

- Covers:
- 1) $A = -kT \ln Q$
 - 2) $G = \mu N$
 - 3) $S = k \sum P_i \ln P_i = k \ln \Omega$

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(A1)

I)

DERIVATION OF BRIDGES EQN.

$$A = -kT \ln Q$$

4) Pathria Sec. 3.3

1) We've derived the canonical distribution FN:

$$P(E_r) = \frac{e^{-\beta E_r}}{Q}$$

where $Q = \sum_{r=1}^Q e^{-\beta E_r}$

2) So, U (macroscopic internal energy for our arbitrary system) is obtained using:

$$U = \sum_r P(E_r) E_r$$
$$= \frac{\sum_r E_r e^{-\beta E_r}}{Q}$$

$$U = -\frac{\partial}{\partial \beta} \ln Q \quad (1.0)$$

3) Now follow Pathria and work out a relationship between U and P

a) FIRST GET SOME DEFINITIONS:
(FOR P, S, μ):

i) $A \equiv U - TS$

ii) ~~DATA~~

$$\therefore dA = dU - Tds - sdt + \mu dN$$

$$= -PdV + Tds - sdt + \mu dN$$

(2.1) $\boxed{dA = -PdV + \mu dN - sdt}$

iii) SO FROM (2.1):

$$\boxed{\begin{aligned} P &= -\frac{\partial A}{\partial V} \bigg|_{N,T} \\ S &= -\frac{\partial A}{\partial T} \bigg|_{N,V} \\ \mu &= \frac{\partial A}{\partial N} \bigg|_{T,V} \end{aligned}} \quad (2.2)$$

b) NOW SHOW THAT

$$\boxed{U = \frac{\partial(A/T)}{\partial(1/T)}} \quad (2.3)$$

$$i) \quad u = A + TS$$

$$= A - T \frac{\partial A}{\partial T} \bigg|_{N, \mu}$$

$$= -T^2 \frac{\partial}{\partial T} (A/T) \bigg|_{N, \mu}$$

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

$$= \frac{\partial (A/T)}{\partial (1/T)}$$

Proof:

$$\oplus \quad \frac{\partial (A/T)}{\partial T} = \frac{\partial (A/T)}{\partial (A/T)} \frac{\partial (A/T)}{\partial T}$$

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

$$\therefore \boxed{\frac{\partial (A/T)}{\partial (1/T)} = -T^2 \frac{\partial (A/T)}{\partial T}}$$

$$\therefore \boxed{u = \frac{\partial (A/T)}{\partial (1/T)}} \quad (3.1)$$

c) FINALLY, COMPARE (3.1) and (1.0) :

$$u = \left[\frac{\partial}{\partial B} \ln Q = \frac{\partial (A/T)}{\partial (1/T)} \right] \quad (3.2)$$

i) try/choose:

$$(4.1) \quad B = \frac{1}{kT}$$

ii) (4.1) in (3.2) $\Rightarrow$

$$(4.2) \quad \left[\frac{\partial(A/T)}{\partial(1/T)} = -k' \ln Q \right]$$

iii) now try/choose

$$A/T = -k' \ln Q$$

$$\Rightarrow \left[A = -k'T \ln Q \right] \quad (4.3)$$

in these notes
⊕ we show that

$k' = k = \text{Boltzmann's const}$

⊕ (4.3) is the BRIDGES
RELATIONSHIP, equivalent
to $S = k \ln \Omega$ for
the microcanonical ensemble

k' doesn't
necessarily
= Boltzmann's
constant;
we can do
show this
by derivation
of
 $S = k \sum p_i \ln p_i$
 $= k \ln \Omega$
in another
part of
these notes

Ex 105 1: prove that
 $G = \mu N$

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AS

$$\begin{aligned} 1) \quad G &\equiv H - TS \\ &= U + PV - TS \\ &= A + PV \end{aligned}$$

$$(A \equiv U - TS)$$

$$G = A - \left. \frac{\partial A}{\partial T} \right|_{N, V}$$

(0) (From derivation
 of $A = -kT \ln Q$)

$$2) \quad \text{Let } a \equiv \frac{A}{N}, \text{ where}$$

a is now a intensive variable

3) so, expressing A in terms
 of its natural variables N, V, T
 (again, see derivation of
 $A = -kT \ln Q$),

$A = A(N, V, T)$ ($A = \text{extensive}$
var)
 Then, in order for a to be
intensive, we must have

$$a \equiv \frac{A}{N} = \tilde{F}(V, T) \quad (1)$$

($\tilde{F}$ cannot depend
 on N)

3a)

However, $\tilde{F}$ cannot depend
 on V either, the way out
 (which preserves the V -dependence
 of A or a while ensuring
 that $\tilde{F}$ is intensive)

is to express $\tilde{F}$ as: lec 17
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(2)
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$$(2) \quad a \equiv A/N = \tilde{F}(\varphi/N, \tau)$$

(this is equivalent to $\frac{1}{\rho}$, $\rho = \text{density}$)

$$4) \therefore (2) \Rightarrow \boxed{A = N \tilde{F}(\varphi/N, \tau)} \quad (3)$$

5) Now use some trial/error/tricks to express (3) in desired form (Let $\tilde{\varphi} \equiv \varphi/N$)

$$a) \quad \varphi \frac{\partial A}{\partial \varphi} \Big|_{N, \tau} = \varphi N \frac{\partial \tilde{F}}{\partial \tilde{\varphi}} \Big|_{N, \tau} \left(\frac{1}{N} \right) \leftarrow \text{using (3)}$$

$$b) \quad N \frac{\partial A}{\partial N} \Big|_{\varphi, \tau} = N \tilde{F} + N^2 \frac{\partial \tilde{F}}{\partial \tilde{\varphi}} \Big|_{N, \tau} \frac{\partial \tilde{\varphi}}{\partial N} \left(\frac{\varphi}{N^2} \right)$$

$$= A - \varphi \frac{\partial \tilde{F}}{\partial \tilde{\varphi}} \Big|_{N, \tau}$$

$$c) \therefore a) + b) \Rightarrow$$

$$\boxed{A = \varphi \frac{\partial A}{\partial \varphi} \Big|_{N, \tau} + N \frac{\partial A}{\partial N} \Big|_{\varphi, \tau}} \quad (4)$$

6) $\therefore$ using (4) in (1):

$$\boxed{G = \mu N}$$

END ASIDES

Microcanonical Ensemble and S

* RIGOROUS PROOF THAT $S = k \sum p_i \ln p_i = k \ln \Omega$

- 1) N replica systems.
- 2) NOW, ~~and~~ ALL N systems restricted to a narrow range of total system energies, $E_0 \leq E \leq E_0 + \Delta E$, where $\Delta E / E_0 \ll 1$.
- 3) $\Omega = \Omega(E_0, N, V)$; $N =$ ^{fixed} ~~no.~~ ^{fixed} ~~no.~~ of units in system; $V =$ ^{fixed} ~~no.~~ ^{fixed} ~~no.~~ Vol. of each unit
= NUMBER OF QUANTUM states that are extent, consistent w/ given V , given N , and given E_0 .
- 4) Assume that the probability of observing your system of interest (having $N-1$ replicants) is any of the quantum states of the available states, is uniform, i.e.,

$$P_r = P(E_r) = \frac{1}{\Omega(E_0, V, N)}$$
 where E_r ~~no~~ runs from E_0 to $E_0 + \Delta E$.

5)

PARTIAL shows
CANONICAL ENSEMBLE

IN Sec. 3.3

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(AS)

that

for a

$$S = -k \sum_i p_i \ln p_i$$

⊕ in the argument leading
to the canonical
distbn, we ~~are~~ allowed
for the possibility
that any replicant
system could assume
any total energy

between 0 and $\tilde{E} = \sum_i n_i E_i$

assumption

We can adapt that to
the microcanonical ensemble (ME)

where now n_i is the number

of systems in the ME

that are in quantum state
where E_i is consistent w/ V, E_0, N .

$E_i \in \Omega$. Thus, the number

of ways of arranging that

the distribution set $\{n_i\}$

can arise w/in the ME

is still given by

$$W\{n_i\} = \frac{\tilde{N}!}{n_1! n_2! \dots}$$

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⊕ Likewise the constraints that apply to the canonical ensemble:

$$\tilde{E} = \sum n_r E_r$$

and

$$\tilde{N} = \sum n_r$$

also apply to the microcanonical ensemble.

⊕ NOW, GOING THROUGH THE SAME ARGUMENT (PATHRIA 3.3 ⊕ LECTURE NOTES) LEADING TO

$$\boxed{P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}} \quad (*)$$

we observe that all available possible E_r 's (= quantum energies) ARE ABOUT THE SAME.

∴ THUS (*) BECOMES:

$$P_r \approx \frac{e^{-\beta E_r} \cancel{N}}{e^{-\beta E_r} \sum_r \cancel{1}} \\ \approx \frac{1}{N}$$

④. So, as claimed by Patricia
system $\in$ constant energy system
in this
(pg 52), for a microcanonical
ensemble:

$$S \stackrel{\text{still}}{=} \text{data}$$

$$= -K \sum p_i \ln p_i$$

$$\stackrel{\sim}{=} -K \sum_{i=1}^{\Omega} \frac{1}{\Omega} \ln \left(\frac{1}{\Omega} \right)$$

$$= -K \frac{1}{\Omega} \ln \left(\frac{1}{\Omega} \right) \sum_{i=1}^{\Omega} 1$$

$$= -K \frac{\Omega}{\Omega} \ln \frac{1}{\Omega}$$

$$\boxed{S = K \ln \Omega}$$

ASIDE 3 ROUGH DERIVATION (8) All
 AND INTERPRETATION OF
 $PdV = dU$

$$U = A + TS$$

$$A = U - TS$$

$$dA = dU - Tds - SdT$$

$$= Tds - PdV + \mu dN - Tds - SdT$$

$$= -PdV + \mu dN - SdT$$

$$A = A(V, N, T)$$

$$P = - \left. \frac{\partial A}{\partial V} \right|_{N, T}$$

$$A = -kT \ln Q$$

$$\left. \frac{\partial A}{\partial V} \right|_{N, T} = -kT \frac{1}{Q} \sum_r \frac{\partial E_r}{\partial V} e^{-\beta E_r}$$

$$= \sum_r \frac{\partial E_r}{\partial V} \left(\frac{e^{-\beta E_r}}{Q} \right)$$

$$\therefore PdV = - \sum_r \frac{\partial E_r}{\partial V} \left(\frac{e^{-\beta E_r}}{Q} \right) dV$$

$$\begin{aligned} \Rightarrow P dU &= - \sum_i (E_{r_i} - E_{r_i}) \frac{e^{-E_{r_i}}}{Q} \\ &= - \sum_i P(E_{r_i}) \Delta E_{r_i} \\ &= - dU \end{aligned}$$

For is low: $dU = -P dU + T dS$

$$\Rightarrow \boxed{dS = 0}$$

$\therefore$ any isothermal process is such that the probability, $P(E_{r_i})$, remain unchanged

$$\begin{aligned} 1) A &= A(N, V, T) \\ 2) A &= N F(\quad) \Rightarrow 3) a = A/N = F(\tilde{V}, T) \end{aligned}$$

F must be fn of intensive prop only

↑
intensive

$$\Rightarrow \boxed{A = N F(\tilde{V}, T)}$$

$$\begin{aligned} 4) G &= A + PV \\ &= A - \frac{\partial A}{\partial V} \bigg|_{N, T} V \\ &= \end{aligned}$$