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System in canonical ensemble.

$\mathcal{N}$; systems sharing energy $\mathcal{E}$.

ϵ_r : $r = 0, 1, 2, \ldots$ possible energies of each system.

n_r : # of systems with energy ϵ_r.

$\{n_r\}$: distribution.

Constraints :

$$\text{①} \begin{cases} \sum_r n_r = \mathcal{N} \\ \sum_r n_r \epsilon_r = \mathcal{E} = \mathcal{N} U \end{cases}$$

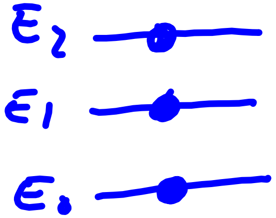
average energy

$U = \frac{\mathcal{E}}{\mathcal{N}}$

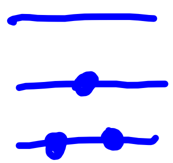
Notice that $\{n_r\}$ have a degeneracy because we can change which member of the ensemble has each energy E_r. Then the degeneracy of $\{n_r\}$ is given by:

$$W\{n_r\} = \frac{N!}{n_0!\,n_1!\,n_2!\cdots}$$

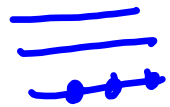
Ex: $N = 3$



$W\{n_r\} = 3! = 6$



$W\{n_r\} = 3 = \frac{3!}{1!\,2!\,0!} = \frac{6}{2} = 3$



$W\{n_r\} = 1 = \frac{3!}{3!\,0!\,0!} = 1$

Now all the states of the ensemble compatible with ① are equally likely. Then the most probable $\{n_r\}$ will be the one with the largest $W\{n_r\}$.

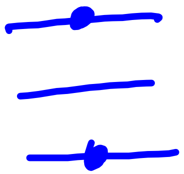
Ex:

$\mathcal{N} = 2 \quad \mathcal{E} = 2\varepsilon$

$\epsilon_2 = 2\varepsilon$

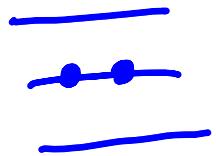
$\epsilon_1 = \varepsilon$

$\epsilon_0 = 0$



$W\{n_r\} = 2$

higher W will be preferred



$W\{n_r\} = 1$

We need to find $\{n_r^*\}$ with maximum W.

We will see that W is very sharp so that if $\{n_r\} \neq \{n_r^*\}$ the probability of the distribution will be negligible.

We will find

→ sum over $\{n_r\}$ satisfying ①

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

We will find n_r^* and $\langle n_r \rangle$ and we will see that $n_r^* = \langle n_r \rangle$ when $N \to \infty$.

1) Method of most probable values:

$$\ln W = \ln N! - \sum_r \ln n_r!$$

Since N and n_r are very large we can use Stirling's approx: $\ln N! \simeq N \ln N - N$

$\therefore$

$$\ln W = N \ln N - N - \sum_r (n_r \ln n_r - n_r) =$$

$$= N \ln N - \cancel{N} - \sum_r n_r \ln n_r + \underbrace{\sum_r n_r}_{\cancel{N}} =$$

$$= N \ln N - \sum_r n_r \ln n_r$$

Let's find $\{n_r^*\}$ that satisfies $\delta W\{n_r^*\} = 0$

$$\delta(\ln W) = -\sum_r \left(\ln n_r + \frac{n_r}{n_r}\right)\delta n_r =$$

$$= -\sum_r (\ln n_r + 1)\,\delta n_r = 0$$

but the sum over r has constraints and this means that:

$$\begin{cases} \sum_r \delta n_r = 0 \\ \sum_r \epsilon_r \delta n_r = 0 \end{cases} \quad \text{constrains.}$$

We can include the constrains via Lagrange multipliers then

$$\delta \ln W = 0 = \sum_r \left[-(\ln n_r + 1) - \alpha - \beta \epsilon_r\right] \delta n_r$$

unrestricted sum

Since δn_r are now arbitrary we have that

$$-(\ln n_r + 1) - \alpha - \beta \epsilon_r = 0$$

$$\therefore \ln n_r^* = -\beta \epsilon_r - \alpha - 1$$

$$\boxed{n_r^* = c\, e^{-\beta \epsilon_r}}$$

(+)

We can use the constraints ① to find c and β:

$$\mathcal{N} = \sum_r n_r = \sum_r n_r^* = c \sum_r e^{-\beta \epsilon_r}$$

$$\therefore \; c = \frac{\mathcal{N}}{\sum_r e^{-\beta \epsilon_r}}$$

Then $$\frac{n_r^*}{\mathcal{N}} = \frac{e^{-\beta \epsilon_r}}{\sum_r e^{-\beta \epsilon_r}} \qquad \overline{++}$$

Also

$$\mathcal{N} U = \mathcal{E} = \sum_r \varepsilon_r n_r = \sum_r \varepsilon_r n_r^* =$$

(++)

$$= \mathcal{N} \frac{\sum_r \varepsilon_r e^{-\beta \varepsilon_r}}{\sum_r e^{-\beta \varepsilon_r}} \Rightarrow$$

$$U = \frac{\mathcal{E}}{\mathcal{N}} = \frac{\sum_r \epsilon_r e^{-\beta \epsilon_r}}{\sum_r e^{-\beta \epsilon_r}}$$

If you know U from the above equation you can obtain β.

Method of Mean Values:

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

Trick:

Define

$$\tilde{W}\{n_r\} = \frac{N!\, w_0^{n_0} w_1^{n_1} w_2^{n_2} \cdots}{n_0!\, n_1!\, n_2! \cdots}$$

Notice that $\tilde{W}\{n_r\}\Big|_{\forall w_r = 1} \equiv W\{n_r\}$

Define:

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

You can see that

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

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

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

The problem to evaluate Γ or W is dealing with the constraint on the sum over $\{n_r\}$:

Construct

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

generating function power series in z with $\Gamma(N,U)$ as the coefficients.

$$= \sum_{U=0}^{\infty} \left[\sum_{\{n_r\}}{}' \frac{N!}{n_0!\, n_1! \cdots} (w_0 z^{\epsilon_0})^{n_0} (w_1 z^{\epsilon_1})^{n_1} \cdots \right]$$

Using $\sum_i n_i \epsilon_i = NU$

$$G(N,z) = (\omega_0 z_0^{\epsilon_0} + \omega_1 z_1^{\epsilon_1} + \dots)^N = f(z)^N$$

Now read in the book (and ask me questions if you have them) the derivation that leads to

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

Replacing $\ln \Gamma(N,U)$ in the expression for $\langle n_r \rangle$ (*):

$$\langle n_r\rangle = w_r \frac{\partial}{\partial w_r}\ln \Omega\Big|_{\forall w_r=1} =$$

$$= w_r \frac{\partial}{\partial w_r}\left[N \ln\left\{\sum_r w_r e^{-\beta\epsilon_r}\right\} + N\beta U\right]_{\forall w_r=1} =$$

$\beta=\beta(w_r)$

$$= w_r \left[\frac{N e^{-\beta\epsilon_r}}{\sum_r w_r e^{-\beta\epsilon_r}} + \left\{-\underbrace{\frac{N\sum_r w_r \epsilon_r e^{-\beta\epsilon_r}}{\sum_r w_r e^{-\beta\epsilon_r}}}_{NU|_{\text{for } w_r=1}} + NU\right\}\frac{\partial\beta}{\partial w_r}\right]_{\forall w_r=1} =$$

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

We see that $\frac{\langle n_r \rangle}{\mathcal{N}} \equiv \frac{\{m_r^*\}}{\mathcal{N}}$ (in $++$).

Let's calculate the fluctuations of $\langle n_r \rangle$:

homework

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

then

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

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

Then

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

homework

You see that when $N \to \infty \Rightarrow \langle n_r \rangle \to \infty$

so the fluctuations $\to 0$ and $\langle n_r \rangle \equiv n_r^*$

Physical meaning of statistical quantities in the canonical ensemble:

We found the canonical distribution

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

$\sum_r \rightarrow$ sum over all states (as opposed to accessible states only as in microcanonical).

β is obtained from
$$U = \frac{\sum_r \epsilon_r e^{-\beta \epsilon_r}}{\sum_r e^{-\beta \epsilon_r}} = -\frac{\partial}{\partial \beta} \ln \left\{ \sum_r e^{-\beta \epsilon_r} \right\}$$

Make contact with thermodynamics:

We know:

$$F = U - TS$$

$$dF = dU - TdS - SdT = T\cancel{dS} - PdV + \mu dN$$

$$- T\cancel{dS} - SdT = -PdV - SdT + \mu dN$$

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

ξ

V, N, T are the variables that control the canonical ensemble.

We know that

$$U = F + TS \overset{\text{?}}{=} F - T\frac{\partial F}{\partial T}\Big|_{V,N} =$$

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

But we also found that

$$U = -\frac{\partial}{\partial\beta}\ln\left\{\sum_r e^{-\beta\varepsilon_r}\right\}$$

Comparing the 2 expressions if we identify

$\beta = \frac{1}{kT}$ then $\ln\sum_r e^{-\beta\varepsilon_r} = -\frac{F}{kT}$

Then

$$F(N,V,T) = -kT \ln \sum_r e^{-\beta \epsilon_r} \equiv$$

$$= -kT \ln Z_N(V,T)$$

$$\underbrace{Z_N(V,T)}_{\text{partition function}} = \sum_r e^{-\beta \epsilon_r} \equiv \sum_r e^{-\frac{\epsilon_r}{kT}}$$

(caution: Pathria uses Q for Z!)

Notice that all the states r appear in the sum but the weight (probability) will kill most of them.

Now if you find F from Z_N you can find all the other properties through derivatives of F.

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