

# Chapter 3

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

$\downarrow$   
generalize a bit

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

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

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

$$U_B = U - U_A$$

$$dU_B = -dU_A$$

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

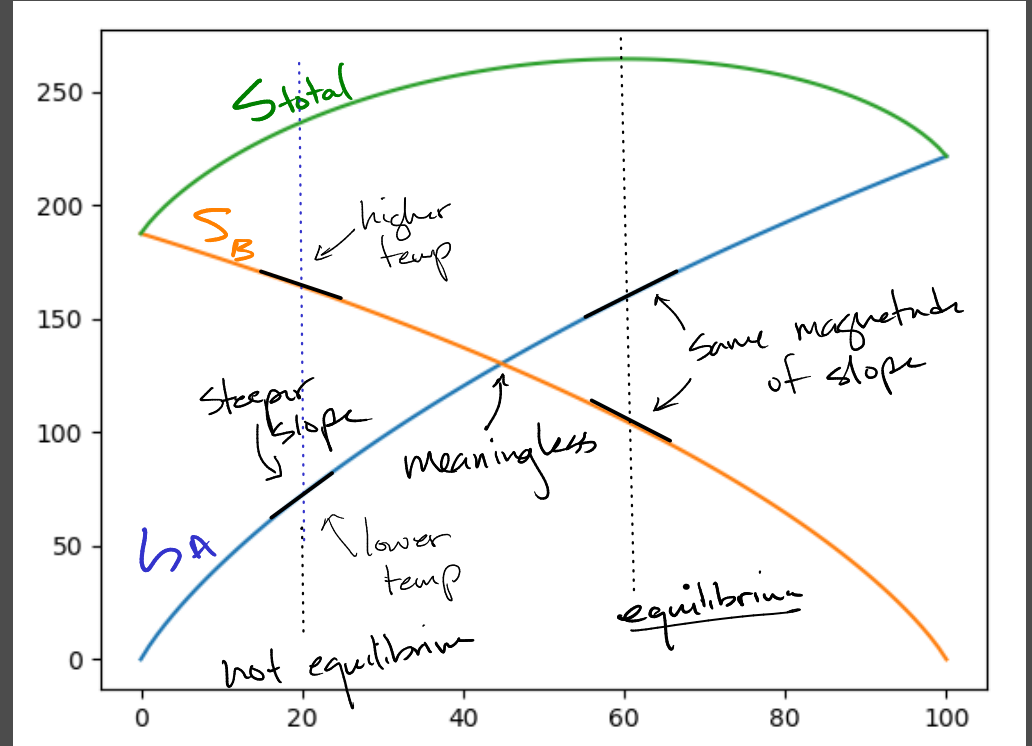
$$\left| \frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \right|$$

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

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

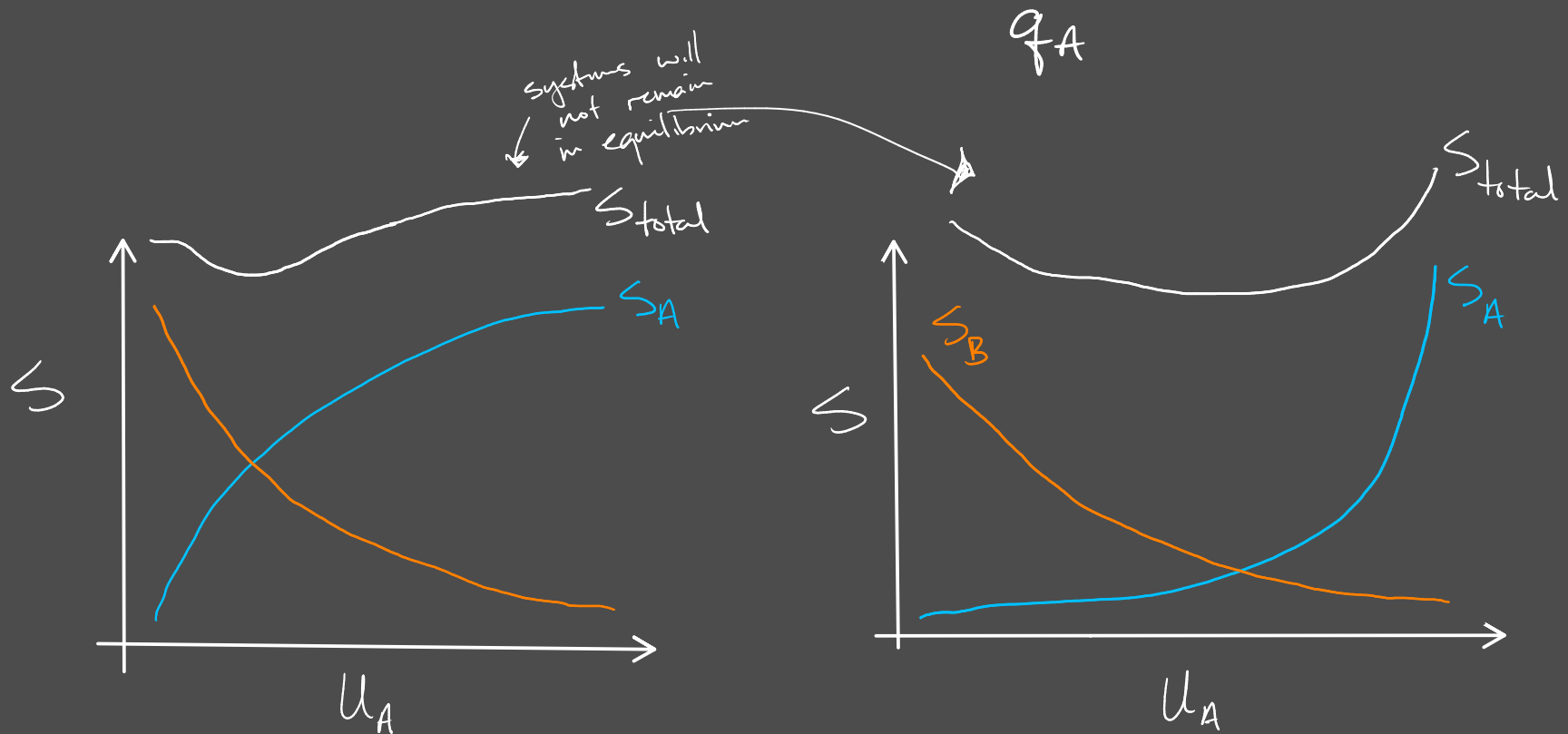
↑ this the definition of temperature

Entropy



HW: 1, 3

Anaconda  
miniconda



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  $\Omega$  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.

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

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

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

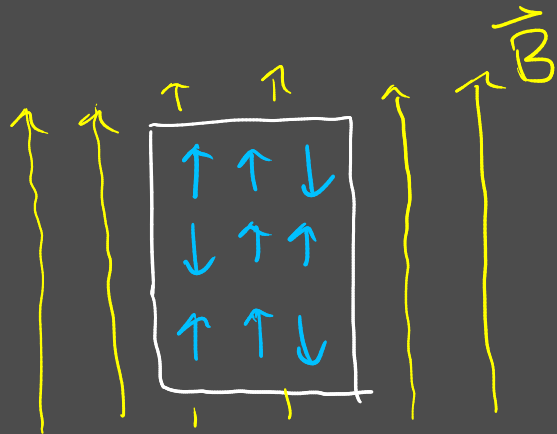
$$dU = T dS - p dV$$

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

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

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

## Paramagnetism

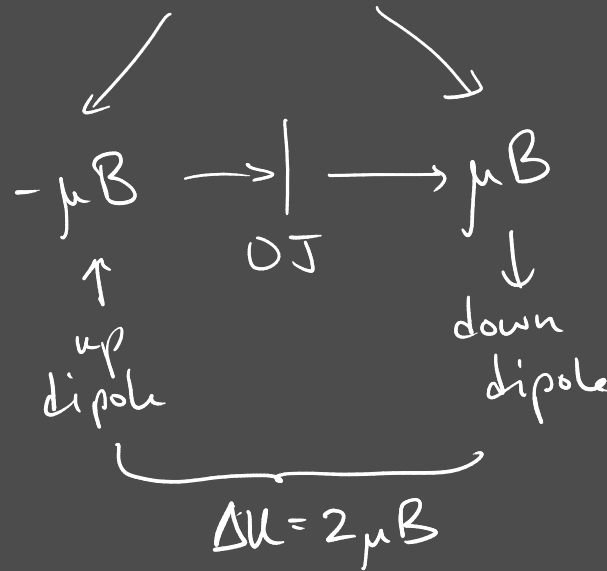


- dipoles aligned parallel to the  $\vec{B}$  have lower energy state
  - antiparallel requires  $U$  to turn it around
  - $U$  is determined by number of  $\uparrow$  and  $\downarrow$  dipoles
- others are not allowed by QM

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

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

↓  
plotted in jupyter

Analytic Solution

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

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

$$\frac{1}{T} = \frac{\partial S}{\partial U} \quad U = \mu_B (N - 2N_{\uparrow}) \Rightarrow N_{\uparrow} = \frac{N}{2} - \frac{U}{2\mu_B}$$

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

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

↓  
Solve for  $U$

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

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

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

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

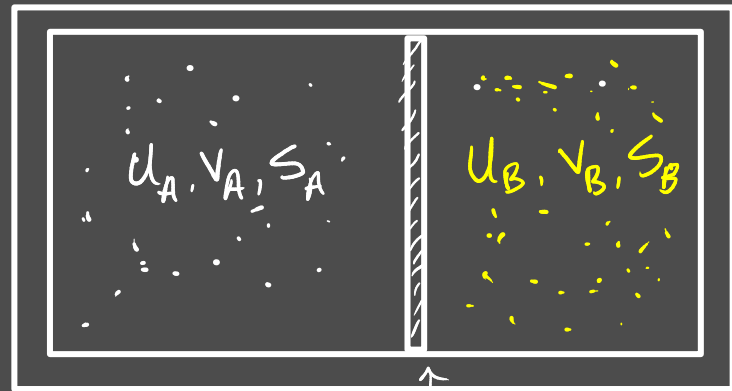
# Pressure

For 2 ideal gases in contact:

$$\Omega_{\text{total}} = [f(N)]^2 (V_A V_B)^N (U_A U_B)^{3N/2}$$

↳ very sharp peak

$$S_{\text{total}} = k_B \ln \Omega_{\text{total}}$$



← highest multiplicity

$$\text{equilibrium} \left\{ \frac{\partial S_{\text{total}}}{\partial U_A} = 0 \right.$$

thus defined  
the same  
T for Einstein  
solids

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

new

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

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

$$dV_A = -dV_B$$

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

$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}$$

at equilibrium  
→ constant  $U, N$

From intuition



At equilibrium the pressure is the same in both gases.  
If the pressure were not the same, the partition would move until the pressure was the same.

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

$$\left[ \frac{\text{J}}{\text{K m}^3} \right] = \left[ \frac{\text{N} \cdot \text{m}}{\text{K m}^3} \right] = \left[ \frac{\text{N}}{\text{m}^2} \cdot \frac{1}{\text{K}} \right] = \left[ \frac{\text{Pa}}{\text{K}} \right]$$

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

↑  
we need to multiply  
by a  $T$ !

is this right?

- CHECK w/ ideal gas

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

$$S = k_B [\ln f(N) + N \ln V + N \ln u^{3/2}]$$

$$p \stackrel{?}{=} T \left( \frac{\partial S}{\partial V} \right) = T \cdot k_B \cdot N \left( \frac{\partial \ln V}{\partial V} \right)$$

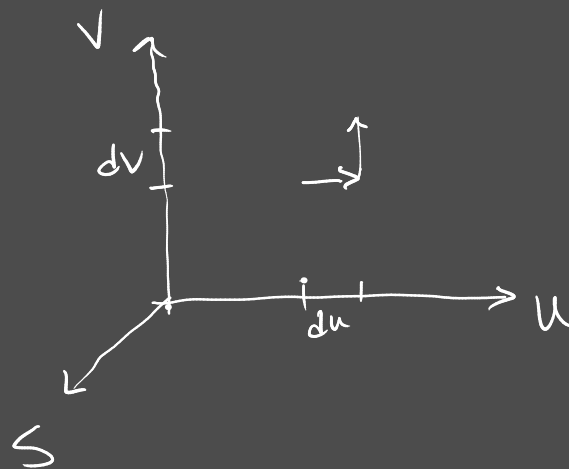
$$\underbrace{\quad}_{\frac{1}{V}}$$

$$p \stackrel{?}{=} \frac{T k_B N}{V} \Leftrightarrow pV = N k_B T \quad \checkmark \checkmark$$

$$dS(u, v) = \underbrace{\left(\frac{\partial S}{\partial u}\right)_v}_{\frac{1}{T}} du + \underbrace{\left(\frac{\partial S}{\partial v}\right)_u}_{\frac{P}{T}} dv$$

$$dS = \frac{1}{T} du + \frac{P}{T} dv$$

$$T dS = du + p dv$$



$du = T dS - p dv$  } true for any infinitesimal change  
 as long as  $T$  &  $P$  are the  
 same throughout the system  
 • and, no other relevant variable (i.e.  $N$ )  
 is changing

thermodynamic identity

Compare to 1st law of thermo

$$du = \delta Q + \delta W$$

$$\delta Q \stackrel{?}{=} T dS$$

$$\delta W \stackrel{?}{=} -p dv$$

$$\delta Q = T dS$$

TRUE IF:

- $dv$  happen quasistatically
- no non-compression work sources
- no other relevant variables change ( $N$ )

So, an adiabatic and quasi-static process is therefore called isentropic.

$$\delta Q = 0 = dS$$

So now even for non-constant volume

$$\delta Q = T dS$$

$$dS = \frac{\delta Q}{T} \Rightarrow \frac{Q}{T}$$

↳ temp does not change.

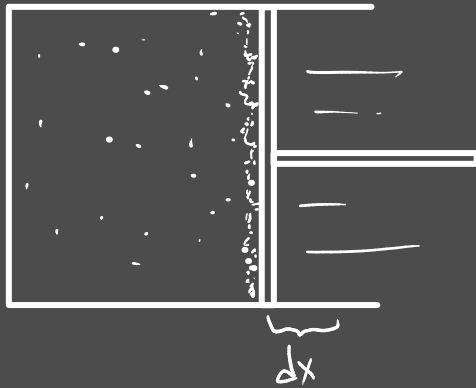
boil 1L of water:  $\rightarrow$  2260 kJ heat added

$$\Delta S = \frac{2260,000 \text{ J}}{373} = 6060 \text{ J/K}$$

- heat capacity to measure entropy

$$(\Delta S)_p = \int_{T_i}^{T_f} \frac{C_p}{T} dT \leftarrow \text{much more practical}$$

What about a not-quasistatic process?



$$W > p dV$$

will not change much for small  $dV$

$$\underbrace{\delta W}_{\text{I do this work}} + \underline{\delta Q} = dU = \underline{T dS} - p dV$$

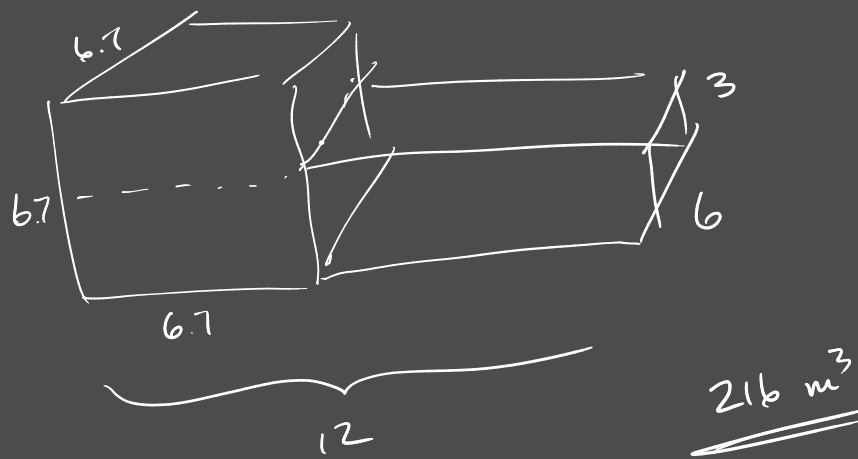
greater than

$$\delta Q < T dS.$$

$$\boxed{dS \geq \frac{\delta Q}{T}}$$



$$\sqrt[3]{300} = 6.7 \text{ m}$$



3 b)  $\Delta S = S_f - S_i$

$$= k_B \ln \Omega_f - k_B \ln \Omega_i$$

$$= k_B \ln \frac{\Omega_f}{\Omega_i} \quad \Omega_f = f(N) V_f^N U_f^{3N/2}$$

$$= k_B N \ln \left( \frac{V_f U_f^{3/2}}{V_i U_i^{3/2}} \right)$$

$$k_B N \ln \left( \left( \frac{1}{20} \right) \cdot \left( \frac{U_f}{U_i} \right)^{3/2} \right)$$

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

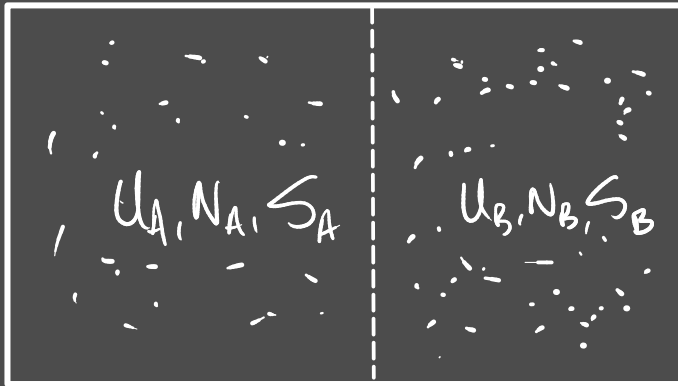
$$\frac{U_f}{U_i} = \frac{T_f}{T_i} = \left( \frac{V_i}{V_f} \right)^{2/3}$$

$$\ln \left( \left( \frac{1}{20} \right) \cdot \left( \left( \frac{20}{1} \right)^{2/3} \right)^{3/2} \right)$$

$$\ln(1) = 0 = \Delta S$$

# Chemical Potential

- thermal equil  $\rightarrow$  Temps same
- mechanical equil  $\rightarrow$  pressure same
- diffusive equil  $\rightarrow$  ?



$$\left( \frac{\partial S_{\text{total}}}{\partial N_A} \right)_{U,V} = 0 \quad \text{at equilibrium}$$

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}$$

$$-T \frac{\partial S_A}{\partial N_A} = -T \frac{\partial S_B}{\partial N_B}$$

$$\mu_A = \mu_B$$

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

$\hookrightarrow$  particles move from higher  $\mu$  to lower  $\mu$ .

modify thermodynamic identity

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

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

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

↓ constant  $S, V$

$$dU = \mu dN$$

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

→  $\mu$  is the energy  
to add/remove a particle  
+ keep entropy constant  
(usually remove energy)  
so  $\mu$  is negative