

8/29

Last time:

$$\beta = \left. \frac{\partial \ln \Omega(E)}{\partial E} \right|_{E=\bar{E}, N, V} \quad (1)$$

Equilibrium: $\beta_1 = \beta_2$

Zeroth Law: there is a common parameter T that characterizes 2 or more systems in thermal equilibrium.

T : temperature

We expect that β will be related to T .

We know from thermodynamics:

$$d\bar{E} = T dS - P dV + \mu dN \quad \therefore \quad E = E(\underbrace{S, V, N}_{\text{extensive variables}})$$

Then: $dS = \frac{1}{T} d\bar{E} + \frac{P}{T} dV - \frac{\mu}{T} dN$ (2')

$$\left. \frac{\partial S}{\partial \bar{E}} \right|_{V, N} = \frac{1}{T} \quad (2)$$

Compare (2) with (1):

$$\text{Then } S \propto \ln \Omega(N, V, \bar{E})$$

$$\frac{1}{T} \propto \beta$$

$$\text{or } \frac{\Delta S}{\Delta(\ln \Omega)} = \frac{1}{\beta T} = \text{constant}$$

Planck noticed this and he defined:

$$S \equiv k \ln \Omega(N, V, E) \quad (2)$$

$$\therefore k = \frac{1}{\beta T} \Rightarrow \boxed{\beta = \frac{1}{kT}} \quad (3)$$

S (entropy) is well defined in terms of Ω .

If $S=0 \Rightarrow \Omega=1$. (one single microstate).

Third law: $S \rightarrow 0$ as $T \rightarrow 0$.

When $T \rightarrow 0$ system \rightarrow ground state
 (usually non-degenerate)
 $S \ll 1$ for degenerate ground states.

Second law: In any process in an isolated system S increases or stays the same.

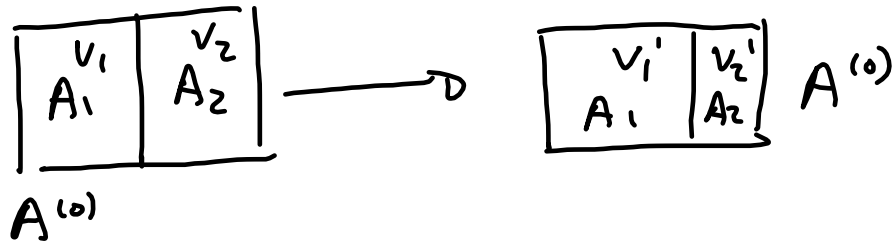
S is related to the amount of information we have on the system.

When the system is ordered, S is small, and Ω is small. For $S=0$, $\Omega=1$ and we know the exact microstate of the system.

When S is large, Ω is very large and there are many microstates compatible with the macrostate. The system is disordered and we ~~do~~ not know in which particular microstate the system is.

More relationships between thermodynamics and statistics:

- Assume that the wall between A_1 and A_2 can move so that $V_1 + V_2 = V^{(0)}$



Now: $\Omega^{(0)}(V^{(0)}, E^{(0)}, V_1, E_1)$

At equilibrium:

$$\left. \frac{\partial \ln \Omega_1}{\partial E_1} \right|_{N_1, V_1, E_1 = \bar{E}_1} = \left. \frac{\partial \ln \Omega_2}{\partial E_2} \right|_{N_2, V_2, E_2 = \bar{E}_2}$$

$$\therefore \beta_1 = \beta_2 \text{ or } T_1 = T_2 \text{ but also}$$

$$\left. \frac{\partial \ln \Omega_1}{\partial V_1} \right|_{N_1, E_1, V_1 = \bar{V}_1} = \left. \frac{\partial \ln \Omega_2}{\partial V_2} \right|_{N_2, E_2, V_2 = \bar{V}_2}$$

following the same steps as for β and knowing that $V_2 = V^{(0)} - V_1$.

Define:

$$\gamma = \left. \frac{\partial \ln \Omega}{\partial V} \right|_{N, E, V = \bar{V}} \quad (4)$$

then at equilibrium

$$\gamma_1 = \gamma_2 \quad \text{if } V_i \text{ changes.}$$

- If particles can go through the wall between A_1 and A_2 :

$$\left. \frac{\partial \ln \Omega_1(N_1, V_1, E_1)}{\partial N_1} \right|_{V_1, E_1, N_1 = \bar{N}_1} = \left. \frac{\partial \ln \Omega_2(N_2, V_2, E_2)}{\partial N_2} \right|_{E_1, V_2, N_2 = \bar{N}_2}$$

define:

$$\xi = \left. \frac{\partial \ln \Omega(N, V, E)}{\partial N} \right|_{V, E, N = \bar{N}} \quad (5)$$

at equilibrium:

$$\xi_1 = \xi_2$$

Thermodynamical meaning of η and μ :

We know that

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

$$\therefore dE = TdS - PdV + \mu dN \quad (6')$$

$$\text{and } dE = \left. \frac{\partial E}{\partial S} \right|_{N,V} dS + \left. \frac{\partial E}{\partial V} \right|_{S,N} dV + \left. \frac{\partial E}{\partial N} \right|_{S,V} dN \quad (6)$$

then comparing 6 and 6':

$$\left. \frac{\partial E}{\partial S} \right|_{N,V} = T \quad \left. \frac{\partial E}{\partial V} \right|_{S,N} = -P \quad \left. \frac{\partial E}{\partial N} \right|_{S,V} = \mu$$

$$E = \underbrace{TS + \mu N - PV}_{\text{conjugate variables}}$$

We defined:

$$S = k \ln \Omega$$

$$dS = \frac{dE}{T} + \frac{P}{T} dV - \frac{\mu}{T} dN \quad (\text{see } \textcircled{2'})$$

$$\eta = \left. \frac{\partial \ln \Omega}{\partial V} \right|_{N, E} = \frac{1}{k} \left. \frac{\partial S}{\partial V} \right|_{N, E} \stackrel{\textcircled{2'}}{=} \frac{P}{kT}$$

$$\therefore \boxed{\eta = \frac{P}{kT}} \quad \textcircled{7}$$

and

$$\xi = \left. \frac{\partial \ln \Omega}{\partial N} \right|_{V, E} = \frac{1}{k} \left. \frac{\partial S}{\partial N} \right|_{V, E} \stackrel{\textcircled{2'}}{=} - \frac{\mu}{kT} \quad \therefore \boxed{\xi = - \frac{\mu}{kT}} \quad \textcircled{8}$$

Then we see that statistical equilibrium means that

$$T_1 = T_2 \quad \mu_1 = \mu_2 \quad \text{and} \quad P_1 = P_2$$

which are the conditions for thermodynamical equilibrium.

Recipe to obtain thermodynamics from sketches of a system:

- 1) For macrostate (N, V, E) find $\Omega(N, V, E)$
- 2) Find $S = k \ln \Omega(N, V, E)$

3) Obtain T , P and μ from derivatives of S with respect to \bar{E} , V and N .

$$\frac{1}{T} = \frac{\partial S}{\partial \bar{E}} \bigg|_{N,V} \quad \textcircled{9} \quad \frac{P}{T} = \frac{\partial S}{\partial V} \bigg|_{N,\bar{E}} \quad \textcircled{10} \quad \frac{-\bar{\mu}}{T} = \frac{\partial S}{\partial N} \bigg|_{V,\bar{E}} \quad \textcircled{11}$$

4) Alternatively from 9, 10 and 11:

$$T = \frac{\partial \bar{E}}{\partial S} \bigg|_{N,V} \quad P = \frac{\frac{\partial S}{\partial V} \big|_{N,\bar{E}}}{\frac{\partial S}{\partial \bar{E}} \big|_{N,V}} = - \frac{\partial \bar{E}}{\partial V} \bigg|_{S,N}$$

$$\frac{\partial x}{\partial y} \bigg|_z = - \frac{\frac{\partial z}{\partial x} \big|_y}{\frac{\partial z}{\partial y} \big|_x} = - \frac{\partial z}{\partial x} \bigg|_y$$

$$\mu = \frac{-\partial S / \partial N |_{V, E}}{\frac{\partial S}{\partial E} |_{V, N}} = \frac{\partial \bar{E}}{\partial N} |_{S, V}$$

You need to obtain $E = E(S, V, N)$ from $S(E, V, N) = k \ln \Omega$.

Other thermodynamical functions:

To obtain P, T and μ from \bar{E} we need to know $\bar{E} = \bar{E}(S, V, N)$ but S is difficult to measure in the lab. What do we do if we know $\bar{E} = \bar{E}(T, V, N)$? We cannot get S !

We can actually define a useful function:

Helmholtz free energy F (A in the book):

$$F = E - TS$$

this will change S to T in the differential expression:

$$dF = dE - TdS - SdT = TdS - PdV + \mu dN - TdS - SdT =$$

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

$$F = F(V, N, T) \quad \text{Now } S = - \left. \frac{\partial F}{\partial T} \right|_{V, N}$$

V, T easier to measure than S .

Gibbs free energy G :

$$G = F + PV = E - TS + PV \equiv \underbrace{TS - PV + \mu N}_E - TS + PV =$$

$$= \mu N$$

$$dG = dF + PdV + VdP = -SdT + VdP + \mu dN$$

$$\therefore G = G(T, P, N)$$

useful when V does not
matter as in phase
coexistence.

Enthalpy H (or heat function)

$$H = E + PV$$

$$dH = dE + PdV + v dP = \underbrace{T dS + \cancel{PdV} + \mu dN + \cancel{PdV} + v dP}_{dE}$$

$$= T dS + v dP + \mu dN$$

$$H = H(S, P, N)$$

$$dH = T dS = dQ \quad (\text{heat exchanged}) \quad \text{if } dP = dN = 0$$

- Knowing two non-conjugate variables in addition to N allows to know everything about a system.

Specific heat:

$$Q = C \Delta T$$

$\overset{\text{heat}}{\curvearrowright}$
 $\underset{T \Delta S}{\underbrace{Q}}$ $\underset{\text{process dependent heat capacity}}{\underbrace{C}}$

$$C_V = T \frac{\partial S}{\partial T} \Big|_{V, N} = \frac{\partial \bar{E}}{\partial T} \Big|_{V, N}$$

$$d\bar{E} = T dS - P dV + \mu dN$$

$= T dS \text{ if } dV = dN = 0$

$$C_P = T \frac{\partial S}{\partial T} \Big|_{P, N} = \frac{\partial H}{\partial T} \Big|_{P, N}$$

The classical ideal gas (monoatomic).

$\Omega(N, V, E)$ can be evaluated

- High T and low density of particles n .
- N non-interacting particles confined to a volume V .
- No spatial correlation between molecules.
(probability of 1 particle at \vec{r} independent of the position of the other particles).
- Negligible interactions.
- Classical because wave packets for each particle
do not overlap.