Phys 301 Fall 2020

Lecture #4 : Interactions Continued (ch 3)

Entropy $S(U,V,N)$ take N constant for now then

$$dS = \underbrace{\left(\frac{\partial S}{\partial U}\right)_{V,N}}_{=\frac{1}{T}} dU + \underbrace{\left(\frac{\partial S}{\partial V}\right)_{U,N}}_{=P/T} dV$$

$\left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{P}{T}$ is plausible. Consider monatomic ideal gas,

$$\Omega = f(N)\left(V U^{3/2}\right)^N$$

$$\frac{S}{k} = \ln \Omega = N \ln V + \frac{3}{2} N \ln U + \ln f(N)$$

$$\frac{1}{k}\left(\frac{\partial S}{\partial V}\right)_U = \frac{N}{V} = \frac{1}{k}\left(\frac{P}{T}\right)$$

then we have the "<u>thermodynamic identity</u>"

$$dS = \frac{dU}{T} + \frac{P}{T} dV$$

or $$dU = T\,dS - P\,dV$$

Valid for any infinitessimal change that leaves T, P well defined called <u>quasistatic</u> process

This identity is not as general as first law which holds for any process

$$\Delta U = Q + W$$

if change is <u>quasistatic</u>, then

$$W = -p\,dV$$
$$Q = T\,dS$$

<u>Non-quasistatic examples</u>

① rapid heating of monatomic gas by contact with heat reservoir, $T_i \to T_f \gg T_i$

$$\Delta U = \frac{3}{2} Nk (T_f - T_i) \quad \text{(equipartition)}$$

$$= Q \qquad (W = 0)$$

$\Delta S \neq \frac{Q}{T}$ how would we define T for this process?

Consider small, quasistatic temperature change ΔT due to heating Δq

$$\Delta q = \frac{3}{2} Nk \Delta T$$

$$\Delta S = \sum \frac{\Delta Q}{T} = \int_{T_i}^{T_f} \frac{3}{2} Nk \frac{dT}{T} = \frac{3}{2} Nk \ln\left(\frac{T_f}{T_i}\right)$$

Since $S(U,V,N)$ state variable, this is the change in ΔS in either case.

Moreover, back to Ω for monatomic gas

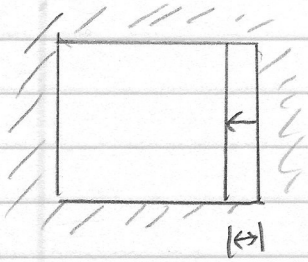
$$\frac{S}{k} = N \ln V + \frac{3}{2} N \ln U + \ln f(N)$$

$$\frac{\Delta S}{k} = \frac{3}{2} N \ln\left(\frac{U_f}{U_i}\right) = \frac{3}{2} N \ln\left(\frac{T_f}{T_i}\right)$$

↑ equipartition

<u>Non quasistatic example 2</u>

rapid compression of thermally isolated gas
Fig 3.16



$\Delta V \ll V$

$$W_{nq} > -p\Delta V = p|\Delta V|$$

↑ non-quasistatic work

if speed of compression ~ molecular speed, gas molecules colliding with piston increase in momentum, giving work $W_{nq} > p|\Delta V|$

Equivalent quasistatic compression requires absorption of heat Q_{qs} from environment

$$\Delta U = W_{nq} = Q_{qs} + p|\Delta V|$$

then assuming change in T is negligible,

$$T\Delta S = \Delta U + p\Delta V = Q_{qs} - p\Delta V + p\Delta V$$

then $$\Delta S = \frac{Q_{qs}}{T}$$

<u>Heat capacity</u> thermodynamic identity

at constant V,

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

at constant pressure,

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$ H is enthalpy

$$H = U + pV$$

$$dH = dU + d(pV) = dU + pdV + Vdp$$

$$= TdS - pdV + pdV + Vdp$$

$$dH = TdS + Vdp = \overset{=T}{\left(\frac{\partial H}{\partial S}\right)_P} dS + \overset{=V}{\left(\frac{\partial H}{\partial P}\right)_V} dP$$

So $H(S,P,N)$ another Legendre transformation change of variables

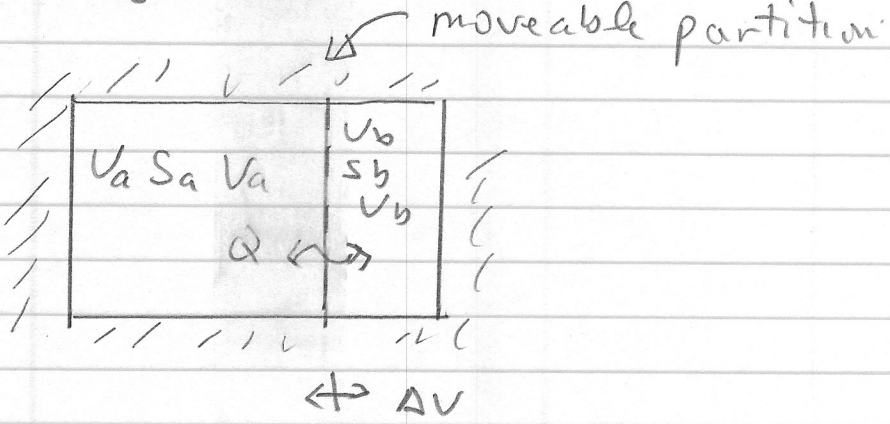
$$dU = TdS - pdV$$

$$U(S,V,N) \xrightarrow[V \to P]{} H(S,P,N)$$

Then

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial H}{\partial S}\right)_P \left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

Mechanical Equilibrium



$$V_a + V_b = \text{const} \Rightarrow dV_a = -dV_b$$
$$S = S_a + S_b$$

at equilibrium $\frac{dS}{dt} = 0$ or $\Delta S = 0$

$$\frac{\partial S}{\partial V_a} = 0 = \frac{\partial S_a}{\partial V_a} + \frac{\partial S_b}{\partial V_a} = \frac{\partial S_a}{\partial V_a} - \frac{\partial S_b}{\partial V_b}$$

then at equilibrium

$$\boxed{\frac{\partial S_a}{\partial V_a} = \frac{\partial S_b}{\partial V_b}} \quad \text{and } T_a = T_b$$

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

general definition of pressure

Diffusion equilibrium

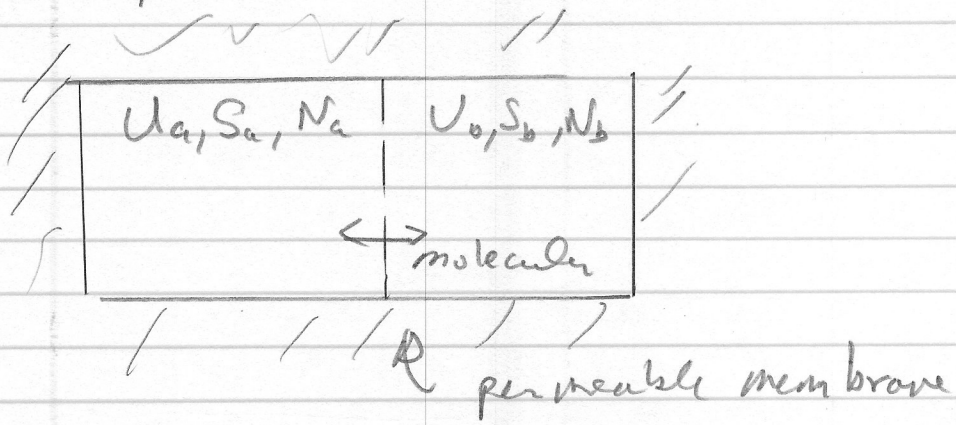
Now take $S(U,V,N)$

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

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

where we have defined the chemical potential

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



$N = N_a + N_b$ constant

in equilibrium what determines N_a, N_b?

$$\frac{dS}{dt} = 0 \qquad \Delta S = 0$$

$$S = S_a + S_b$$

in equilibrium, total entropy is maximal

$$S = S_a + S_b \qquad \frac{dS}{dt} = 0$$

① $\left(\frac{\partial S}{\partial U_a}\right)_{N_a, V_a} = 0$ ② $\left(\frac{\partial S}{\partial V_a}\right)_{N_a, U_a} = 0$

③ $\left(\frac{\partial S}{\partial N_a}\right)_{U_a, V_a} = 0$

from which follows,

① $T_a = T_b$

② $P_a = P_b$

③ $$\frac{\partial (S_a + S_b)}{\partial N_a} = \frac{\partial S_a}{\partial N_a} + \frac{\partial S_b}{\partial N_a}$$

$$\underset{N = N_a + N_b = \text{const}}{=} \frac{\partial S_a}{\partial N_a} - \frac{\partial S_b}{\partial N_b} = 0$$

$$-\frac{\mu_a}{T} = -\frac{\mu_b}{T}$$ from def. of chemical potential

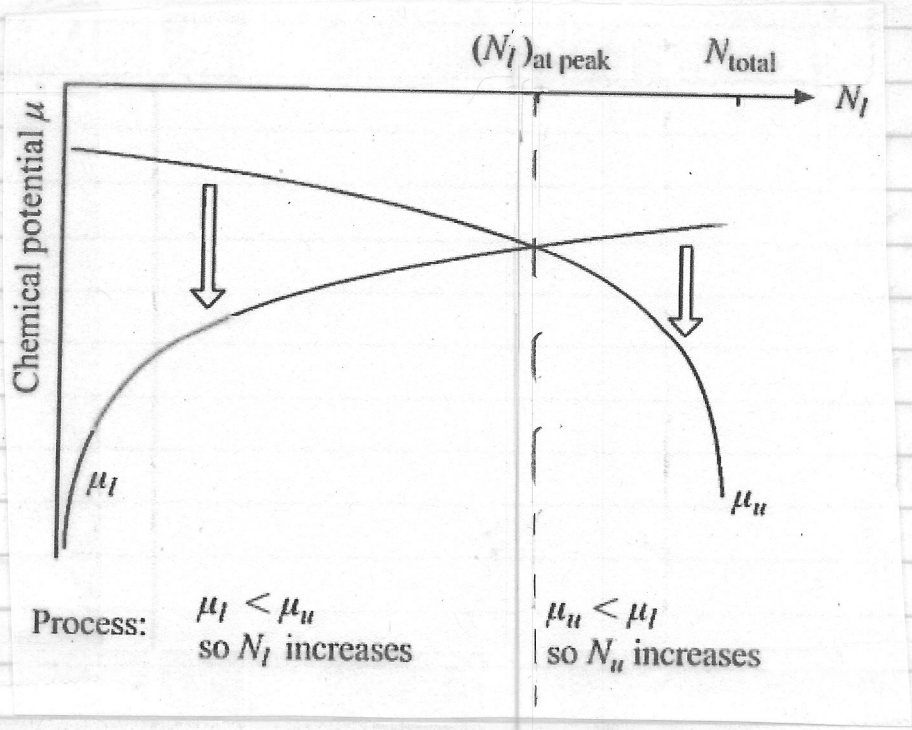
equilibrium condition is chemical potentials are equal.

Choice of sign of <u>chemical potential</u>

maximum entropy ⇒ minimal chemical potential. System evolves to minimum chemical potential in equilibrium, just as mechanical system evolves to minimum of mechanical potential.

From Baierlein. Two volumes "u" and "l"

Δ(chemical potential) analogous to mechanical force driving particle to minimum potential.



Chemical potential has dimension of energy

$$dU = T\,dS - p\,dV + \mu\,dN$$

other relations follow as

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

<u>Example 3.36 large Einstein solid</u>

$N, q \gg 1$ so

$$\Omega(N,q) \cong \left(\frac{q+N}{q}\right)^{q} \left(\frac{q+N}{N}\right)^{N}$$

$$\frac{S}{k} = q \ln\left(1+\frac{N}{q}\right) + N \ln\left(1+\frac{q}{N}\right)$$

$$\frac{1}{k}\frac{\partial S}{\partial N} = \frac{q}{1+\frac{N}{q}}\left(\frac{1}{q}\right) + \ln\left(1+\frac{q}{N}\right)$$

$$+ \left(\frac{N}{1+\frac{q}{N}}\right)\left(\frac{-q}{N^2}\right) = \ln\left(1+\frac{q}{N}\right)$$

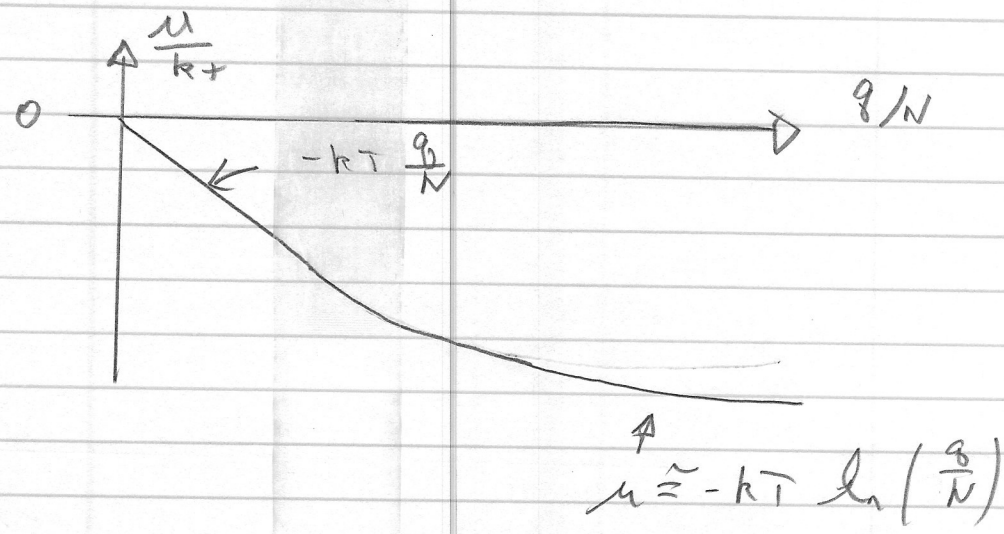
So $\mu = -T\frac{\partial S}{\partial N} = -kT \ln\left(1+\frac{q}{N}\right)$

limits

$q/N \ll 1 \qquad \mu = -kT\,\frac{q}{N}$

$q/N \gg 1 \qquad \mu = -kT \ln\left(\frac{q}{N}\right)$

sketch μ for large Einstein solid



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

Chemical potential of monatomic ideal gas

Sackur-Tetrode:

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

combine as $N^{-5/2}$

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

$[\,] \equiv B$ independent of N

$$\boxed{-\frac{\mu}{kT} = \frac{1}{k}\left(\frac{\partial S}{\partial N}\right)_{U,V}} = \ln B - \frac{5}{2}\ln N - \frac{5}{2} + \frac{5}{2}$$

$$= \ln\left(\frac{B}{N^{5/2}}\right) = \ln\left[\frac{V}{Nh^3}\left(\frac{4\pi}{3} m \frac{U}{N}\right)^{3/2}\right]$$

equipartition $U = \frac{3}{2} NkT$

$$-\frac{\mu}{kT} = \ln\left[\frac{V}{N}\left(\frac{2\pi m kT}{h^2}\right)^{3/2}\right]$$

thermal de Broglie wavelength

$$l_Q \equiv \frac{h}{\sqrt{2\pi m kT}}$$

$$\left[\begin{array}{l} \frac{p^2}{2m} \sim \frac{3}{2} kT \\ p_Q \sim \sqrt{mkT} \\ l_Q = \frac{h}{p_Q} \end{array}\right]$$

then $$\boxed{-\frac{\mu}{kT} = \ln\left(\frac{V}{N}\frac{1}{l_Q^3}\right)}$$

l_Q for N_2 gas at $T = 300K$, $P = 10^5$ Pa

$m(N_2) = 2(14)\,u$ $\qquad uc^2 = 0.9315 \times 10^9$ eV
atomic mass unit

$\hbar c = 2\pi(197\ \text{eV}\cdot\text{nm})$

$$kT\Big|_{298K} = \frac{1}{38.9}\ \text{eV}$$

$$l_Q = \frac{2\pi(197\ \text{eV}\cdot\text{nm})}{\left[2\pi\left(\frac{\text{eV}}{38.9}\right)(28)(0.93\times10^9\ \text{eV})\right]^{1/2}}$$

$$= 1.97\times10^{-2}\left[\frac{2\pi(38.9)}{28(9.3)}\right]^{1/2}\ \text{nm}$$

$$= 0.019\ \text{nm} \cong 0.2\ \text{Å}$$

for 1 mole $N = N_A$, $p = 10^5\ \text{Pa} = 10^5\ \frac{\text{J}}{\text{m}^3}$

$$\frac{V}{N} = \frac{kT}{P} = \frac{1.38\times10^{-23}\ \frac{\text{J}}{\text{K}}\ (300\text{K})}{10^5\,(10^{-9})^3\ \frac{\text{J}}{(\text{nm})^3}}$$

$$= (1.38\times3\times10\ \text{nm})^3 = 41.4\ \text{nm}^3$$

$$\left(\frac{V}{N}\right)^{1/3} = 3.5\ \text{nm} \gg l_Q \qquad \text{classical regime.}$$

$$-\frac{\mu}{RT} = 3\ln\left(\frac{3.5\ \text{nm}}{0.02\ \text{nm}}\right) = 15.5$$

$$\mu = -15.5\left(\frac{1}{40}\ \text{eV}\right) = -0.39\ \text{eV}$$

increasing N @ fixed T increases μ.
increasing density always increases μ. System more likely to give particle to other systems.

Another way to get chemical potential

From $dS = \frac{1}{T} dU + \frac{p}{T} dV - \mu dN$

$$dU = TdS - pdV + \mu dN$$

$U(S, V, N)$

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

Chemical potential and Einstein Solid

$N = 3;\ q = 3 \qquad \Omega(3,3) = \frac{(N+q-1)!}{q!\,(N-1)!} = 10$

for example, micro state

$$*\,|\,**\,|\,|$$

increase N by 1,

$$*\,|\,**\,|\,|\,|$$

$\Omega(3,4) = 5$

to keep Ω the same, must remove 1 unit of energy ε

$$\Omega(2,4) = \frac{(4+2-1)!}{2!\,(4-1)!} = \frac{5\cdot4\cdot3\cdot2}{2\cdot2\cdot3} = 10$$

So

$$\left(\frac{\Delta U}{\Delta N}\right)_S = \frac{-\varepsilon}{1} = \mu$$