I.4.7 An example

Helmholtz free energy

$$F = F(T, V, n) = -nRT - nRT\ln\left[\left(\frac{V}{V_0}\right)\left(\frac{n_0}{n}\right)\left(\frac{T}{T_0}\right)^{3/2}\right]$$

Equation of state: $-P = \left(\frac{\partial F}{\partial V}\right)_{T,n} = -\frac{nRT}{V} \Rightarrow PV = nRT \Rightarrow$ ideal gas

entropy: $S = -\left(\frac{\partial F}{\partial T}\right)_{V,n} = nR + nR\ln\left[\left(\frac{V}{V_0}\right)\left(\frac{n_0}{n}\right)\left(\frac{T}{T_0}\right)^{3/2}\right] + \frac{3}{2}\frac{nRT}{T}$

$$= \frac{5}{2}nR + nR\ln\left[\left(\frac{V}{V_0}\right)\left(\frac{n_0}{n}\right)\left(\frac{T}{T_0}\right)^{3/2}\right]$$

"Sackur - Tetrode equation"

chemical potential: $\mu = \left(\frac{\partial F}{\partial n}\right)_{T,V} = -RT - RT\ln\left[\left(\frac{V}{V_0}\right)\left(\frac{n}{n_0}\right)\left(\frac{T}{T_0}\right)^{3/2}\right] + \frac{nRT}{n}$

$$= -RT\ln\left[\left(\frac{V}{V_0}\right)\left(\frac{n}{n_0}\right)\left(\frac{T}{T_0}\right)^{3/2}\right]$$

Gibbs free energy:

$$G = F + PV = -nRT - nRT\ln\left[\left(\frac{V}{V_0}\right)\left(\frac{n_0}{n}\right)\left(\frac{T}{T_0}\right)^{3/2}\right] + PV$$

$$\overset{V=\frac{nRT}{P}}{=} -nRT\ln\left[\left\{\frac{nRT}{P}\frac{P_0}{n_0RT_0}\frac{n_0}{n}\left(\frac{T}{T_0}\right)^{3/2}\right]= -nRT\ln\left[\left(\frac{P_0}{P}\right)\left(\frac{T}{T_0}\right)^{5/2}\right]$$

check: $G = \mu' N = \mu n$ ✓

Internal energy:

$$U = F + TS = -nRT - nRT\ln\left[\left(\frac{V}{V_0}\right)\left(\frac{n_0}{n}\right)\left(\frac{T}{T_0}\right)^{3/2}\right] + \frac{5}{2}nRT + nRT\ln\left[\left(\frac{V}{V_0}\right)\left(\frac{n_0}{n}\right)\left(\frac{T}{T_0}\right)^{3/2}\right] = \frac{3}{2}nRT$$

solve for temperature as a function of entropy

$$\frac{S}{nR} - \frac{5}{2} = \ln\left[\left(\frac{V}{V_0}\right)\left(\frac{n_0}{n}\right)\left(\frac{T}{T_0}\right)^{3/2}\right]$$

$$\Rightarrow \quad \frac{T}{T_0} = e^{\frac{2S}{3nR} - \frac{5}{3}} \left(\frac{V_0}{V}\right)^{2/3}\left(\frac{n}{n_0}\right)^{2/3}$$

$$U = \frac{3}{2} n R T_0 \left(\frac{V_0}{V}\right)^{2/3}\left(\frac{n}{n_0}\right)^{2/3} e^{\frac{2S}{3nR} - \frac{5}{3}}$$

Enthalpy

$$H = G + TS$$

$$= -nRT \ln\left[\left(\frac{p_0}{p}\right)\left(\frac{T}{T_0}\right)^{5/2}\right] + TS$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_V = nR \ln\left[\left(\frac{p_0}{p}\right)\left(\frac{T}{T_0}\right)^{5/2}\right] + \frac{5}{2}nR$$

$$H = -nRT \ln\left[\left(\frac{p_0}{p}\right)\left(\frac{T}{T_0}\right)^{5/2}\right] + nRT \ln\left[\left(\frac{p_0}{p}\right)\left(\frac{T}{T_0}\right)^{5/2}\right] + \frac{5}{2}nRT$$

$$= \frac{5}{2} nRT$$

check: $\quad H = U + pV \quad \checkmark$

solve for temperature as a function of entropy

$$\frac{S}{nR} - \frac{5}{2} = \ln\left[\left(\frac{p_0}{p}\right)\left(\frac{T}{T_0}\right)^{5/2}\right]$$

$$\Rightarrow \quad \frac{T}{T_0} = e^{\frac{2S}{5nR} - 1}\left(\frac{p}{p_0}\right)^{2/5}$$

$$H = \frac{5}{2} n R T_0 \left(\frac{p}{p_0}\right)^{2/5} e^{\frac{2S}{5nR} - 1}$$

Grand Potential

$$\Omega = F - \mu' N = F - \mu n$$

$$= -nRT - nRT \ln\left[\left(\frac{V}{V_0}\right)\left(\frac{n_0}{n}\right)\left(\frac{T}{T_0}\right)^{3/2}\right] + nRT \ln\left[\left(\frac{V}{V_0}\right)\left(\frac{n}{n_0}\right)\left(\frac{T}{T_0}\right)^{3/2}\right]$$

$$= -nRT$$

check: $\Omega = XY = -PV$ ✓

solve for ~~[illegible]~~ n as a function of μ

$$\frac{V}{V_0}\frac{n}{n_0}\left(\frac{T}{T_0}\right)^{3/2} = e^{-\frac{\mu}{RT}}$$

$$n = n_0 \frac{V_0}{V}\left(\frac{T}{T_0}\right)^{-3/2} e^{-\frac{\mu}{RT}}$$

$$\Omega = -n_0 \frac{V_0}{V} R \left(\frac{T}{T_0}\right)^{-3/2} T e^{-\frac{\mu}{RT}}$$

10/14

I.5 Response functions

- thermodynamic quantities that are easiest to measure
- describe how a state variable changes as experimental parameters are tuned

I.5.1 Thermal response function (heat capacity)

$$\text{“} C = \frac{dQ}{dT} \text{”}$$

different heat capacities if different variables are kept constant while varying temperature.

a) $C_{X,\{N_j\}}$: change in heat as temperature is varied at constant X and $\{N_j\}$

$$dQ = dU - YdX - \sum_j \mu_j' dN_j = \left(\frac{\partial U}{\partial T}\right)_{X,\{N_j\}} dT + \left[\left(\frac{\partial U}{\partial X}\right)_{T,\{N_j\}} - Y\right] dX$$
$$+ \sum_j \left[\left(\frac{\partial U}{\partial N_j}\right)_{T,X,\{N_{i\neq j}\}} - \mu_j'\right] dN_j$$

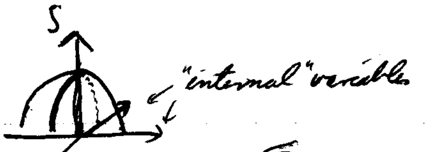
First reading assignment 10/14 (28)

1) How can entropy decrease during fluctuations?
Does it mean the system can move into new equilibrium state with lower entropy?
What about infinite system size?

2) How to go from
$$\Delta S = (\ \ )\Delta U + (\ \ )\Delta V - \sum (\ \ )\Delta N_j$$
to $T_A = T_B$, — ?
is ΔS always 0 or can it be negative?

3) i'th particle, chemical potentials, physical picture (A),
relation between conditions and equalities (B)

ad 1)
- Thermodynamic laws in strict sense apply only to infinite systems, no fluctuations in infinite systems
- finite systems have fluctuations that do not have to respect thermodynamic laws → QM, ideal gas of few particles
- but: system has to return to equilibrium state at <u>fixed</u> external conditions.



ad 2) If any of the ( ) is non-zero,
we can choose a $(\Delta U_A, \Delta V_A, \{\Delta N_j\})$ that increases the entropy
⇒ all ( ) are zero
but, there are higher order terms that can decrease the entropy → next class, picture

ad 3)
wall moveable ⟷ $P_A = P_B$
heat exchange ⟷ $T_A = T_B$
particle exchange ⟷ $\mu_{i,A} = \mu_{i,B}$

osmosis: water/sugar