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Last time:

$$\Gamma(N,U) = \sum_{\{n_r\}}{}' \tilde{W}\{n_r\} = N! \sum_{\{n_r\}}{}' \frac{\omega_0^{n_0}}{n_0!} \frac{\omega_1^{n_1}}{n_1!} \cdots$$

and we saw that:

$$\langle n_r \rangle = \frac{\sum_{\{n_r\}}' n_r \, W\{n_r\}}{\underbrace{\sum_{\{n_r\}}' W\{n_r\}}_{\text{unknown}}} = \omega_r \frac{\partial \ln \Gamma}{\partial \omega_r}\Bigg|_{\forall \omega_r = 1} \quad (*)$$

We need to calculate $\Gamma(\mathcal{N}, \upsilon)$.

For that we construct:

$$G(\mathcal{N}, z) = \sum_{\upsilon=0}^{\infty} \Gamma(\mathcal{N}, \upsilon)\, z^{\mathcal{N}\upsilon} =$$

Now they are the coefficients of a power series on $z^{\mathcal{N}}$

$$= \sum_{\upsilon=0}^{\infty} \left[\sum_{\{m_i\}}' \frac{\mathcal{N}!}{n_0!\, n_1! \dots} (w_0 z^{\epsilon_0})^{n_0} (w_1 z^{\epsilon_1})^{n_1} \dots \right] =$$

Using that $\sum_i m_i \cdot \epsilon_i = \mathcal{N}\upsilon$

$$= \sum_{n_0+n_1+\dots=\mathcal{N}} \binom{\mathcal{N}}{n_0, n_1, \dots} \prod_{t=1} (w_t z^{\epsilon_t})^{m_t} = (w_0 z^{\epsilon_0} + w_1 z^{\epsilon_1} + \dots)^{\mathcal{N}} =$$

multinomial theorem

$$(x_1 + x_2 + \dots)^n = \sum_{k_1+k_2+\dots=n} \binom{n}{k_1, k_2, \dots} \prod_{t=1} x_t^{k_t}$$

$$= [f(z)]^{\mathcal{N}}$$

Then we need to obtain $\Gamma(\mathcal{N},\nu)$ which are the coefficients of a power expansion in powers of z:

$$[f(z)]^{\mathcal{N}} \equiv \sum_{\nu=0}^{\infty} \Gamma(\mathcal{N},\nu)\, z^{\mathcal{N}\nu}$$

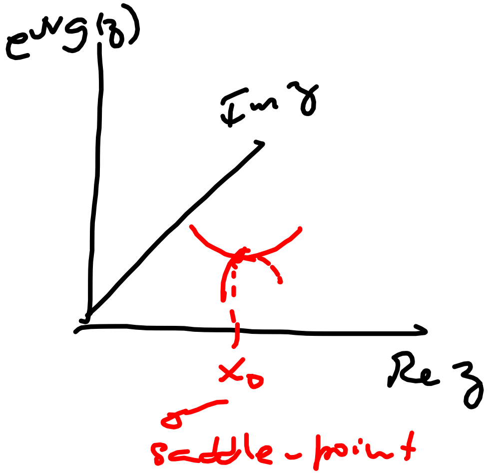
For all details look at section 3.2 in book.

$$\Gamma(\mathcal{N},\nu) = \frac{1}{2\pi i} \oint \underbrace{\boxed{\frac{[f(z)]^{\mathcal{N}}}{z^{\mathcal{N}\nu+1}}}}_{g(z)}\, dz$$

This integral is solved using the steepest descent method.

In order to obtain $\Gamma(\mathcal{N},\nu)$ a point

(*) $z = x_0 = e^{-\beta}$ needs to be found.



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

(3.2.31)

where β is such that

$$\boxed{x_0 = e^{-\beta}}$$

Replacing the solution for $\Gamma(N,U)$ in our expression for $\langle n_r\rangle^{(*)}$ we find:

$$\langle n_r\rangle = w_r \left.\frac{\partial \ln\Gamma}{\partial w_r}\right|_{\forall w_r = 1} = w_r \frac{\partial}{\partial w_r}\left[N\ln\left\{\sum_s w_s e^{-\beta\epsilon_s}\right\} + \beta U\right]_{\forall w_r=1} =$$

assume that $\beta = \beta(w_r)$

$$= w_r\left[\frac{N e^{-\beta\epsilon_r}}{\sum_s w_s e^{-\beta\epsilon_s}} + \Bigg(\underbrace{\frac{-\sum_s \epsilon_s w_s e^{-\beta\epsilon_s} N}{\sum_s w_s e^{-\beta\epsilon_s}} + N U}_{0\ (3.2.24)}\Bigg)\frac{\partial\beta}{\partial w_r}\right]_{\forall w_r=1} =$$

(3.2.24) shows that

$$U \approx \frac{\sum_s w_s \epsilon_s x_0^{\epsilon_s}}{\sum_s w_s x_0^{\epsilon_s}} = \frac{\sum_s w_s \epsilon_s e^{-\beta \epsilon_s}}{\sum_s w_s e^{-\beta \epsilon_s}}$$

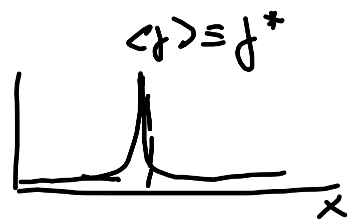
Then

$$\langle n_r \rangle = w_r \frac{N e^{-\beta \epsilon_r}}{\sum_s w_s e^{-\beta \epsilon_s}} \Bigg|_{\forall w_r = 1} = \frac{N e^{-\beta \epsilon_r}}{\sum_r e^{-\beta \epsilon_r}} \equiv n_r^*$$

found last time

This means that the average value of the distribution coincides with its maximum:

Ex: $f(x)$



vs

Fluctuations of $\langle n_r \rangle$:

Homework

$$\langle n_r^2 \rangle = \frac{\sum_{\{n_r\}}' n_r^2 \, W\{n_r\}}{\sum_{\{n_r\}}' W\{n_r\}} = \frac{1}{\Gamma}\left(\omega_r \frac{\partial}{\partial \omega_r}\right)^2 \Gamma \Big|_{\forall \omega_r = 1}$$

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

$$= \langle n_r^2 \rangle - 2 \langle n_r \rangle^2 + \langle n_r \rangle^2 = \langle n_r^2 \rangle - \langle n_r \rangle^2 =$$

homework

$$= \left(\omega_r \frac{\partial}{\partial \omega_r}\right)\left(\omega_r \frac{\partial}{\partial \omega_r}\right) \ln \Gamma \Big|_{\forall \omega_r = 1}$$

and

homework

$$\left\langle \left(\frac{\Delta n_r}{\langle n_r \rangle}\right)^2 \right\rangle = \frac{1}{\langle n_r \rangle} - \frac{1}{\mathcal{N}} \left\{ 1 + \frac{(\epsilon_r - U)^2}{\langle (\epsilon_r - U)^2 \rangle} \right\} \longrightarrow 0$$

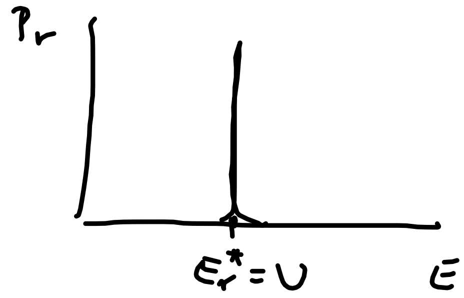
if $\mathcal{N} \to \infty$

since $\langle n_r \rangle \to \infty$

Physical interpretation of statistical quantities in the canonical ensemble:

Canonical probability distribution:

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



β is obtained from:

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

solving this if you know U you get β

$$= -\frac{\partial}{\partial \beta} \ln Z_N$$

$Z_N = \sum_r e^{-\beta E_r}$ is the canonical partition function (called Q_N in the book).

N is the total number of particles in each member of the ensemble.

We know from thermodynamics that:

$F = U - TS$

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

$TdS - PdV + \mu dN$

Then:

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

and since

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

$$-T^2 F\left(-\frac{1}{T^2}\right) - \frac{T^2}{T}\frac{\partial F}{\partial T}\Big|_{V,N}$$

$$= \left[\frac{\partial (F/T)}{\partial (1/T)}\right]_{N,V} \quad 2$$

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

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

Comparing ① with ② we find that:

$$\left.\frac{\partial(F/T)}{\partial(1/T)}\right|_{N,V} \equiv -\frac{\partial}{\partial\beta}\ln Z_N$$

this is satisfied if we identify:

$$\beta \equiv \frac{1}{kT} \quad \text{and then} \quad \ln Z_N = \ln \sum_r e^{-\beta \epsilon_r} \equiv -\frac{F}{kT}$$

k: universal constant.

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

where $Z_N(V,T) = \sum_r e^{-\frac{\epsilon_r(V)}{kT}}$

Now all the thermodynamical properties can be obtained from F:

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

$$= -T\frac{\partial^2}{\partial T^2}(-kT \ln Z_N)$$

Notice that

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

$$-\frac{\partial}{\partial V}\left[-kT \ln Z\right]\Big|_{N,T} = +kT\frac{\sum_r \frac{\partial \epsilon_r}{\partial V}\frac{e^{-\epsilon_r/kT}}{-kT}}{\sum_r e^{-\frac{\epsilon_r}{kT}}} = -\frac{\sum_r \frac{\partial \epsilon_r}{\partial V} e^{-\frac{\epsilon_r}{kT}}}{\sum_r e^{-\epsilon_r/kT}}$$

$\therefore$

$$P\,dV = -\frac{\sum_r \overbrace{e^{-\epsilon_r/kT}}^{P_r}\, d\epsilon_r}{\sum_r e^{-\epsilon_r/kT}} = -\sum_r P_r\, d\epsilon_r = -dU$$

Δ change in the average energy of the system during a process that changes E_r leaving the probability constant occurs when we change V but we are not changing S which only changes when P_r changes. Thus, it is a transformation in which $TdS = Q = 0$ (no heat exchanged). adiabatic.

Entropy relation to probability distribution:

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

$$\langle \ln P_r \rangle = -\beta \langle E_r \rangle - \ln Z_N = -\beta U + \beta F =$$

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

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

This is the expression for the entropy used in information theory (with $k \equiv 1$!).

You see that if $T = 0$ the system is in the ground state and $P_r = 1$. $\Rightarrow$ $S = 0$ (third law).