

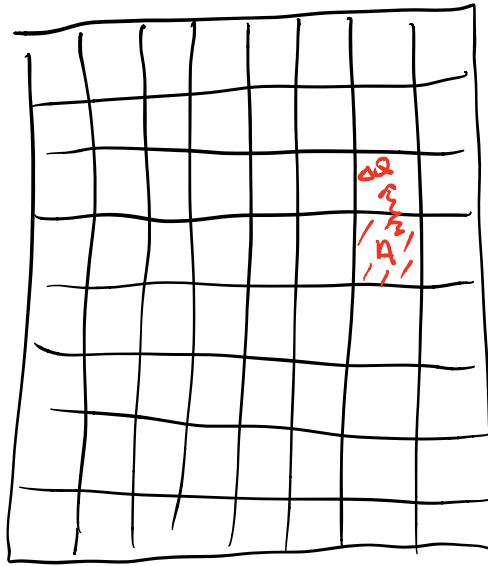
# PHYS 425 - w9ll

Last Time:

Microcanonical Ensemble - For an isolated system  $S = k_B \ln W$  where  $W$  is the no. of quantum states that satisfy all constraints  $(U, V, N, \dots)$  on the system

Today: The Canonical Ensemble

Imagine an ensemble of systems all w/  
identical  $N, V, \vec{B}, \vec{E}$  { in thermal contact  
with each other. As a whole, the ensemble  
acts as a thermal reservoir that maintains  
the temp of each system in the ensemble  
at a const. value  $T$ .



$U_A$  of system  
A can vary

Canonical Ensemble  
useful b/c in many  
experimental meas.  
keep system temp  
const.

$$U_T, \bar{T} \text{ const}$$

The ensemble is isolated from the rest of the universe  $\{\}$  has const. total internal energy  $U_T$ . However, energy can pass from one system in the ensemble to another.

Consider system A w/ internal energy  $U_A$   $\{\}$  the remaining system as the reservoir with internal energy  $U_R = U_T - U_A$ .

The combined system has:

$$W = W(U_A) = W_A(U_A)W_R(U_T - U_A)$$

accessible quantum states.

If one particular state of A is chosen, say

$$\Psi_i \text{ w/ } U_A = E_i \text{ then } W_A(E_i) = 1$$

$$\rightarrow W(E_i) = W_R(U_T - E_i)$$

←  
system A in  
state  $\Psi_i$   
w/ energy  $E_i$

First law of Thermodynamics

$$dU = TdS - PdV$$

$$\therefore \frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_V = k_B \left( \frac{\partial (\ln W_R)}{\partial U_e} \right)_V$$

since for reservoir  $S = k_B \ln W_R$

$$\therefore \frac{1}{k_B T} = \left( \frac{\partial (\ln W_R)}{\partial U_R} \right)_V \quad \{ \text{since } T = \text{const.} \}$$

$$\frac{1}{k_B T} \int dU_R = \int d(\ln W_R)$$

or  $\frac{U_R}{k_B T} = \ln W_R - \underbrace{\ln \gamma}_{\text{integration const.}}$

$$\therefore W_R = \gamma e^{\frac{U_R}{k_B T}}$$

$$\therefore W(E_i) = W_R \underbrace{(U_T - E_i)}_{\substack{\uparrow \\ \text{no. of quantum states}}} e^{\frac{U_T}{k_B T} - \frac{E_i}{k_B T}}$$

of entire ensemble when  
 $U_A = E_i$ .

$$N_{\text{tot}} = \sum_j W(E_j) = \gamma e^{\frac{U_A}{k_B T}} \sum_j e^{-E_j/k_B T}$$

↑      j ←  
 no. of possible quantum states for ensemble when  $U_A$  is allowed to vary.  
 Sum over all possible states of A.

The prob. that system A is in state w/ energy  $E_i$  is :

$$P_i = \frac{W(E_i)}{\sum_j W(E_j)} = \frac{\cancel{\gamma e^{\frac{U_A}{k_B T}}} e^{-E_i/k_B T}}{\cancel{\gamma e^{\frac{U_A}{k_B T}}} \sum_j e^{-E_j/k_B T}}$$

$$\therefore P_i = \frac{e^{-E_i/k_B T}}{Z}$$

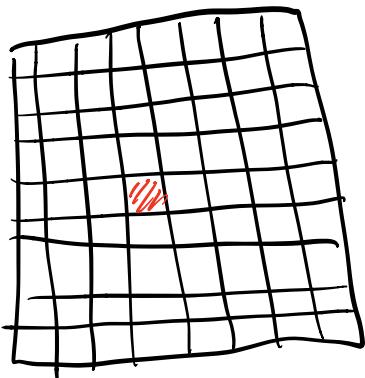
Boltzmann prob. dist'n

$$Z = \sum_i e^{-E_i/k_B T}$$

Partition Function

(sum over quantum mechanical energy states available to system A)

## Entropy & The Canonical Ensemble



System A in contact w/  
 $M-1$  replica systems that  
together form a canonical  
ensemble.

Note  $S = k_B \ln W$  valid for the whole ensemble b/c it is isolated from outside universe. However  $k_B \ln W$  is not valid for system A in the ensemble b/c it exchanges energy w/ adjacent systems.

Of the  $M$  systems, suppose  $n_i$  in quantum state  $\Psi_i$       i.e.  $n_1$  in  $\Psi_1$ ,  
 $n_2$  in  $\Psi_2$   
⋮

In this case,  $\sum_i n_i = M$

There are  $W = \frac{M!}{n_1! n_2! n_3! \dots}$  ways to form  
this arrangement.

$$\begin{aligned}\ln W &= \ln M! - \ln n_1! - \ln n_2! - \ln n_3! \dots \\ &= \ln M! - \sum_i \ln n_i!\end{aligned}$$

Use Stirling's approx for large factorials

$$\ln N! \approx N \ln N - N \text{ when } N \gg 1$$

$$\frac{S_M}{k_B} = \ln W \approx M \ln M - M - \sum_i (n_i \ln n_i - n_i)$$

$$= \underbrace{M \ln M}_{\sum_i n_i} - \sum_i n_i \ln n_i + \sum_i n_i \cancel{M}$$

$$= \sum_i n_i \ln M - \sum_i n_i \ln n_i$$

$$= \sum_i n_i (\ln M - \ln n_i)$$

$$\begin{aligned}\therefore \frac{S_m}{k_B} &\approx -M \sum_i \frac{n_i}{M} (\ln n_i - \ln M) \\ &= -M \sum_i \frac{n_i}{M} \ln \frac{n_i}{M}\end{aligned}$$

for large  $M$   $\frac{n_i}{M} = p_i$  where  $p_i$  is the prob. that any system in the canonical ensemble is in state  $i$ .

$$\frac{S_m}{M} = -k_B \sum_i p_i \ln p_i$$

$\therefore$  average entropy of a system in the canonical ensemble is:

$$S = \frac{S_m}{M} = -k_B \sum_i p_i \ln p_i$$

$p_i$  is given by the Boltzmann dist'n

$$p_i = e^{-\epsilon_i/k_B T} / Z$$

Connection between Q.M. partition fcn  $Z$   
 & Classical Thermodynamic Quantities.

$$\ln p_i = -\frac{E_i}{k_B T} - \ln Z$$

$$\therefore S = k_B \sum_i p_i \left( \frac{E_i}{k_B T} + \ln Z \right)$$

$$= \underbrace{\frac{1}{T} \sum_i p_i E_i}_{\bar{U}} + k_B \ln Z \underbrace{\sum_i p_i}_1$$

average internal  
energy of systems  
in the ensemble

$$\therefore TS = \bar{U} + k_B T \ln Z$$

$$\text{or } \bar{U} - TS = -k_B T \ln Z$$

$$\underbrace{U - TS}$$

$F$  : average value of the Helmholtz Free Energy .

Summary of key results for Canonical ensemble:

$$p_i = \frac{e^{-E_i/k_B T}}{Z} \quad \text{Boltz. dist'n}$$

$$Z = \sum_j e^{-E_j/k_B T} \quad \text{Partition Fun}$$

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

$$F = -k_B T \ln Z$$

$F$  can be measured/deduced experimentally.

∴ Partition fun is a link between the quantum mechanical energy states of

a system & the macroscopic (observable) thermodynamic behaviour of the system.

To experimentally deduce F

① Meas.  $C_V$  vs T

② Use  $C_V = \left(\frac{\partial U}{\partial T}\right)_V$  to find U

③ use  $C_V = T \left(\frac{\partial S}{\partial T}\right)_V$  to find S

Find  $F = U - TS$ .

Relation between  $F(z)$  & other thermodynamic quantities.

$$F = U - TS$$

$$\begin{aligned} dF &= dU - TdS - SdT \\ &= (\cancel{TdS} - PdV) - \cancel{TdS} - SdT \end{aligned}$$

$$\therefore dF = -PdV - SdT$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \quad S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_V = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_V$$

How about  $\bar{U} = TS + F$

$$\therefore \bar{U} = -T \left( \frac{\partial F}{\partial T} \right)_V + F$$

use  $F = -k_B T \ln Z$

$$\rightarrow \frac{\partial F}{\partial T} = -k_B \ln Z - k_B T \left( \frac{\partial (\ln Z)}{\partial T} \right)_V$$

$$\rightarrow \bar{U} = \cancel{k_B T \ln Z} + k_B T^2 \left( \frac{\partial (\ln Z)}{\partial T} \right)_V - \cancel{k_B T \ln Z}$$

$$\therefore \bar{U} = k_B T^2 \left( \frac{\partial (\ln Z)}{\partial T} \right)_V$$

Once we know  $Z$ , can calc.  $F \& \bar{U}, P, S, C_V, \dots$