1. <u>The System</u>

Fixed:

- E
- V
- N
- $\vec{M}$ or $\vec{H}$
- $\vec{\mathcal{P}}$ or $\vec{\mathcal{E}}$

E < energy < $E+\Delta$

$\Delta \ll E$

A complete set of independent thermodynamic variables is fixed.

Many micro-states satisfy the conditions.

2. Probability Density

All accessible microscopic states are equally probable.

Classical

$$
\begin{aligned}
p(\{p,q\}) &= 1/\Omega \qquad E < \mathcal{H}(\{p,q\}) \le E + \Delta \\
&= 0 \qquad \text{elsewhere}
\end{aligned}
$$

$$\Omega \equiv \int_{\text{accessible}} \{dp, dq\} = \Omega(E, V, N)$$

Quantum

$$p(k) = 1/\Omega \qquad E < \langle k|\mathcal{H}|k\rangle \leq E + \Delta$$

$$= 0 \qquad \text{elsewhere}$$

$$\Omega \equiv \sum_{k,\ \text{accessible}} (1) = \Omega(E, V, N)$$

Let X be a state of the system specified by a subset { p'' ,q'' } of { p,q}

$$\begin{aligned}
p(X) &= \int_{\text{except } \{p'',q''\}} p(\{p,q\})\,\{dp,dq\} \\
&= \frac{1}{\Omega}\int_{\text{except } \{p'',q''\}} \{dp,dq\} \\
&= \frac{\Omega'(\text{consistent with } X)}{\Omega} \\
&= \frac{\text{volume consistent with } X}{\text{total volume of accessible phase space}}
\end{aligned}$$

3. Quantities Related to Ω

$$\Phi(E,V,N) \equiv \int_{\mathcal{H}(\{p,q\})<E} \{dp,dq\}$$
$$= \text{cumulative volume in phase space}$$

$$\omega(E,V,N) \equiv \frac{\partial \Phi(E,V,N)}{\partial E}$$
$$= \text{density of states as a function of energy}$$

$$\Rightarrow \Omega(E,V,N) = \omega(E,V,N)\Delta$$

Example Ideal Monatomic Gas

$q_i = x, y, z$ in a box $V = L_x L_y L_z$

$p_i = m\dot{x}, m\dot{y}, m\dot{z}$ $-\infty < p_i < \infty$

N atoms $\mathcal{H}(\{p, q\}) = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$

$$
\begin{aligned}
\Omega &= \int \{dp, dq\} = \int \{dq\} \int \{dp\} \\
&= \left[\int_0^{L_x} dx\right]^N \left[\int_0^{L_y} dy\right]^N \left[\int_0^{L_z} dz\right]^N \int \{dp\} \\
&= V^N \int_{E<\mathcal{H}<E+\Delta} \{dp\}
\end{aligned}
$$

$$
\Phi(E, V, N) = V^N \int_{\mathcal{H}<E} \{dp\}
$$

$$E = \sum_{i=1}^{3N} \frac{p_i^2}{2m} \quad \Rightarrow \quad 2mE = \sum_{i=1}^{3N} p_i^2$$

This describes a $3N$ dimensional spherical surface in the p part of phase space with a radius $R = \sqrt{2mE}$.

Math:

- Volume of an α dimensional sphere of radius R is

$$\frac{\pi^{\alpha/2}}{(\alpha/2)!}R^{\alpha}$$

- Sterling's approximation for large M

$$\ln(M!) \approx M \ln M - M$$

$$\rightarrow M! \approx \left(\frac{M}{e}\right)^{M}$$

$$\Phi(E,N,V) = V^N \frac{\pi^{3N/2}}{(3N/2)!}(2mE)^{3N/2}$$

$$\approx \left\{ V^N \left(\frac{4\pi emE}{3N}\right)^{3N/2} \right\}$$

$$\omega(E,N,V) = \left(\frac{3N}{2}\,\frac{1}{E}\right)\{\quad\}$$

$$\Omega(E,N,V) = \left(\frac{3N}{2}\,\frac{\Delta}{E}\right)\{\quad\}$$

$$p(x_i) = \frac{\Omega'}{\Omega} = \frac{V^{N-1}L_yL_z}{V^N} = \frac{1}{L_x} \qquad 0 \leq x < L_x$$

$$p(x_i, y_j) = \frac{\Omega'}{\Omega} = \frac{V^{N-2}L_yL_zL_xL_z}{V^N} = \frac{1}{L_xL_y} = p(x_i)p(y_j) \Rightarrow \text{S.I.}$$

$$p(p_{x_i}) = \int \underbrace{p(\{p,q\})}_{1/\Omega}\{\underbrace{dp}_{p \neq p_{x_i}}, dq\} = \frac{\Omega'}{\Omega}$$

Note that Ω' differs on each of the three lines, being a generic symbol for the reduced phase volume consistent with some constraint.

$\epsilon \equiv p_x^2/2m$ $\qquad$ $E - \epsilon$ distributed over other variables

$$\Omega' = \left(\frac{3N-1}{2}\,\frac{\Delta}{E-\epsilon}\right) V^N \left(\frac{4\pi e m (E-\epsilon)}{3N-1}\right)^{(3N-1)/2}$$

$$\frac{\Omega'}{\Omega} = \underbrace{\left(\frac{3N-1}{3N}\right)}_{\approx 1} \underbrace{\left(\frac{E}{E-\epsilon}\right)}_{\approx 1} \left(\frac{4\pi e m}{3}\right)^{-1/2}$$

$$\times \quad \underbrace{\left(\frac{(N-\frac{1}{3})^{-\frac{3N}{2}+\frac{1}{2}}}{N^{-\frac{3N}{2}}}\right)}_{A} \quad \underbrace{\left(\frac{(E-\epsilon)^{\frac{3N}{2}-\frac{1}{2}}}{E^{\frac{3N}{2}}}\right)}_{B}$$

$$A = \sqrt{N - \frac{1}{3}}\ \left(1 - \frac{1}{3N}\right)^{-\frac{3N}{2}} = \sqrt{N - \frac{1}{3}}\ \left(1 + \frac{1/2}{-3N/2}\right)^{-\frac{3N}{2}}$$

but $\quad \lim_{\zeta\to\infty}\left(1 + \frac{x}{\zeta}\right)^{\zeta} = e^x$

so $A \approx \sqrt{N}\ e^{1/2}$

$$B = \frac{1}{\sqrt{E-\epsilon}} \;\left(1 - \frac{\epsilon}{E}\right)^{\frac{3N}{2}} = \frac{1}{\sqrt{E-\epsilon}} \;\left(1 - \frac{\frac{1}{2}\epsilon/ < \epsilon >}{3N/2}\right)^{\frac{3N}{2}}$$

where we have used $< \epsilon > \equiv E/3N$ and $E = 3N < \epsilon >$.

so $B \approx \frac{1}{\sqrt{3N{<}\epsilon{>}}}\; e^{-\epsilon/2<\epsilon>}$

$$p(p_x) \; = \; \left(\frac{\sqrt{3}}{\sqrt{4\pi m}} \; e^{-1/2} \right) \left(\sqrt{N} \, e^{1/2} \right) \frac{1}{\sqrt{3N < \epsilon >}} \; e^{-\epsilon/2<\epsilon>}$$

$$= \; \frac{1}{\sqrt{4\pi m < \epsilon >}} \; e^{-\epsilon/2<\epsilon>}$$

Now use $\epsilon = p_x^2/2m$ and $< \epsilon > = < p_x^2 > /2m$.

$$p(p_x) = \frac{1}{\sqrt{2\pi < p_x^2 >}} \; e^{-p_x^2/2<p_x^2>}$$