η : # of systems in the same ensemble

We can also use the ensemble approach:

$$E = \sum_j n_j E_j \quad ; \; \underline{n_j = \text{\# of systems w/ energy } E_j}$$

The total # of systems in the ensemble is $\eta = \sum_j n_j$

(# possible configs in the ensemble) $\Omega_{\{n_j\}} = \dfrac{\eta!}{\prod_j n_j!}$; The total number of possible configurations is

$$\Omega(E, \eta, V, N) = \sum_{\{n_j\}} \Omega_{\{n_j\}}$$

We can now calculate the thermodynamics by finding $S = k_B \ln \Omega$.

However the behavior will be dominated by that $\{n_j\}$ that gives the biggest contribution to $\sum_j \Omega(\{n_j\})$

We propose to Maximize $\Omega(\{n_j\})$ over all variations of the n_j's with the constraints

$$\sum_j n_j = \eta \quad \text{and} \quad \sum_j n_j E_j = E$$

We use Lagrange Multipliers to do this.

Consider $\ln \Omega_{\{n_j\}} - \alpha \sum_j n_j - \beta \sum_j n_j E_j$

α, β = Lagrange multipliers.

$$\delta\left[\ln\Omega - \alpha\sum n_j - \beta\sum n_j E_j\right] = 0$$

$$\ln\Omega = \eta\ln\eta - \eta - \sum_j (n_j \ln n_j - n_j)$$

$$\therefore \delta[\,] = \sum_j \left(-\ln n_j\,\delta n_j + \cancel{\delta n_j} - \alpha\,\delta n_j - \cancel{\delta n_j} - \beta E_j\,\delta n_j\right) = 0$$

$$\sum_j \left(\ln n_j + \alpha + \beta\right)\delta n_j = 0$$

$\therefore$ we require $n_j = e^{-\alpha} e^{-\beta E_j}$

but $\sum_j n_j = \eta = e^{-\alpha}\sum_j e^{-\beta E_j}$

and $\sum_j E_j n_j = E = e^{-\alpha}\sum_j E_j e^{-\beta E_j}$

$$\therefore\ U = \frac{E}{\eta} = \text{Average Energy per system} = \frac{\sum_j E_j e^{-\beta E_j}}{\sum_j e^{-\beta E_j}}$$

We identify β through the average entropy per subsystem,

$$S = \frac{k}{\eta}\ln\Omega_{max} = \frac{k_B}{\eta}\left\{\eta\ln\eta - \eta - \sum_j \left(n_j \ln n_j - n_j\right)\right\}$$

$$\sum_j n_j = \eta$$

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$$\therefore S = \frac{k}{\eta}\left\{\eta \ln \eta - \sum_j e^{-\alpha} e^{-\beta E_j}\left(-\beta E_j - \alpha\right)\right\}$$

recall $e^{-\alpha} = \eta \Big/ \sum_j e^{-\beta E_j} \equiv \eta / Z$

$$\therefore S = \frac{k}{\eta}\left\{\eta \ln \eta - \frac{\eta}{Z}\left[\sum_j e^{-\beta E_j}\left[-\beta E_j + \ln \frac{\eta}{Z}\right]\right]\right\}$$

$$= \frac{k}{\eta}\left\{\cancel{\eta \ln \eta} + \beta \eta U - \cancel{\eta \ln \eta} + \eta \ln Z\right\}$$

$S = k\beta U + k \ln Z$; since Z only depends on E_j and β (NOT U)

$$\left.\frac{\partial S}{\partial U}\right|_{V,N} = \frac{1}{T} = k\beta \quad \text{or} \quad \boxed{\beta = \frac{1}{kT}} \quad \text{consistant!}$$

Probability that any member of ensemble is in microstate w/ Energy E_j

$$\frac{n_j}{\eta} = P_j = \frac{e^{-\beta E_j}}{Z}$$

probability that any member of the ensemble w/ Energy E_j

$$\therefore S = -k \sum_j P_j \ln P_j$$

Shannon Entropy!

$k\beta U + k \ln Z = k\beta \sum_j \frac{e^{-\beta E_j}}{Z} E_j + k \ln Z = k \ln Z + \frac{k\beta}{\beta} \sum_j P_j\left(-\ln P_j - \ln Z\right)$
$= -k \sum P_j \ln P_j$

This is also true for Microcanonical formalism

$$P_j = \frac{1}{\Omega} \quad \text{(Each microstate is equally probable)}$$

$$S = -k \sum_j P_j \ln P_j = -k \sum \frac{1}{\Omega} \ln \frac{1}{\Omega}$$

$$S = +k \ln \Omega$$

$\Rightarrow$ "Shannon Entropy" is more fundamental than than thermodynamics.

More on Information theory later!

Applications of the Canonical Partition function:

Consider Non-interacting system of identical constituents.

$$\hat{H} = \sum_{i=1}^{N} \hat{H}_i$$

$$Q_N = \mathrm{Tr}\, e^{-\beta \hat{H}} = \mathrm{Tr}\, e^{-\sum_i \beta H_i} = \prod_i \mathrm{Tr}\, e^{-\beta H_i}$$

$$\therefore Q_N = [Q_1]^N$$

For the ideal gas

$$Q_N = \frac{1}{N!}\frac{1}{h^{3N}}\int \prod_i d\vec{q}_i d\vec{p}_i \; e^{-\beta H}$$

$$Q_N = \frac{1}{N!} Q_1^N ; \quad Q_1 = \int \frac{d\vec{p}_i d\vec{q}_i}{h^3} e^{-\beta H^{(1)}(p_i, q_i)}$$

$$Q_1 = \frac{V}{h^3}\int d^3p \, e^{-\beta p^2/2m} = \frac{V}{h^3}\left(2\pi m k_B T\right)^{3/2}$$

$$\therefore Q_N = \frac{1}{N!}\left(\frac{V}{h^3}\right)^{3N}\left(2\pi m k T\right)^{3N/2}$$

$$A = -kT \ln Q_N \simeq -kTN\left[1 + \ln\left[\frac{V}{h^3 N}\left(2\pi m k T\right)^{3/2}\right]\right]$$

U, S, C_v, etc. follow from thermo.

Consider an average of $\mathbb{F}(q, p)$,

$$\langle \mathbb{F} \rangle = \frac{\frac{1}{N!}\int \frac{d^{3N}p \, d^{3N}q}{h^{3N}} \mathbb{F}(q,p) \, e^{-\beta H(q,p)}}{\int \frac{d^{3N}p \, d^{3N}q}{h^{3N} N!} e^{-\beta H(p,q)}} \equiv \int \rho \, \mathbb{F} \, d\Gamma$$

$$\left(d\Gamma = \frac{d^{3N}p \, d^{3N}q}{h^{3N}} \right)$$

$\Rightarrow$ the density of particles is

$$\rho(p,q) = e^{-\beta H(q,p)} \Big/ \int d^{3N}p \, d^{3N}q \, e^{-\beta H(p,q)}$$

Recall

$$Q_N(\beta) = \int \frac{dE}{\Delta}\, \Omega(E)\, e^{-\beta E}$$

Q_N is Laplace transform of $\Omega(E)$

$\frac{\Omega}{\Delta}$ is inverse Laplace transform of Q_N

$$\frac{\Omega(E)}{\Delta} = \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} d\beta\, e^{\beta E}\, Q_N(\beta) \quad ; \beta' > 0$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(\beta' + i\beta'')} Q_N(\beta' + i\beta'')\, d\beta''$$

$$\beta' = \mathrm{Re}\,\beta = 0^+$$

$\therefore$ Thermodynamic potentials, which are

S vs. $\frac{A}{T}$

Legendre transforms of one another, have ensemble partition functions that are Laplace transforms of each other.

Virial Thm: $\left\langle X_i \frac{\partial H}{\partial X_j} \right\rangle = kT\, \delta_{ij}$

is a general result for classical systems.

X_i, X_j are any of the 6N generalized coordinates $\{\vec{q}, \vec{p}\}$

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{\prod_k \int dq_k dp_k\, x_i \frac{\partial H}{\partial x_j} e^{-\beta H}}{\prod_k \int dq_k \int dp_k\, e^{-\beta H}}$$

Integrate by parts: $\frac{\partial H}{\partial x_j} e^{-\beta H} = \frac{\partial}{\partial x_j} e^{-\beta H} \left(\frac{1}{-\beta}\right)$

$$= \left(-\frac{1}{\beta}\right) \int' dq_k dp_k\, x_i\, e^{-\beta H} \Big|_{x_j^{(1)}}^{x_j^{(2)}} + \frac{1}{\beta} \int dp_k dq_k\, \underbrace{\delta_{ij}}_{\frac{\partial x_i}{\partial x_j}} e^{-\beta H}$$

$\int'$ = integration of coordinates (except x_j)

Boundary term vanishes because $e^{-\beta H} \to 0$ @ ∂

$$\therefore \left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = kT\, \delta_{ij}$$

if $x_i = x_j = p_i \Rightarrow \langle p_i \dot{q}_i \rangle = kT$

" " " $q_i \Rightarrow -\langle q_i \dot{p}_i \rangle = kT$

Traditional expression

$$\sum_i \langle p_i \dot{q}_i \rangle = 3NkT$$

$$-\sum_i \langle q_i \dot{p}_i \rangle = 3NkT$$