Thermodynamics 4230

Sept 20, 2011

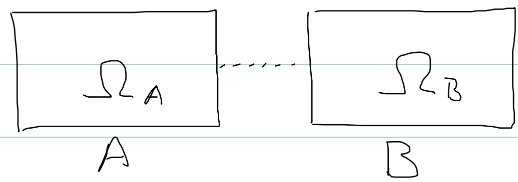
Lecture Set 3

(Leo Radzihovsky)

Interacting Systems

- Temperature
- Pressure
- chemical potential
- Entropy - heat relation
- 3^{rd} law of thermodynamics

1. Temperature in μ-canonical ensemble



$$\Omega_{AB}(E_A, E) = \Omega_A(E_A)\,\Omega_B(E - E_A)$$

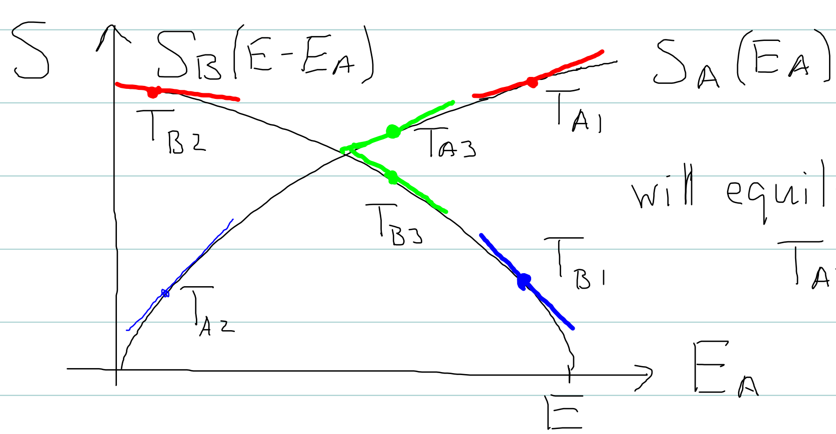
$$\Rightarrow S_{AB}(E_A) = S_A(E_A) + S_B(E - E_A)$$

maximize: $\dfrac{\partial S_{AB}}{\partial E_A} = 0 = \dfrac{\partial S_A}{\partial E_A} + \dfrac{\partial S_B}{\partial E_A}$

$$0 = \frac{\partial S_A}{\partial E_A} - \frac{\partial S_B}{\partial E_B}$$

$\Rightarrow$ in equilibrium / S_{AB} max :

$$\frac{\partial S_A}{\partial E_A} = \frac{\partial S_B}{\partial E_B} \Rightarrow \text{define: } \frac{1}{T} \equiv \frac{\partial S}{\partial E}$$



will equilibrate to $T_{A3} = T_{B3}$

- Einstein Solid:

$$\Omega(q,N) \simeq \left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N \simeq \begin{cases} \left(\frac{N}{q}\right)^q, & q \ll N \\ \left(\frac{q}{N}\right)^N, & q \gg N \end{cases}$$

$$S = k_B \ln \Omega$$

$$E = U = \hbar\omega_0 q$$

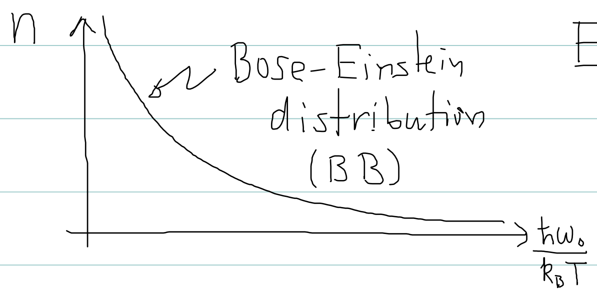
$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{k_B}{\hbar\omega_0} \ln\left(\frac{q+N}{q}\right)$$

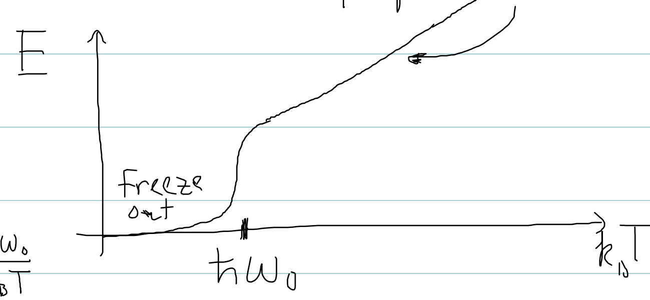
$$\Rightarrow \frac{q}{N} = n = \frac{1}{e^{\frac{\hbar\omega_0}{k_B T}} - 1} \simeq \begin{cases} e^{-\frac{\hbar\omega_0}{k_B T}}, & k_B T \ll \hbar\omega_0 \\ \frac{k_B T}{\hbar\omega_0}, & k_B T \gg \hbar\omega_0 \end{cases}$$

$$\Rightarrow E = \hbar\omega_0 n N = \frac{\hbar\omega_0 N}{e^{\frac{\hbar\omega_0}{k_B T}} - 1} \simeq \begin{cases} N\hbar\omega_0 e^{-\hbar\omega_0/k_B T}, & T \text{ low} \\ k_B T N, & T \text{ high} \end{cases}$$

freeze out for $T \ll \hbar\omega_0/k_B$

equipartition



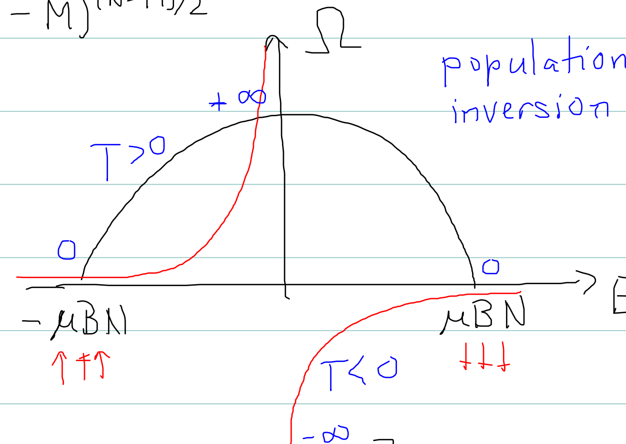


- Ising paramagnet: $\uparrow\ \uparrow\ \uparrow\ \downarrow\ \downarrow\ \uparrow\ \uparrow\ \downarrow\ \uparrow$ $\quad B$

$$\Omega(q,N) = \frac{(2N)^N}{(N+M)^{(N+M)/2}\,(N-M)^{(N-M)/2}}$$

$$S = k_B \ln \Omega$$

$$E = -\underset{g\mu_B}{\mu} B \cdot \underset{\text{net \# of } \parallel B \text{ moments}}{M}$$

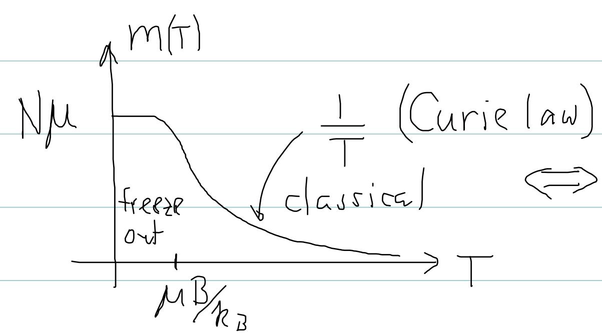


$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{k_B}{\mu B\, 2}\left[\ln(N-M) - \ln(N+M)\right]$$

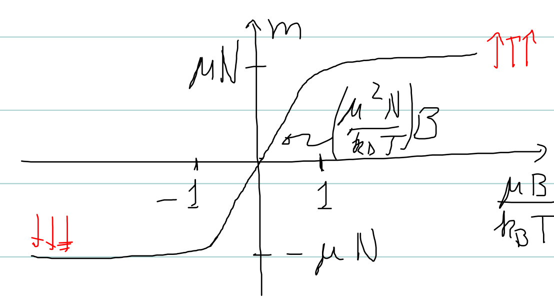
$$\Rightarrow \quad \frac{N-M}{N+M} = e^{\frac{2\mu B}{k_B T}} \Rightarrow \frac{M}{N} = \frac{e^{\frac{\mu B}{k_B T}} - e^{-\frac{\mu B}{k_B T}}}{e^{\frac{\mu B}{k_B T}} + e^{-\frac{\mu B}{k_B T}}} = \tanh\left(\frac{\mu B}{k_B T}\right)$$

$$m = \mu M = \mu N \tanh\frac{\mu B}{k_B T} = \begin{cases} \mu N, & k_B T \ll \mu B, \text{ low } T \\ \left(\dfrac{N\mu^2}{k_B T}\right) B, & k_B T \gg \mu B, \text{ high } T \end{cases}$$

$$(E = -m B)$$

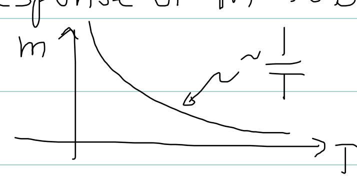


$\Longleftrightarrow$



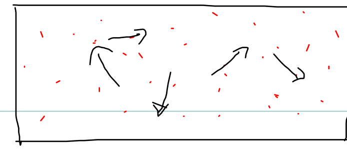
magnetic susceptibility (response of m to B)

$$\chi = \frac{\partial m}{\partial B} \xrightarrow[\text{high } T]{} \frac{\mu^2}{k_B T}$$



general prop. of classical PM.

• Boltzmann gas:



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

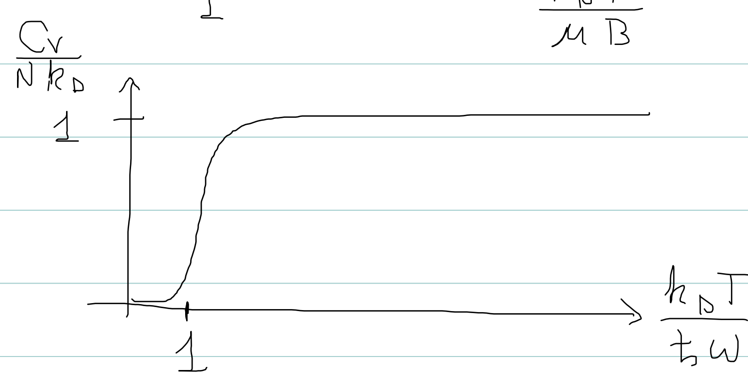
$$= N k_B \ln V + N k_B \ln E^{3/2} + \text{fnc independent of } V, E)$$

$$\Rightarrow \frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{V,N} = \frac{3}{2} \frac{N k_B}{E} \Rightarrow \underbrace{E = \frac{3}{2} N k_B T}_{\text{equipartion}} \checkmark$$

$$C_V = \frac{\partial E}{\partial T} = \frac{3}{2} N k_B \checkmark$$

cf. Ising PM:

• Einstein solid:



heat & entropy: $E \equiv U$

$$\frac{1}{T} = \frac{\partial S}{\partial U} \Rightarrow dS = \frac{dU}{T} \underset{\text{if } W=0}{=} \frac{Q}{T}$$

$$\boxed{dS = \frac{Q}{T}}$$ ← only for reversible process

if $T = \text{const}$ (e.g. 1st order transition / melting, vaporiz)

$$\Rightarrow \Delta S = \frac{Q}{T}$$

measure $\Delta S = \int dS = \int_{T_i}^{T_f} dT \, \frac{C_V}{T}$

$$S_f - S(0) = \int_0^{T_f} \frac{C_V}{T} \, dT$$

$S(0) = 0$, since (typically) unique q.m. ground state

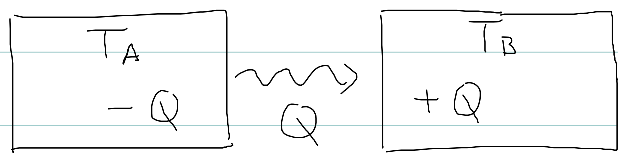
$\Rightarrow \Omega = 1 \Rightarrow S_{T=0} = \ln 1 = 0$, e.g. $\uparrow\uparrow\uparrow\uparrow\uparrow$

$$\Rightarrow \boxed{S(T=0) = C_V(T=0) = 0}$$ 3rd law of thermodynamics

Entropy change

Carried by heat Q

irreversible process:



$\Rightarrow \Delta S_A = -\dfrac{Q}{T_A}$ ↘ $\Rightarrow \Delta S = \Delta S_A + \Delta S_B$

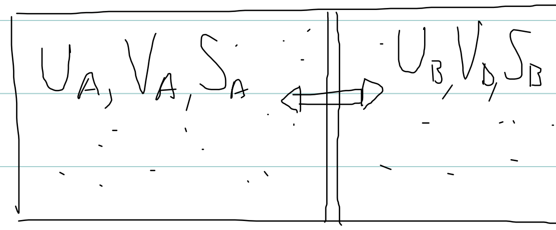
$\Delta S_B = \dfrac{Q}{T_B}$ ↗ $\Delta S = Q\left(\dfrac{1}{T_B} - \dfrac{1}{T_A}\right) \ge 0$

S - increases (irreversible)
or stays the same (reversible)

$\boxed{\Delta S \ge \dfrac{Q}{T}}$ 2^{nd} law of thermodynamics

Mechanical Equilibrium – P

$$S_{AB} = S_A + S_B$$



maximize over V_A

fixed U_A :

$$0 = \frac{\partial S_{AB}}{\partial V_A} = \frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_A} = \frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B} = 0$$

$$\Rightarrow \left.\frac{\partial S_A}{\partial V_A}\right|_{U_A, N_A} = \left.\frac{\partial S_B}{\partial V_B}\right|_{U_B, N_B} \text{ in equilibrium}$$

$\Rightarrow \underline{P_A = P_B}$ mechanical equilibrium

where,

$$\boxed{P = T \left.\frac{\partial S}{\partial V}\right|_{U,N}}$$

maximizes total S_{AB}

for ideal gas: $S(U,V) = N k_B \ln V +$ V - independent terms

$$\Rightarrow P = T N k_B \frac{\partial}{\partial V}(\ln V) = k_B T N / V$$

$$\Rightarrow \underline{PV = N k_B T} \checkmark$$

why $P = T \left.\frac{\partial S}{\partial V}\right|_{U,N}$?

A1. By defn & 2^{nd} law: P is what's equal to max S_{AB}.
& agrees w/ convent. defn.

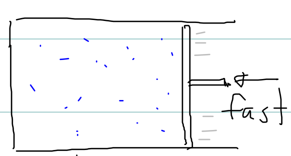
A2. recall 1^{st} law: $dU = Q + W$

$= TdS - PdV$, quasistatic reversible

$$\Rightarrow \underbrace{dS = \frac{1}{T}dU + \frac{P}{T}dV}_{} \underset{\text{calc.}}{\equiv} \left.\frac{\partial S}{\partial U}\right|_{V,N} dU + \left.\frac{\partial S}{\partial V}\right|_{U,N} dV$$

$$\Rightarrow \frac{1}{T} = \left.\frac{\partial S}{\partial U}\right|_{V,N}, \quad \frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_{U,N} \quad \checkmark$$

<u>nonquasistatic process</u>: <u>entropy is created</u>

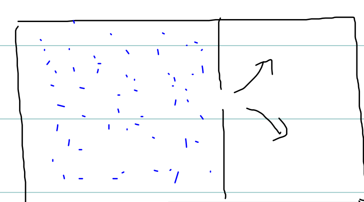


fast compression

$dU = Q + W$

$= TdS - PdV$

but $W \geq -PdV \Rightarrow \underline{Q \leq TdS}$



fast (free) expansion

$Q = 0$

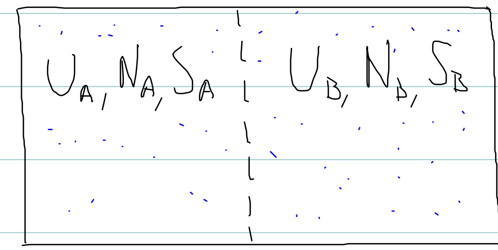
<u>but $S \nearrow$</u> since $V \nearrow$

$\Rightarrow dS > \frac{Q}{T}$

$\Rightarrow$ <u>new entropy S is created</u>

2^{nd} law: S can be created/increased but not decreased — in a closed system

Diffusive equilibrium – μ



- thermal equil: E exchanges until $T_A = T_B$ (max S_{AB})
- mechanical equil: V exchanges until $P_A = P_B$ (max S_{AB})
- diffusive equil: N exchanges until $? = ?$ (max S_{AB})

A: chemical potential μ : $\mu_A = \mu_B$

$$\left.\frac{\partial S_{AB}}{\partial N_A}\right|_{U,V} \underset{max}{=} 0 \Rightarrow \left.\frac{\partial S_A}{\partial N_A}\right|_{U,V} = \left.\frac{\partial S_B}{\partial N_B}\right|_{U,V} \quad (N_A + N_B = N)$$

$$-\frac{\mu_A}{T} = -\frac{\mu_B}{T}$$

i.e. $\boxed{\mu \equiv -T \left.\frac{\partial S}{\partial N}\right|_{U,V}}$ $\Rightarrow \mu_A = \mu_B$ in equilibrium

single species, e.g: liquid water + ice, or water + vapor

if not equil then system w/ bigger $\frac{\partial S}{\partial N}$ will gain particles (since leads to larger ΔS)

$\Rightarrow \mu_A < \mu_B \Rightarrow N_A \nearrow, N_B \searrow$: flow from high to low μ (potential)

Thermodynamic Potential

$$dS = \left(\frac{\partial S}{\partial U}\right)_{N,V} dU + \left(\frac{\partial S}{\partial V}\right)_{N,U} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$$

$$= \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN$$

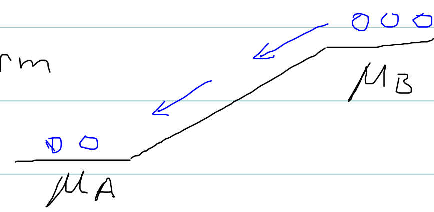
$$\Rightarrow \boxed{dU = T dS - P dV + \mu dN}$$

$-PdV$: mechanical work

μdN: chemical work

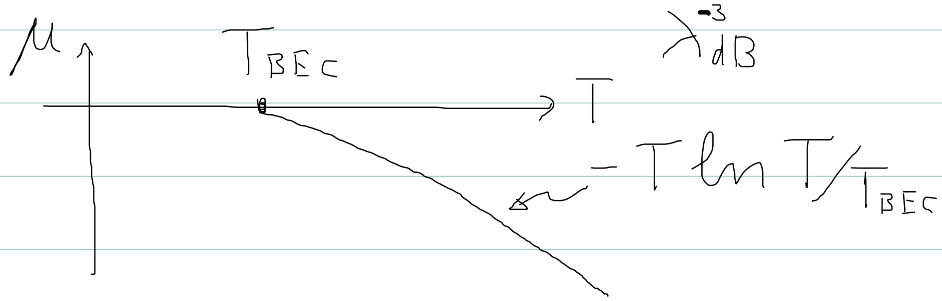
note: $\mu = \left.\frac{\partial U}{\partial N}\right|_{S,V}$ — useful form

μ: energy increase per particle



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

$$\Rightarrow \boxed{\mu} = -k_B T \ln\left[n^{-1} \underbrace{\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2}}_{\lambda_{dB}^{-3}} \right] = \boxed{k_B T \ln\left(n \lambda_{dB}^3\right)}$$



$\mu(n) \nearrow$ w/ $n \nearrow$

- multi-species, e.g. chemical reaction $\Rightarrow$

$$dU = T dS - P dV + \sum_i \mu_i dN_i \Rightarrow \boxed{\mu_i^A = \mu_i^B}$$

(note: $\mu_{chemist} = N_A \mu$)