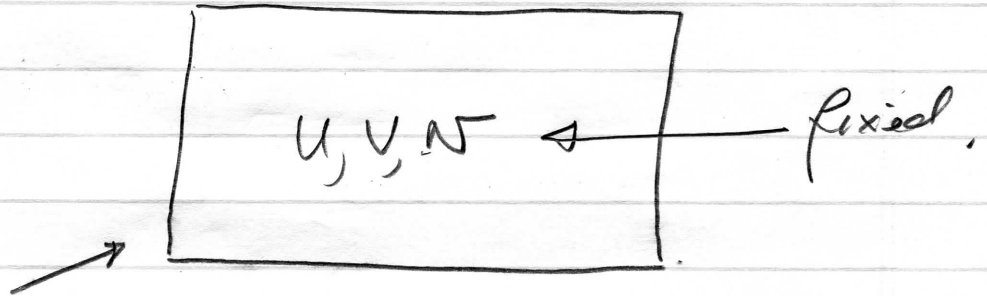


# BOLTZMAN STATISTICS

- Powerful approach to understanding systems
- Equivalent to methods we have used.

So FAR studied systems like:



Isolated system → MICROCANONICAL ENSEMBLE

ENSEMBLE → group of identical systems  
 ↓  
 Perform observations on all of them  
 ↓

Results distributed according to  
 MICROCANONICAL PROBABILITY DISTRIBUTION

PROBABILITY OF SYSTEM being in any accessible microstate

$$P(\text{any accessible } \mu\text{-state}) = \frac{1}{\Omega(u, v, N)}$$

↑ could derive all of thermodynamics from this

In Particular

↳ 2 systems in contact and isolated from Rest of World.

Microcanonical distribution → implies

energy, volume, and number of particles

are distributed between systems such that

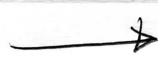
$$S_{1+2} \rightarrow \text{maximized}$$

Can in principle understand all systems in this way.

Technique due to Boltz man

↳ Canonical ENSEMBLE

CANONICAL DISTRIBUTION



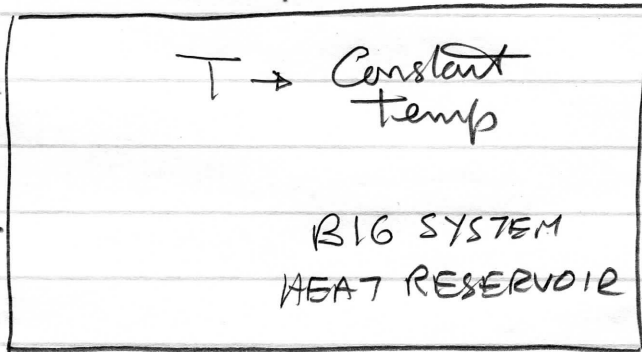
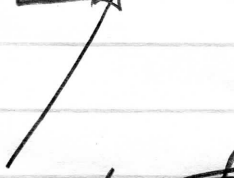
BOLTZMAN DISTRIBUTION

Refers to a system where  $T$ , rather than  $E$  is fixed

KEEP THIS ON BOARD



$T, V, N$



system of interest

fixed  $V, N, T = T_{HEAT BATH}$

can take heat out, but temp  $T$  does not change

(4)

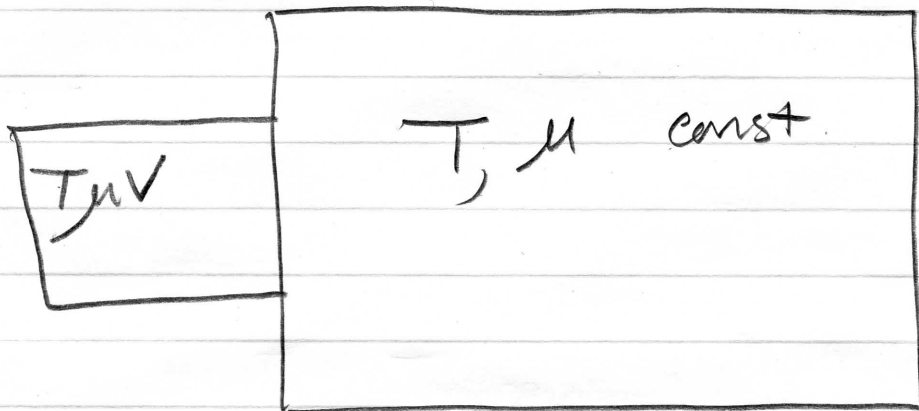
Because of BIGNESS of heat bath  
can derive a simpler description of  
the system than the MICROCANONICAL (ISOLATED)  
approach.

— SYSTEM + HEAT BATH } → One Big ISOLATED SYSTEM.

— EXPLOIT BIGNESS

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ASIDE → ALSO HAVE GRAND CANONICAL ENSEMBLE  
due to Gibbs



System and Bath can exchange particles  
and energy → no time to study  
this.

should be on BOARD



fixed  $\longleftrightarrow$  Can Exchange Energy.

$E =$  Energy of System.

$U_R =$  energy of Reservoir.

$$U_{TOT} = U_R + U_E$$

fixed  $\uparrow$   $\rightarrow$  R + SYSTEM Isolated

Apply Basic Postulate of Stat Mech.

$$\rightarrow \textcircled{1} P(\text{of any accessible } \mu \text{ STATE of SYSTEM } + R) = \frac{1}{\sum_{STR} \Omega(U_{TOTAL})}$$

Don't need to indicate dependence on  $V, N$  of system  $\rightarrow$  fixed

Note that (SYSTEM + Reservoir) → MACROSCOPIC

↓ for fixed  $U_{TOTAL}$

$$\text{System energy} = E$$

$$U_R = U_{TOT} - E$$

$$\Omega_{\text{SYSTEM} + \text{R}}(U_{TOTAL}) = \sum_E \Omega_{\text{SYSTEM}}(E) \Omega_{\text{R}}(U_{TOT} - E)$$

All possible  
allowed values of  $E$



All possible  
Eigenvalues of  
the Hamiltonian

↑  
multiplicity  
of sys  
with  $E$

↑  
multiplicity  
of Reservoir  
with  $(U_{TOT} - E)$

(7)

$$(2) P(\text{any accessible } \mu \text{ state with } U_{TOT}) = \frac{1}{\sum \Omega(E) \Omega_R(U_{TOT} - E)}$$

this depends on Stat Mech Postulate

and fact ~~that~~ system & Reservoir MACROSCOPIC

— What is the prob that SYSTEM is in a

$\mu$  STATE WITH SOME PARTICULAR  $E = E_s$

↳ follows from (2)

↳ system is  $E_s$   $\mu$  STATE

↳ Reservoir  $U_{TOT} - E_s$   $\mu$  STATE

↳ there are  $\Omega_R(U_{TOT} - E_s)$   
 $\mu$  states of R

$$P \left( \begin{array}{c} \text{SYSTEM IN} \\ \text{A STATE} \\ \text{WITH } E_s \end{array} \right) = P \left( \begin{array}{c} \text{SYSTEM + R} \\ \text{IN} \\ \text{ANY} \\ \text{STATE} \end{array} \right) \times \underbrace{\Omega_R (U_{TOT} - E_s)}_{\text{# of } \mu\text{STATES OF SYSTEM + R, such that system is in } \mu\text{STATE WITH } E_s}$$

Prob system in thermodynamic Equilibrium with R

# of  $\mu$ STATES OF SYSTEM + R, such that system is in  $\mu$ STATE WITH  $E_s$

$$P(E_s) = \frac{\Omega_R (U_{TOT} - E_s)}{\sum_E \Omega(E) \Omega_R (U_{TOT} - E)}$$

Only depends on  $E_s$  NOT on any other details of  $\mu$ STATE

All possible energies system can have

↓  
It is just a NORMALIZATION FACTOR



Normalization cancels out for Ratios

$$\frac{P(E_{s1})}{P(E_{s2})} = \frac{\Omega_{LR}(U_{TOT} - E_{s1})}{\Omega_{LR}(U_{TOT} - E_{s2})}$$

we showed weeks ago.

$$\Omega_{LR} = e^{S_R/k} \rightarrow S_R = k \ln \Omega_{LR}$$

$$\frac{P(E_{s1})}{P(E_{s2})} = \frac{\exp(S_R(U_{TOT} - E_{s1})/k)}{\exp(S_R(U_{TOT} - E_{s2})/k)}$$

$$= \exp\{S_R(U_{TOT} - E_{s1}) - S_R(U_{TOT} - E_{s2})\}$$

R is VERY BIG — changes in  $E_s$  only change  $U_{TOT}$  by small amount  
 ↓  
 Expand.

$$S_R(U_{TOT} - E_{s1}) \approx S_R(U_{TOT}) - E_{s1} \frac{\partial S_R(U_{TOT})}{\partial U_R}$$

$$S_R(U_{TOT} - E_{s2}) \approx S_R(U_{TOT}) - E_{s2} \frac{\partial S_R(U_{TOT})}{\partial U_R}$$

$$\frac{P(E_{s1})}{P(E_{s2})} \approx \exp \left[ \frac{1}{k} \left\{ S_R(U_{TOT}) - E_{s1} \frac{\partial S_R}{\partial U_R}(U_{TOT}) \right\} - \frac{1}{k} \left\{ S_R(U_{TOT}) - E_{s2} \frac{\partial S_R}{\partial U_R}(U_{TOT}) \right\} \right]$$

$$= \exp \left[ - \frac{1}{k} (E_{s1} - E_{s2}) \frac{\partial S_R}{\partial U_R}(U_{TOT}) \right]$$

this is just  $\frac{1}{T_R} = \frac{1}{T}$

Heat Bath at Constant Temp.

Distribution of Probabilities of system being in some  $\mu_{STATE}$ , only depends on Temp of Heat Bath

$$\frac{P(E_{s1})}{P(E_{s2})} = e^{- (E_{s1} - E_{s2}) / kT}$$

$$\frac{P(E_{s1})}{e^{-E_{s1}/kT}} = \frac{P(E_{s2})}{e^{-E_{s2}/kT}}$$

This holds for 2 states with ARBITRARY

$E_{s1}$  and  $E_{s2}$ .

↳ so  $\frac{P(E_{s1})}{e^{-E_{s1}/kT}}$  can not depend on energy of  $\mu$  STATE.

generally

$$\frac{P(E_s)}{e^{-E_s/kT}} = Z^{-1}$$

$$P(E_s) = \frac{e^{-E_s/kT}}{Z}$$

Probability that system of T, V, N in some  $\mu$  STATE with energy  $E_s$

Boltzmann Distribution  
Canonical Distribution

What is Z?

- If sum  $P(E_s)$  over all  $\mu$  STATES, and all energies = 1  $\leftarrow$  SYSTEM EXISTS IN SOME STATE

-  $\mu$  state of system is determined by quantum numbers  $(\vec{n}_1, \dots, \vec{n}_N)$  for Ideal Gas.

Energy of  $\mu$  STATE

$E(\vec{n}) = \frac{\pi^2 \hbar^2}{L} \frac{1}{2m} \sum_{i=1}^N \vec{n}_i^2$  quantum #s of  $\mu$  STATES

Many  $\mu$  STATES have SAME ENERGY  $\rightarrow$  drop "s"

$P(E) = \frac{1}{Z} e^{-E/KT}$

$1 = \sum_E P(E) \Omega(E)$  number of  $\mu$  STATES with energy E

energies system can have

$$1 = \sum P(E) N(E)$$

$$= \sum \frac{1}{Z} e^{-E/kT} \cdot N(E)$$

$$= \frac{1}{Z} \sum e^{-E/kT} \cdot N(E)$$

$$Z = \sum_E N(E) e^{-E/kT}$$

allowed energies of system

number of  $\mu$ STATES with energy  $E$

↳ this is  $\Omega(E)$

Can write this as :-

$$Z = \sum_n e^{-E(n)/kT}$$

Sum over all possible quantum numbers

energy of  $\mu$ STATE with quantum number  $n$ .

Can Regard  $Z$  as:-

① Sum over Spectrum (Eigenvalues)

of a system, includes degeneracy

$N(E) \rightarrow$  # of  $\mu$  STATES with  $E$

② Sum over quantum numbers of all  $\mu$  states (= eigenstates of  $\hat{H}$ )

$$\textcircled{1} P \left( \begin{array}{c} \text{any } \mu \text{ STATE} \\ \text{with } E \\ \text{@ } T \end{array} \right) = \frac{1}{Z} e^{-E/kT}$$

$$\textcircled{2} P \left( \begin{array}{c} \text{@ given } T \\ \text{system} \\ \text{has } E \end{array} \right) = \frac{1}{Z} N(E) e^{-E/kT}$$

↑  
number of  $\mu$  STATES with energy  $E$

$$\textcircled{2} \rightarrow = \frac{1}{Z} \Omega(E) e^{-E/kT}$$

$$\uparrow$$

$$\frac{S(E)}{k}$$

$$= \frac{1}{Z} e^{-\left[ \frac{S(E)}{k} - E/kT \right]}$$

or  $P(\text{system has } E \text{ @ given } T) = \frac{1}{Z} e^{-\left[ \frac{E - TS(E)}{kT} \right]}$

$$= \frac{1}{Z} e^{-F(E)/kT}$$

$F = E - TS(E)$  Helmholtz Free Energy

Most likely value of  $E$  is the one where  $F$  is MINIMUM

For

$$\boxed{T, V, N}$$

system.

Most likely  $E$  is when the FREE ENERGY  $F$  is minimized.

$$F = E - TS(E)$$

$$F \equiv F(T, V, N)$$

$$F = E - TS(E)$$

$$E \equiv E(T, V, N)$$

By inserting  $\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{V, N}(E, V, N)$

can get  $E \equiv E(T, V, N)$

and plug this back into

$$F = E(T, V, N) - TS(E, V, N)$$

Partial Derivatives of  $F$   
determine average  $E, \mu, \phi$



Compare this to maximizing  $S(E, V, N)$

Partial Derivatives of  $S$  determine  $T, \mu, P$

$S \rightarrow$  THERMODYNAMIC POTENTIAL for  $(E, V, N)$  system

$F \rightarrow$  THERMODYNAMIC POTENTIAL for  $(T, V, N)$  system

$$F = E - TS$$

$$\text{so } \Delta F = \Delta E - S \cdot \Delta T - T \cdot \Delta S$$

$$= \Delta E - S \cdot \Delta T - T \left\{ \right.$$

$$\frac{1}{T} \longrightarrow \left( \frac{\partial S}{\partial E} \right)_{V, N} \cdot \Delta E$$

$$\frac{P}{T} \longrightarrow + \left( \frac{\partial S}{\partial V} \right)_{E, N} \Delta V$$

$$- \frac{\mu}{T} \longrightarrow + \left( \frac{\partial S}{\partial N} \right)_{E, V} \Delta N \left. \right\}$$

$$= \cancel{\Delta E} - \Delta T \cdot S - T \left\{ \frac{1}{T} \cdot \cancel{\Delta E} + \frac{P}{T} \cdot \Delta V - \frac{\mu}{T} \Delta N \right\}$$

$$= \cancel{\Delta E} - S \cdot \Delta T - \cancel{\Delta E} - P \Delta V + \mu \Delta N$$

So  $\Delta F = -S \cdot \Delta T - P \cdot \Delta V + \mu \Delta N$

can also write as

$$\Delta F = \left( \frac{\partial F}{\partial T} \right)_{N, V} \Delta T + \left( \frac{\partial F}{\partial V} \right)_{T, N} \Delta V + \left( \frac{\partial F}{\partial N} \right)_{T, V} \Delta N$$

So

$$\left. \begin{aligned} S &= - \left( \frac{\partial F}{\partial T} \right)_{N, V} \\ P &= - \left( \frac{\partial F}{\partial V} \right)_{T, N} \\ \mu &= \left( \frac{\partial F}{\partial N} \right)_{T, V} \end{aligned} \right\}$$

For a  $T, V, N$  system  $F(T, V, N)$  is

the THERMODYNAMIC POTENTIAL

↳ measuring its PARTIAL DERIVATIVE determines  $S, P, \mu$  in THERMODYNAMIC EQUILIB.

CANONICAL  
( $T, V, N$ )

MICROCANONICAL  
( $E, V, N$ )

$$F(T, V, N) = E - TS$$

↑  
MINIMIZE  $F$

$$S(E, V, N)$$

↑  
MAXIMIZE  $S$

$$S = \left( -\frac{\partial F}{\partial T} \right)_{V, N}$$

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{V, N}$$

$$P = \left( -\frac{\partial F}{\partial V} \right)_{T, N}$$

$$\frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{E, N}$$

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{T, V}$$

$$\frac{\mu}{T} = - \left( \frac{\partial S}{\partial N} \right)_{V, E}$$

# Free Energy $F(T, V, N)$

① \* Minimum  $\rightarrow$  thermodynamic  
Equilibrium state  
at given  $T$   
(eg water, or ice)

② \* Process at fixed  $T$ , change in  $F$

$$\Delta F = \Delta E - T\Delta S$$

1<sup>st</sup> LAW

$$= Q + W - T\Delta S$$

Quasistatic process  $Q = T\Delta S$

$\hookrightarrow F = W$

$\Rightarrow$  Change in FREE ENERGY  $\rightarrow T_{const}$

QUASI STATIC PROCESS = WORK done  
on / or by  
system.

$F =$  "Energy Free to do Work"

PROPERTY ① is most useful.

$$F = E - TS$$

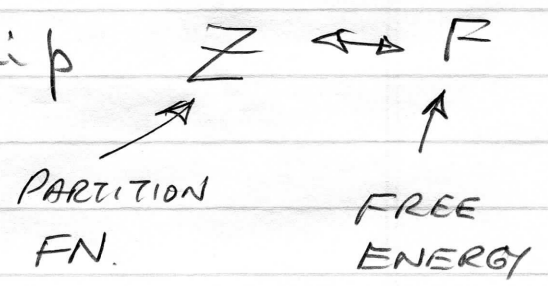
high Temp  
2ND Term  
dominates

$\min(F) \approx \max(S)$   
DISORDERED  
STATE

Low Temp

$F \approx E$   
 $\min(F) = \min(E)$   
↓  
ordered STATE

Look AT Relationship



for TVN system  $Z = \sum_S e^{-E_S/KT}$

determines all  
thermodynamic  
properties.

↑  
sum over  $\mu$  states

have  $\sum_s P(E_s) = 1 = \sum_s \frac{1}{Z} e^{-E_s/kT}$

will show  $F = -kT \ln Z(T, V, N)$

SHOULD  
BE ON  
BOARD

and

$$\left(\frac{\partial F}{\partial T}\right)_{V, N} = -S$$

$$\left(\frac{\partial F}{\partial V}\right)_{T, N} = -P$$

$$\left(\frac{\partial F}{\partial N}\right) = \mu$$

All of  
thermo Dynam  
Properties