Chapter 3

Equilibrium occurs when $\dfrac{\partial S_{total}}{\partial q_A} = 0$ ← Einstein solid

generalize a bit

$$\frac{\partial S_{total}}{\partial U_A} = 0$$

$$\frac{\partial (S_A + S_B)}{\partial U_A} = 0$$

$U_B = U - U_A$

$dU_B = -dU_A$

$$\frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A} = 0$$

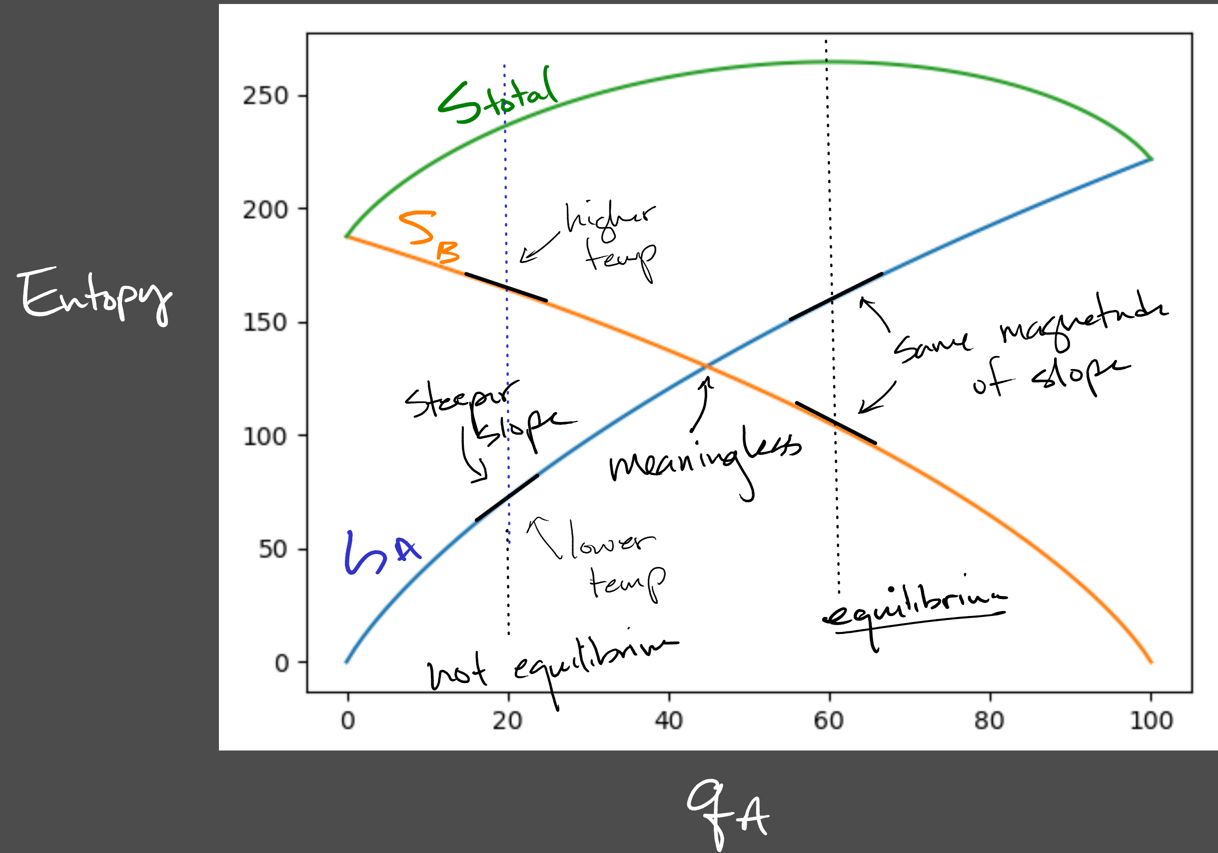
$$\frac{\partial S_A}{\partial U_A} - \frac{\partial S_B}{\partial U_B} = 0$$

$$\boxed{\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}}$$

$$\frac{\partial S}{\partial U} = \frac{1}{T}$$

$$\boxed{T = \left(\frac{\partial S}{\partial U}\right)^{-1}_{N,V}}$$

this the definition of temperature



HW: 1, 3

Anaconda
miniconda

Apply to hot Einstein solid ($q >> N$)

$$\Omega = \left(\frac{eq}{N}\right)^N \qquad q >> N \text{ limit}$$

# of packets of energy

energy of one energy packet

$$U = q \cdot \epsilon$$

$$q = \frac{U}{\epsilon}$$

$$T = \left(\frac{\partial S}{\partial U}\right)^{-1} \qquad S = k_B \ln \Omega = k_B N \ln\left(\frac{eq}{N}\right)$$

$$S = k_B N \left(\ln \frac{U}{N\epsilon} + \cancel{\ln e}^{\,1}\right)$$

$$S = k_B N \ln U - k_B N \ln N\epsilon + k_B N$$

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{k_B N}{U}$$

# of oscillators

$$T = \frac{U}{N k_B} \Rightarrow \underbrace{U = N k_B T}$$

$\hookrightarrow$ Equipartition Theorem

$f = 2$

- $\hookrightarrow$ 1-D kinetic energy
- $\hookrightarrow$ 1-D potential energy

An Einstein solid

# of atoms

$$n = \frac{N}{3} \leftarrow \text{\# of oscillators}$$

$$N = 3n \Rightarrow U = 3 n k_B T$$

What about an ideal gas

Sackur-Tetrode equation

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

$$S = k_B \ln \Omega = k_B \ln V^N + k_B \ln U^{3N/2} + k_B \ln f(N)$$

$$= k_B N \left(\ln V + \frac{3}{2} \ln U + \ln f(N) \right)$$

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{3}{2} \frac{k_B N}{U}$$

$$U = \frac{3}{2} N k_B T \quad \checkmark\checkmark$$

$f = 3 \rightarrow$ 3-D kinetic energy

Entropy + Heat

Experiment to determine heat capacity.

Also have a theory to make a prediction

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

$\hookrightarrow U(T)$

high temp solid

$$C_V = \frac{\partial}{\partial T}(Nk_BT)$$

$$= Nk_B = n_m R$$

ideal gas (monoatomic)

$$C_V = \frac{3}{2}Nk_B = \frac{3}{2}n_m R$$

Review the process for any material to predict heat capacity

1. Use combinatorics + QM to find an expression for Ω in terms of U, V, N etc. } probably impossible!
2. $S = k_B \ln \Omega$
3. $T = \left(\frac{\partial S}{\partial U}\right)^{-1}_{N,V\ etc}$
4. solve for U in terms of T
5. take partial of U w.r.t. $T \rightarrow C_V$

stat mech give an alternative $\rightarrow$ Ch. 6

We can measure S, by going <u>backwards</u>.

$$dS = \underbrace{\frac{\partial S}{\partial U}}_{\frac{1}{T}} \cdot dU$$

$$dS = \frac{dU}{T}$$

constant volume (isochoric)

$$đW = 0$$

$$dU = đQ$$

$$\boxed{dS = \frac{đQ}{T}}$$

original definition of entropy

T does not change much w/ a little $đQ$ added

$$\Delta S = \frac{Q}{T} \Big\} \text{ phase change}$$

rewrite in terms of heat capacity

$$dS = \frac{C_V dT}{T}$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V dT}{T}$$

can be constant but can also be a function of temp itself.

$$đW = pdV$$

$$dU = đQ + đW$$

$$dU = đQ - pdV$$

$$dU = TdS - pdV$$

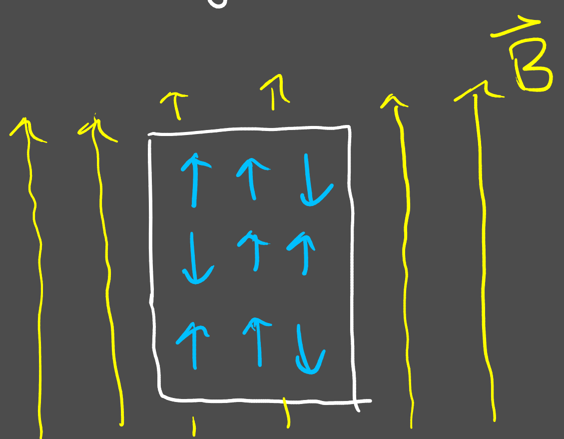
$$S(T_f) - S(0) = \int_0^{T_f} \frac{C_V}{T}\, dT$$

→ need to know all the way to zero.

→ 0 or some constant → residual entropy

→ much experimental data for many substances tabulated by chemists!

Paramagnetism



- dipoles aligned parallel to the $\vec{B}$ have lower energy state
- antiparallel requires U to turn it around
- U is determined by number of $\underbrace{\uparrow \text{ and } \downarrow}_{\text{others are not allowed by QM}}$ dipoles

$$\Omega = \frac{N!}{N_\uparrow!\, N_\downarrow!} = \frac{N!}{N_\uparrow!\,(N-N_\uparrow)!}$$

Energy is dependent $N_\uparrow$ or $N_\downarrow$ and the strength of $\vec{B}$.

↳ energy to flip one dipole = $2\mu B$

$$-\mu B \longrightarrow \underset{0\,J}{|} \longrightarrow \mu B$$

$\uparrow$ up dipole (at $-\mu B$)

$\downarrow$ down dipole (at μB)

$$\Delta U = 2\mu B$$

$$U = \mu B(\underbrace{N_\downarrow}_{N-N_\uparrow} - N_\uparrow) = \mu B(N - 2N_\uparrow)$$

magnetization = total magnetic moment

$$M = \mu(N_\uparrow - N_\downarrow) = \frac{U}{B}$$

goal: how does M + U depend on temperature?

$$T = \left(\frac{\partial S}{\partial U}\right)^{-1}$$

$$S = k_B \ln \Omega$$

$$\Omega = \frac{N!}{N_\uparrow (N-N_\uparrow)!}$$

$N_\uparrow$ is macrostate

$N = 100$ dipoles

↓

plotted in jupyter

Analytic Solution

$$\frac{S}{k_B} = \underbrace{\ln N! - \ln N_\uparrow! - \ln (N-N_\uparrow)!}$$

↓

$$\frac{S}{k_B} = N \ln N - N_\uparrow \ln N_\uparrow - (N-N_\uparrow)\ln(N-N_\uparrow)$$

$$\frac{1}{T} = \frac{\partial S}{\partial U} \qquad U = \mu B (N - 2N_\uparrow) \Rightarrow N_\uparrow = \frac{N}{2} - \frac{U}{2\mu B}$$

$$\frac{1}{T} = \frac{\partial S}{\partial N_\uparrow} \cdot \frac{\partial N_\uparrow}{\partial U} \Rightarrow \frac{k_B}{2\mu B} \cdot \ln\left(\frac{N - U/\mu B}{N + U/\mu B}\right) = \frac{1}{T}$$

Solve for U

$$e^{i\theta} = \cos\theta + i\sin\theta$$

$$U = N\mu B \left(\frac{1 - e^{2\mu B/kT}}{1 + e^{2\mu B/kT}} \right)$$

$$\underbrace{\left(\frac{1 - e^{2\mu B/kT}}{1 + e^{2\mu B/kT}} \right)}_{-\tanh\left(\frac{\mu B}{kT}\right)}$$

$$\rightarrow U = -N\mu B \tanh\left(\frac{\mu B}{kT}\right)$$

$$M = \frac{U}{B}$$

$$M = -N\mu \tanh\left(\frac{\mu B}{kT}\right)$$