^{3N/2}}{(3N/2-1)!} \quad \text{--- (7)}$$

Now combining (2), (3), (4), (5), (6) & (7), we get.

$$\Omega(E, V, N) = V^N \frac{2 \pi^{3N/2}}{(3N/2-1)!} (2mE)^{(3N-1)/2} A_R \quad \text{--- (8)}$$

The entropy is thus obtained as below

$$S(E, V, N) = k_B \left[ N \ln V + \frac{3N}{2} \ln(2\pi m E) - \frac{3N}{2} \ln\left(\frac{3N}{2}\right) + \frac{3N}{2} \right]$$
$$= N k_B \ln \left[ V \left( \frac{4\pi m E}{3N} \right)^{3/2} \right]$$

Properties of the ideal gas can be recovered from

$$T ds = dE + P dv - \mu dN$$

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{N, V} = \frac{3}{2} \frac{N k_B}{E}$$

$\therefore$  the internal energy  $E = \left(\frac{3}{2}\right) N k_B T$  is only a function of  $T$ .

The heat capacity is thus

$$C = \left( \frac{\partial E}{\partial T} \right) = \frac{3}{2} N k_B$$

The equation of state is obtained from

$$\frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{N, E} = \frac{N k_B}{V}$$

$\therefore PV = N k_B T$  Ideal gas law.