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1 Method of Mean values (Canonical formalism):

We want to evaluate

$$\langle n_r \rangle = \frac{\sum'_{\{n_r\}} n_r W\{n_r\}}{\sum'_{\{n_r\}} W\{n_r\}}$$

$\leadsto$ satisfying constraints.

Define:

$$\tilde{W}\{n_r\} = \frac{\mathcal{N}! \; \omega_0^{n_0} \omega_1^{n_1} \cdots}{n_0! \, n_1! \cdots}$$

Notice:

$$W\{n_r\} = \tilde{W}\{n_r\} \Big|_{\forall \omega_r = 1}.$$

Define:

$$\Gamma(\mathcal{N}, U) = \sum'_{\{n_r\}} \tilde{W}\{n_r\}$$

$\mathcal{N}$: # of ensemble members

U: average energy

We see that:

$$\langle n_r \rangle = \omega_r \frac{\partial}{\partial \omega_r} (\ln \Gamma) \Big|_{\forall \omega_r = 1}$$

P/ $$\omega_r \frac{\partial \ln \Gamma}{\partial \omega_r}\Big|_{\forall \omega_r = 1} = \omega_r \frac{\partial}{\partial \omega_r} \ln \sum'_{\{n_r\}} \frac{\mathcal{N}! \; \omega_0^{n_0} \omega_1^{n_1} \cdots}{n_0! \, n_1! \cdots} \Big|_{\forall \omega_r = 1} =$$

$$= \omega_r \frac{\sum'_{\{n_r\}} n_r \, \omega_r^{n_r - 1} \tilde{W}\{n_r\}}{\sum'_{\{n_r\}} \tilde{W}\{n_r\}}\Bigg|_{\forall \omega_r = 1} = \frac{\sum'_{\{n_r\}} n_r \, \tilde{W}\{n_r\}}{\sum'_{\{n_r\}} \tilde{W}\{n_r\}}\Bigg|_{\forall \omega_r = 1} =$$

$\leadsto$ it does not have ω_r.

$$= \frac{\sum'_{\{n_r\}} n_r W\{n_r\}}{\sum'_{\{n_r\}} W\{n_r\}} \equiv \langle n_r \rangle \quad (*)$$

Then we need to be able to find Γ or W to obtain $\langle n_r \rangle$:

$$\Gamma(\mathcal{N}, U) = \mathcal{N}! \sum'_{\{n_r\}} \frac{\omega_0^{n_0} \omega_1^{n_1} \cdots}{n_0! \quad n_1! \cdots}$$

Let's construct $G(\mathcal{N}, z)$ such that it is a power series in z with $\Gamma(\mathcal{N}, U)$ as coefficients.

Let's construct $G(N, z)$ such that it is a power series in z with $\Gamma(N, U)$ as coefficients.

$$G(N, z) = \sum_{U=0}^{\infty} \Gamma(N, U)\, z^{NU} = \qquad NU = \epsilon_0 m_0 + \epsilon_1 m_1 + \dots$$

$$= \sum_{U=0}^{\infty} \left[\sum_{\{m_r\}}' \frac{N!}{m_0!\, m_1! \dots} (w_0 z^{\epsilon_0})^{m_0} (w_1 z^{\epsilon_1})^{m_1} \dots \right] =$$

$$= (w_0 z^{\epsilon_0} + w_1 z^{\epsilon_1} + \dots)^N = [f(z)]^N \equiv \sum_{U=0}^{\infty} \Gamma(N, U)\, z^{NU}$$

since: $$(x_1 + x_2 + \dots + x_m)^n = \sum_{\substack{k_1 + k_2 + \dots + k_m = n \\ \sum_{t=1}^{m} k_t = n}} \binom{n}{k_1, k_2, \dots, k_m} \prod_{t=1}^{m} x_t^{k_t}$$

$$\binom{n}{k_1, k_2, \dots, k_m} \to \frac{n!}{k_1!\, k_2! \dots k_m!}$$

$x_t = w_t z^{\epsilon_t}$

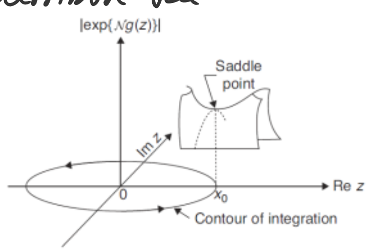
$k_t = m_t$

$n = N$

Notice that the Γ as coefficients of the expansion in powers of z of $G(N, z)$ is given by:

$$\Gamma(N, U) = \frac{1}{2\pi i} \oint \frac{[f(z)]^N}{\quad}$$

We need to find the values of the integrand ($e^{Ng(z)}$) that contribute the most to the integral:



The value of z that contributes the most is x_0 (a saddle-point) and it can be found with the steepest-descent technique. (See Ch. 3 Sec. 2.)

if $z = x_0 \equiv e^{-\beta}$ (β is a "new variable")

$$\frac{1}{N} \ln \Gamma(N, U) = \ln \left\{ \sum_r w_r e^{-\beta \epsilon_r} \right\} + \beta U \qquad (3.2.31)$$

Replacing in (*):

$$\langle m_r \rangle = w_r \frac{\partial \ln \Gamma}{\partial w_r}\bigg|_{\dots} = w_r \frac{\partial}{\quad} \left\{ \left[N \ln \sum_s w_s e^{-\beta \epsilon_s} \right] \right.$$

$$\langle n_r \rangle = \omega_r \frac{\partial \ln \Gamma}{\partial \omega_r}\Bigg|_{\forall \omega_r = 1} = \omega_r \frac{\partial}{\partial \omega_r}\Bigg\{\Big[\mathcal{N} \ln \sum_s \omega_s e^{-\beta \epsilon_s}\Big]$$

$$+ \mathcal{N}\beta U\Bigg\}\Bigg|_{\forall \omega_r=1} \quad \beta = \beta(\omega_r)$$

$$= \omega_r \left[\frac{\mathcal{N} e^{-\beta\epsilon_r}}{\sum_s \omega_s e^{-\beta \epsilon_s}} + \underbrace{\left[\frac{\mathcal{N}\sum_s \omega_s(-\epsilon_s)e^{-\beta\epsilon_s}}{\sum_s \omega_s e^{-\beta\epsilon_s}} + \mathcal{N}U\right]}_{0 \text{ since } U = \frac{\sum_s \omega_s \epsilon_s x_0^{\epsilon_s}}{\sum_s \omega_s x_0^{\epsilon_s}} \ (3.2.24)}\frac{d\beta}{d\omega_r}\right]\Bigg|_{\forall \omega_r=1} =$$

$$x_0^{\epsilon_s} \equiv e^{-\beta\epsilon_s}$$

$$= \frac{\mathcal{N} e^{-\beta\epsilon_r}}{\sum_s e^{-\beta\epsilon_s}} \equiv$$

s: dummy index

$$= \frac{\mathcal{N} e^{-\beta\epsilon_r}}{\sum_r e^{-\beta\epsilon_r}} \equiv \langle n_r \rangle$$

Notice that $\langle n_r \rangle \equiv n_r^*$ if we identify the β's appearing in both expressions.

Fluctuations of $\langle n_r \rangle$:

$$\langle n_r^2 \rangle = \frac{\sum'_{\{n_r\}} n_r^2 W\{n_r\}}{\sum'_{\{n_r\}} W\{n_r\}} \overset{\text{homework}}{=} \frac{1}{\Gamma}\left(\omega_r \frac{\partial}{\partial \omega_r}\right)^2 \Gamma \Bigg|_{\forall \omega_r=1}$$

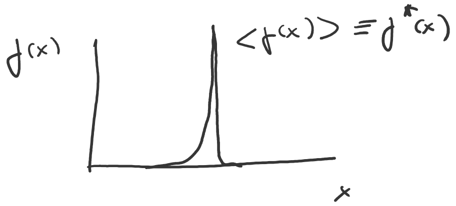
$$\therefore \langle (\Delta n_r)^2 \rangle \equiv \langle \{n_r - \langle n_r\rangle\}^2 \rangle = \langle n_r^2 \rangle - \langle n_r \rangle^2 =$$

$$\overset{\text{hw}}{=} \left(\omega_r \frac{\partial}{\partial \omega_r}\right)\left(\omega_r \frac{\partial}{\partial \omega_r}\right) \ln \Gamma \Bigg|_{\forall \omega_r = 1}$$

and

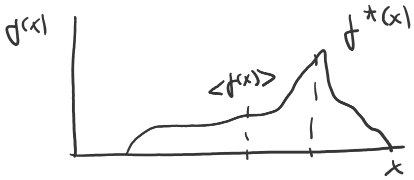
$$\left\langle \left(\frac{\Delta n_r}{\langle n_r \rangle}\right)^2 \right\rangle \overset{\text{hw}}{=} \frac{1}{\langle n_r \rangle} - \frac{1}{\mathcal{N}}\left\{1 + \frac{(\epsilon_r - U)^2}{\langle (\epsilon_r - U)^2 \rangle}\right\}$$

As $\mathcal{N} \to \infty$ $\langle n_r \rangle \to \infty$ $\therefore \langle \ \rangle \to 0$



very sharp peak

versus

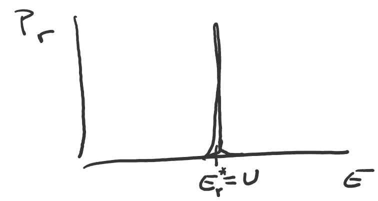


in wide function
$\langle f(x)\rangle \neq f^*(x)$
Not the case for canonical distribution

Physical meaning and statistical quantities in the canonical ensemble:

Canonical distribution:

$$P_r = \frac{\langle n_r\rangle}{\mathcal{N}} = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$



β is obtained from:

$$U = \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = -\frac{\partial}{\partial \beta} \ln \underbrace{\left\{\sum_r e^{-\beta E_r}\right\}}_{Z_N} \quad (1)$$

Z_N partition function for system with N particles.

(Pathria uses Q instead of Z).

All members of the canonical ensemble have N particles each.

Thermodynamical functions:

$$F = U - TS \quad (2)$$

$$dF = dU - TdS - SdT = -PdV - SdT + \mu dN$$

$$\therefore \quad S = -\frac{\partial F}{\partial T}\Big|_{V,N} \qquad P = -\frac{\partial F}{\partial V}\Big|_{T,N} \qquad \mu = \frac{\partial F}{\partial N}\Big|_{T,V}$$

$$\text{and} \quad U \overset{(2)}{=} F + TS = F - T\frac{\partial F}{\partial T}\Big|_{V,N} = -T^2 \underbrace{\left[\frac{\partial}{\partial T}\left(\frac{F}{T}\right)_{N,V}\right]}_{-T^2 \frac{F}{(-T^2)} - \frac{T^2}{T}\frac{\partial F}{\partial T}\big|_{V,N}}$$

$$= \left[\frac{\partial (F/T)}{\partial (1/T)}\right]_{N,V} \quad (3)$$

$$\frac{\partial (F/T)}{\partial T} \underbrace{\frac{\partial T}{\partial (1/T)}}_{} \equiv -T^2 \frac{\partial (F/T)}{\partial T}$$

$$\left[\frac{\partial (1/T)}{\partial T}\right]^{-1} = \left(-\frac{1}{T^2}\right)^{-1} = -T^2$$

Comparing ① and ③:

$$U = -\frac{\partial}{\partial \beta} \ln Z_N = \frac{\partial (F/T)}{\partial (1/T)}\Big|_{N,V} \qquad \text{if } \beta = 1/kT$$

identifying $\ln \sum_r e^{-\beta \epsilon_r} \equiv -F/kT$

$$\therefore \quad F(N,V,T) \equiv -kT \ln Z_N(V,T)$$

($Z_N \equiv Q_N$ in book)

where

$$Z_N(V,T) = \underbrace{\sum_r}_{\text{over ALL states}} e^{-\epsilon_r/kT}$$

$\epsilon_r(N,V)$

Now we can obtain all the thermodynamical properties:

$$c_V = \frac{\partial U}{\partial T}\Big|_{N,V} = T\frac{\partial S}{\partial T} = -T\frac{\partial^2 F}{\partial T^2}\Big|_{N,V}$$

$$\therefore \; c_V = -T\frac{\partial^2(-kT\ln Z)}{\partial T^2}$$

Notice that

$$P = -\frac{\partial F}{\partial V}\Big|_{N,T} = \frac{\partial\, kT \ln Z}{\partial V}\Big|_{N,T} =$$

$$= kT\frac{\partial}{\partial V}\Big(\ln \sum_r e^{-\epsilon_r/kT}\Big)\Big|_{N,T} = kT\frac{\sum_r \left(-\frac{1}{kT}\right)\frac{\partial \epsilon_r}{\partial V} e^{-\epsilon_r/kT}}{\sum_r e^{-\epsilon_r/kT}} =$$

$$= -\frac{\sum_r \frac{\partial \epsilon_r}{\partial V} e^{-\epsilon_r/kT}}{\sum_r e^{-\epsilon_r/kT}}$$

$$\therefore \; P\,dV = -\sum_r \underbrace{\frac{e^{-\epsilon_r/kT}}{\sum_r e^{-\epsilon_r/kT}}}_{P_r} d\epsilon_r = -\sum_r P_r\, d\epsilon_r$$

$$= -dU$$

the change in average energy of the system during a process that changes ϵ_r leaves the probabilities P_r constant.

Entropy:

$$P_r = \frac{e^{-\beta \epsilon_r}}{Z_N} \Rightarrow \ln P_r = -\beta \epsilon_r - \ln Z_N$$

Then

$$\langle \ln P_r \rangle = -\beta \langle \epsilon_r \rangle - \underbrace{\ln Z_N}_{-\frac{F}{kT} = -\beta F} = \beta(-\underbrace{\langle \epsilon_r \rangle}_{U} + F) =$$

$$= \beta(F - U) = \frac{1}{kT}(U - TS - U) = -\frac{S}{k}$$

$$\therefore \quad S = -k \langle \ln P_r \rangle = -k \sum_r P_r \ln P_r$$

This is the definition of entropy used in information theory. (with $k \equiv 1$).

- S is determined by P_r.
- if $T = 0$ the system is in the ground state. for a nondegenerate ground state $P_r = P_0 = 1$ and $S = -k \ln 1 = 0$ (3^{rd} law).
- $S = 0$ corresponds to knowing everything about the state of the system.
- large $S \Rightarrow$ large disorder $\Rightarrow$ large lack of information

For microcanonical ensemble:

$P_r = \frac{1}{\Omega}$ where $\Omega = \#$ of accessible states

$$\boxed{S} = -k \sum_{r=1}^{\Omega} \frac{1}{\Omega} \ln\left(\frac{1}{\Omega}\right) = -k \frac{\overset{1}{\widetilde{\Omega}}}{\Omega} \ln\left(\frac{1}{\Omega}\right) =$$

$$= \boxed{k \ln \Omega}$$