

Chapter 3

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

↓ $\frac{\partial q_A}{\partial U_A}$
generalize a bit

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

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

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

$$U_B = U - U_A$$

$$dU_B = -dU_A$$

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

$$\left| \frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \right|$$

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

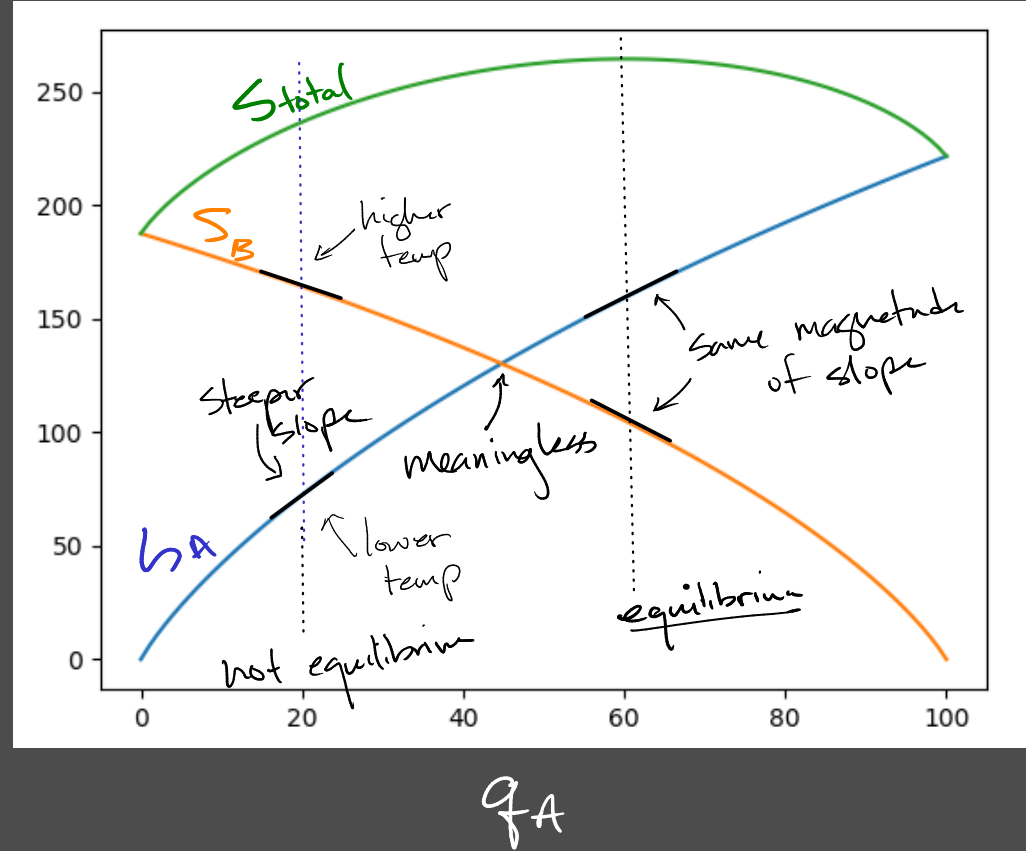
$$T = \left(\frac{\partial S}{\partial U} \right)^{-1}_{N,V}$$

↑ this the definition of
temperature

HW: 1, 3

Anaconda
miniconda

Entropy



Apply to hot Einstein solid ($q \gg N$)

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

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

$$S = k_B \ln \Omega = k_B N \ln \left(\frac{eq}{N}\right)$$

of packets of energy \swarrow energy of one energy packet

$$U = q \cdot \epsilon$$

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

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

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

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

of oscillators

$$T = \frac{U}{Nk_B} \Rightarrow U = Nk_B T$$

Equipartition Theorem

$$f = 2$$

1-D kinetic energy

1-D potential energy

An Einstein solid

of atoms

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

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

What about an ideal gas

Sackur-Tetrode equation

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

$$\begin{aligned} S &= k_B \ln \Omega = k_B \ln V^N + k_B \ln U^{3N/2} + k_B \ln f(N) \\ &= k_B N \left(\ln V + \frac{3}{2} \ln U + \ln f(N) \right) \end{aligned}$$

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

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

$f=3 \rightarrow 3\text{-D kinetic energy}$

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

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

$$= Nk_B = n_m R$$

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

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 backwards.

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

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

constant volume (isochoric)

$$\pm W = 0$$

$$dU = \pm Q$$

$$dS = \frac{\pm Q}{T}$$

original definition
of entropy

T does not change
much w/ a little $\pm Q$
added

rewrite in terms of heat capacity

$$\Delta S = \frac{Q}{T} \quad \left. \vphantom{\Delta S} \right\} \text{phase change}$$

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

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

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

$$\pm W = p dV \rightarrow$$

$$dU = \pm Q + \pm W$$

$$dU = \pm Q - p dV$$

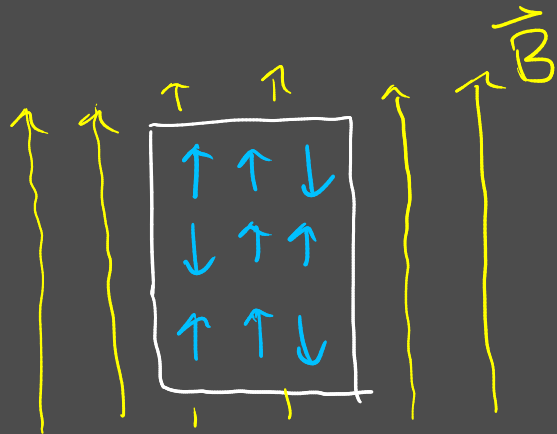
$$dU = T dS - p dV$$

$$S(T_f) - S(0) = \int_0^{T_f} \frac{C_v}{T} dT \rightarrow \text{need to know all the way to zero.}$$

$\rightarrow 0$ or some constant \rightarrow residual entropy

\rightarrow much experimental data for many substances tabulated by chemists!

Paramagnetism

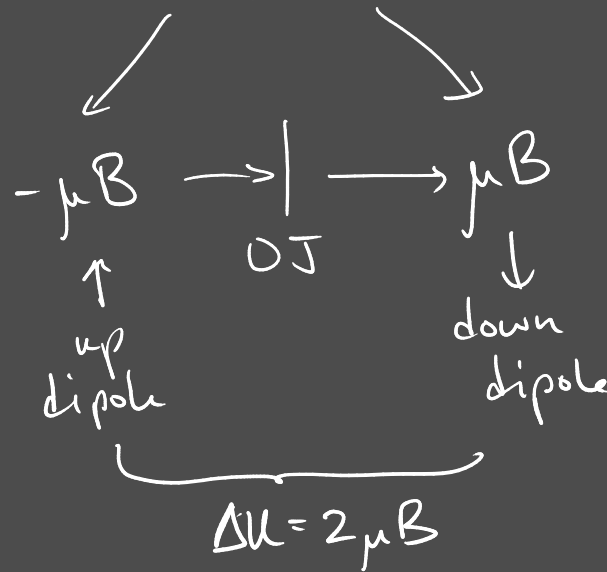


- dipoles aligned parallel to the \vec{B} have lower energy state
 - antiparallel requires U to turn it around
 - U is determined by number of \uparrow and \downarrow dipoles
- others are not allowed by QM

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

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

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



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

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
