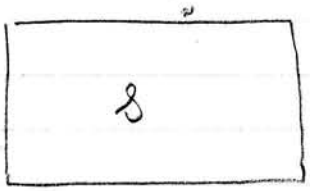
Lecture 7

We've dealt with 2 statistical ensembles so far

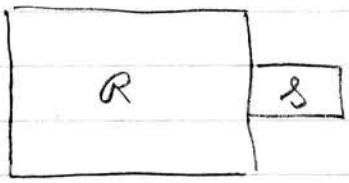
Microcanonical ensemble :



S is isolated so:
U_S is fixed (V_S also.*)

We showed that S_S increases until equilibrium is reached: S_S is an extremum, $dS_S = 0$

Canonical ensemble :



S is in thermal contact with reservoir R so:
$T = T_S = T_R$ is fixed (V_S also*)

$U = U_R + U_S$ is also fixed
but U_R, U_S can vary

Total system $R+S$ is isolated so S_{R+S} is an extremum

But, is there a quantity of the system S alone that is an extremum? We don't care about R so we don't want to have to calculate S_R!

$$dS_{R+S} = dS_R + dS_S$$

$$dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$$

$$= \frac{1}{T} dU + \underbrace{\frac{P}{T} dV}_{0 \text{ if } V \text{ is fixed}}$$

* Again we consider that N is fixed

$$\therefore \quad dS_{R+S} = dS_R + dS_S$$

$$= \frac{dU_R}{T_R} + dS_S \qquad \text{but} \quad U = U_R + U_S$$

$$\text{so} \quad 0 = dU_R + dU_S$$

$$T = T_S = T_R$$

$$= -\frac{dU_S}{T} + dS_S$$

$$= -T\, d\underbrace{(U_S - TS_S)}$$

This quantity is a property of S alone
And if S_{R+S} is an extremum, so must $U_S - TS_S$ by this equality

Define Helmholtz free energy

$$\boxed{F \equiv U - TS}$$

At equilibrium $dS_{R+S} = 0 = -T\, dF_S$
Notice that S_{R+S} is a maximum, but − sign means F_S is a minimum

So in canonical ensemble F of system S tends to decrease until a minimum is reached

Can we write a thermodynamic identity for F?

$$dF = dU - T\,dS - S\,dT \qquad \text{but} \quad dU = T\,dS - p\,dV$$

$$= \cancel{T\,dS} - p\,dV - \cancel{T\,dS} - S\,dT$$

$$= -S\,dT - p\,dV$$

$$= \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

$\therefore \quad F = F(T, V)$ Makes sense. Canonical ensemble is a constant T, V ensemble

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

In microcanonical ensemble $S_g = k_B \ln \Omega_g$

Suggests that F_g and Z_g in canonical ensemble are related (recall that Z_g is like Ω_g in counting states)

Propose that $F_g = -k_B T \ln Z_g$. Let's check

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

Show that $\tilde{F} = -k_B T \ln Z$ satisfies this equation

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

$$= -k_B \ln Z + \frac{1}{T} \frac{\partial}{\partial \beta} \ln Z \qquad \frac{\partial}{\partial T} = \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} = -\frac{1}{k_B T^2} \frac{\partial}{\partial \beta}$$

$$= \frac{\tilde{F}}{T} - \frac{U}{T} \quad \checkmark$$

So $F, \tilde{F}$ satisfy the same 1st-order differential eq'n In principle $\tilde{F} = F + \text{const.}$ To show $\tilde{F} = F$ I must check that they match for one value of T. Let's take T=0

$$F(T=0) = U(T=0)$$

$$\tilde{F}(T=0) = \lim_{T \to 0} -k_B T \ln Z = \lim_{T \to 0} -k_B T \ln \sum_i e^{-E_i / k_B T}$$

As $T \to 0$ only 1st term in Z, with lowest energy (the ground state) will contribute

$$Z(T\to 0) = e^{-E_0/k_BT} + \underbrace{e^{-E_1/k_BT} + \cdots}_{\text{negligible as } T\to 0} \approx e^{-E_0/k_BT}$$

So $$\tilde{F}(T=0) = \lim_{T\to 0} -k_BT \ln e^{-E_0/k_BT} = E_0 \quad \checkmark$$

$$F = U(T=0) = -\frac{\partial}{\partial\beta} \ln Z(T=0) = -\frac{\partial}{\partial\beta} \ln e^{-\beta E_0} = E_0 \quad \checkmark$$

It matches so

$$\boxed{F = -k_BT \ln Z}$$ very important eq'n

Now we have simple ways to calculate p, S from Z

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{\partial}{\partial V} k_BT \ln Z \qquad S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{\partial}{\partial T} k_BT \ln Z$$

Look at ideal monatomic gas $Z_N = \frac{(n_Q V)^N}{N!}$

$$p = \frac{\partial}{\partial V}\left(k_BT \ln V^N + \cdots\right) = \frac{Nk_BT}{V}$$

$$\therefore \quad pV = Nk_BT \qquad \text{Ideal gas law}$$

$$S = \frac{-\partial F}{\partial T} = \frac{U - F}{T} = \frac{U}{T} + k_B \ln Z \qquad U = \frac{3}{2} N k_B T$$

$$= \frac{3}{2} N k_B + k_B \ln\left(\frac{1}{N!} V^N n_Q^N\right)$$

$$= \frac{3}{2} N k_B + N k_B \ln V + N k_B \ln n_Q \underbrace{- k_B \ln N!}_{-N k_B \ln N + N k_B}$$

$$= \frac{5}{2} N k_B + N k_B \ln\left(\frac{n_Q V}{N}\right)$$

$$S = N k_B \left[\underbrace{\ln\left(\frac{n_Q V}{N}\right)}_{} + \frac{5}{2} \right]$$

$$\frac{n_Q V}{N} = \frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} = \frac{V}{N}\left(\frac{2\pi m}{h^2}\,\frac{U}{\frac{3}{2}N}\right)^{3/2} = \frac{V}{N}\left(\frac{4\pi m U}{3 N h^2}\right)^{3/2}$$

$$\therefore S = N k_B \left[\ln\left[\frac{V}{N}\left(\frac{4\pi m U}{3 N h^2}\right)^{3/2} \right] + \frac{5}{2} \right]$$

This is the Sackur-Tetrode eq'n, which we derived earlier (Lecture 4)

Before we go on, let's summarize

Microcanonical ensemble

For isolated system S:

Fixed: U, V

Extremum: $S(U,V)$ maximum

Counting states:

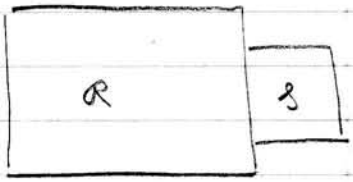
$$\Omega = \sum_{\text{States } i} 1$$

$$S = k_B \ln \Omega$$

$$dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$$

$$= \frac{1}{T} dU + \frac{p}{T} dV$$

Canonical ensemble



For system S in contact with R:

Fixed: T, V

Extremum: $F(T,V)$ minimum

Counting states:

$$Z = \sum_{\text{States } i} e^{-\beta E_i}$$

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

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

$$= -S\, dT - p\, dV$$

Gibbs's paradox + entropy of mixing

We've encountered $N!$ factor due to indistinguishability:

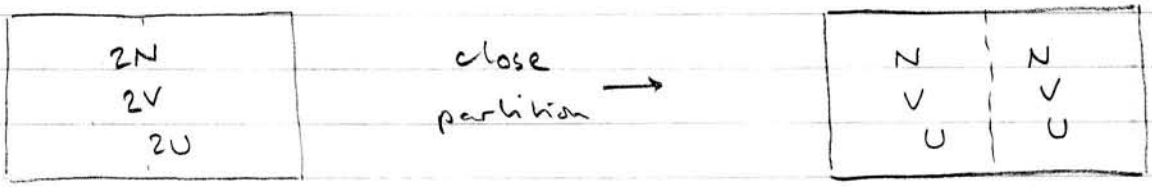
$Z_N = \frac{Z_1^N}{N!}$ ⇒ What would happen if we ignored it?

$Z_N = Z_1^N$ so $S_{inc} = \frac{3}{2} N k_B + N k_B \ln V + N k_B \ln n_Q$

$$= N k_B \left[\ln (n_Q V) + \frac{3}{2} \right]$$

$$= N k_B \left[\ln \left[V \left(\frac{4\pi m U}{3Nh^2} \right)^{3/2} \right] + \frac{3}{2} \right]$$

What are the consequences?
Consider a container with a gas of identical particles



Partition is closed so ½ are on each side

Entropy of both should be the same but, ignoring $N!$ factor

$$S_{inc}^i = (2N) \times k_B \left[\ln \left[2V \left(\frac{4\pi (2U) m}{3(2N) h^2} \right)^{3/2} \right] + \frac{3}{2} \right]$$

$$S_{inc}^f = 2 \times N k_B \left[\ln \left[V \left(\frac{4\pi U m}{3Nh^2} \right)^{3/2} \right] + \frac{3}{2} \right]$$

$$\Delta S_{inc} = S_{inc}^f - S_{inc}^i = -2N k_B \ln 2$$

S decreases!
Violates 2nd law
S_{inc} cannot be right

This is called Gibbs paradox, and is resolved by $N!$ factor

Check:

$$S^i_{correct} = 2N \cdot k_B \left[\ln \left[\frac{V}{N} \left(\frac{4\pi m U}{3 N h^2} \right)^{3/2} \right] + \frac{5}{2} \right]$$

$$S^f_{correct} = 2 \cdot N k_B \left[\ln \left[\frac{V}{N} \left(\frac{4\pi m U}{3 h^2} \right)^{3/2} \right] + \frac{5}{2} \right]$$

$\Delta S = 0$ as it should be. Indistinguishability is essential

Notice form of $S = N f\left(\frac{V}{N}, \frac{U}{N}\right)$ so if $N, U, V \to 2N, 2U, 2V$ then $S \to 2S$

Extensive quantities: S, U, F

Intensive quantities: $p, T, n = \frac{N}{V}$