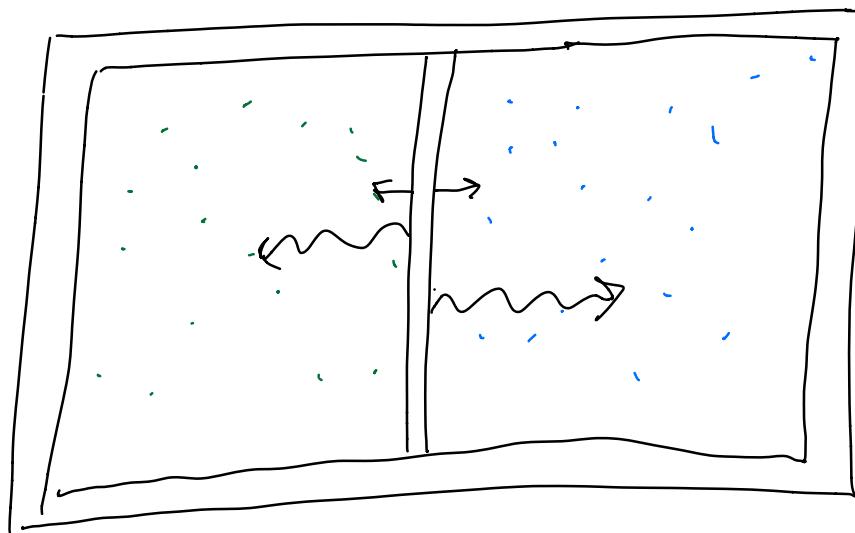


Consider:

Two ideal gases in a container

- Separated by movable partition  $V_{\text{tot}} = V_A + V_B$

- Allowed to exchange energy  $U_{\text{tot}} = U_A + U_B$



The total entropy  $S_{\text{tot}}$  of the system of both gases is just  $S_A + S_B$

For fixed  $N$ , entropy is a function of  $U, V$

$S(U_A, V_A)$  forms a surface

Equilibrium @  $S_{\text{max}}$

To find  $S_{\max}$ :

$$\boxed{\frac{\partial S_{\text{tot}}}{\partial U_A} = 0}, \quad \frac{\partial S_{\text{tot}}}{\partial V_A} = 0$$

This gave us  
the defn  
of temperature

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

$$\frac{\partial S_B}{\partial V_A} = - \frac{\partial S_B}{\partial V_B} \quad \partial V_A = \partial (V - V_{BS})$$

$$\left( \frac{\partial S_A}{\partial V_A} \right) = \left( \frac{\partial S_B}{\partial V_B} \right)$$

$$@ \text{ equilibrium} \quad \frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}$$

What else is true @ equilibrium?

$$\bar{T}_A = \bar{T}_B$$

$V_A = V_B$ ? Not always, only if  $N_A = N_B$

$$\bar{P}_A = \bar{P}_B$$

Suggests a relationship between

$$\frac{\partial S}{\partial V} + \text{pressure}$$

Check the ideal gas!

$$S = Nk \ln(CV) + Nk \ln \frac{S}{Z}$$

assume  $U$  is const

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

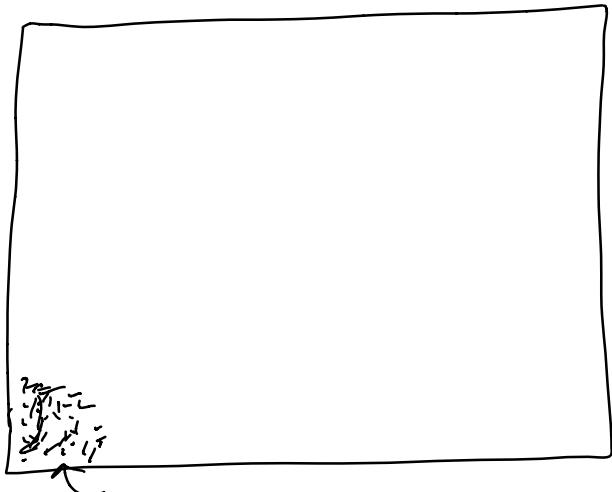
$$PV = NkT$$
$$\frac{PV}{T} = \frac{1}{V}$$

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

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

- Pressure is the amount of entropy gained by expansion

Consider:



all gas is concentrated here

- gas at higher pressure than surroundings

gas pressure creates a net outward force  
causing gas to expand

$$\frac{\Delta S}{\Delta V} \text{ large}$$

- increasing the volume dramatically raises the entropy

$P$  is  
large

- As gas expands further  $\frac{\Delta S}{\Delta V}$  decreases  
+ so pressure decreases ( $S \sim \ln V$ )

- All scaled by temperature

For a given  $\frac{\Delta S}{\Delta V}$ , P is greater at higher T

For gas-in-corner example,  $\frac{\Delta S}{\Delta V}$  doesn't depend on T, but pressure does

Higher T  $\rightarrow$  rapid expansion (higher pressure)

---

In 3.2, we saw that for a const V process,  $dS = \frac{Q}{T}$

What about a process where U + V both change?

$$S = S(U, V)$$

$$dS = ?$$

Recall: Calc 3

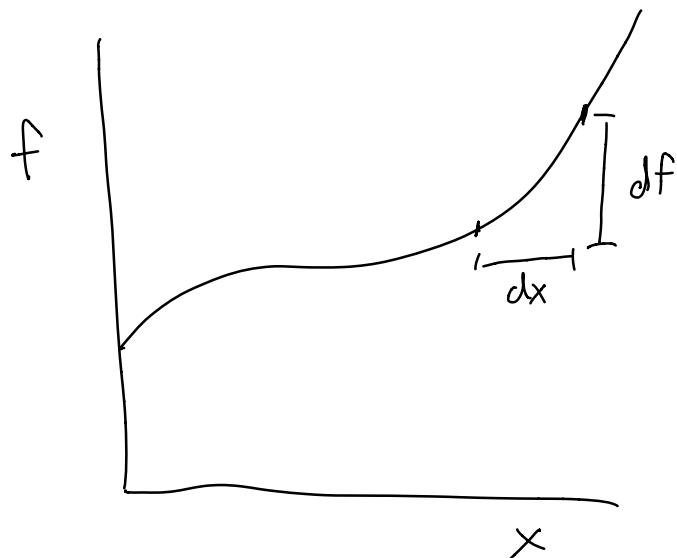
$$f = f(x, y)$$

$$df = f(x+dx, y+dy) - f(x, y)$$

$$f(x+dx, y+dy) = f(x, y) + \left(\frac{\partial f}{\partial x}\right) dx + \left(\frac{\partial f}{\partial y}\right) dy$$

$$df = \left(\frac{\partial f}{\partial x}\right) dx + \left(\frac{\partial f}{\partial y}\right) dy$$

In 1D



$$df = \left(\frac{df}{dx}\right) dx \quad 1D, \text{ use total deriv}$$

$$f(x_1, x_2, \dots, x_n)$$

$$df = \sum_{i=1}^n \left(\frac{\partial f}{\partial x_i}\right)_{\{x_j, j \neq i\}} dx_i$$

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

First increase  
 energy @ const  
 volume

then increase volume  
 @ const  
 energy

$$dS = \frac{1}{T} dU + \frac{P}{T} dV$$

Rearrange:

$$dU = T dS - P dV$$

Memorize this!

If you know this, you can get derivatives for  $T$  &  $P$

$$dS = \frac{1}{T} (dU + P dV)$$

$$dS = \frac{\partial S}{\partial U} dU + \frac{\partial S}{\partial V} dV$$

$$\Rightarrow \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}, \quad \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{P}{T}$$

$$dU = TdS - PdV$$

Compare to

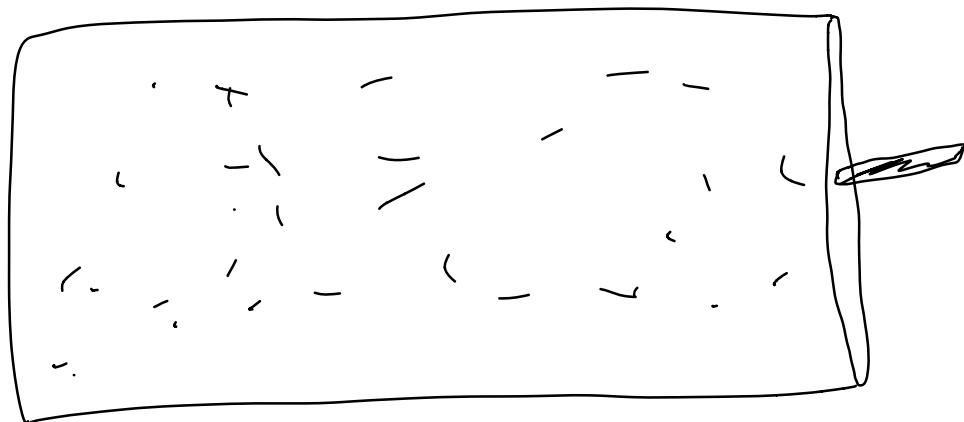
$$dU = Q + W$$

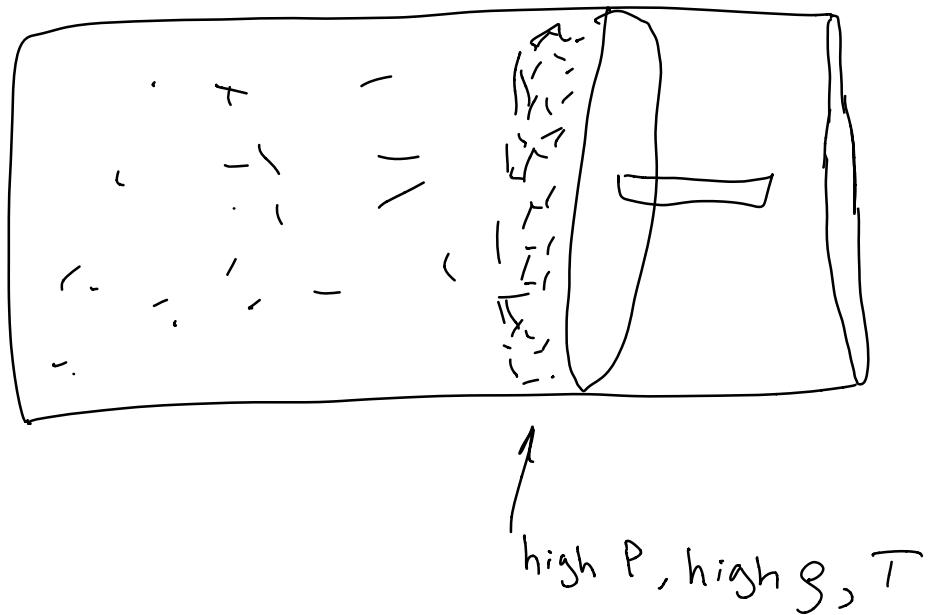
so Shouldn't we write  $Q = TdS$   
 $W = -PdV$  ?

Only if the process is quasistatic

What does this mean?

Consider a box of air with a piston on one end





- Gas is not at uniform  $P, T, S$
- Pressure wave propagates w/ speed of sound  $c_s = \sqrt{\frac{\gamma kT}{m}}$   
in air,  $c_s \approx 340 \text{ m/s}$

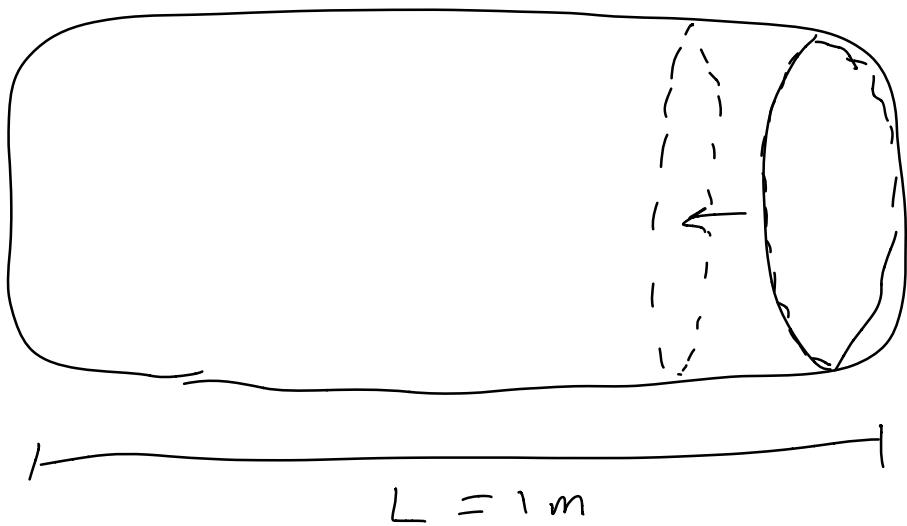
Time for pressure to equalize:  $t \sim \frac{L}{c_s}$

In this room:

$$L = 10 \text{ m}$$

$$t \sim 0.03 \text{ s}$$

If gas is in a small tank



$$t \sim 3 \text{ ms}$$

Before this time, the temp & pressure for the entire gas are not well-defined

- Our pressure wave is still propagating

$P, V, \text{ & } T$  are not uniform throughout

Time to equilibrate:  $\tau$

In a quasistatic process, the distance the piston moves over time  $\tau$  is insignificant

$$V_{\text{piston}} \ll C_s$$

If we want to move the piston a distance "d", imagine doing it over & over again, moving  $\Delta x$  @ a time.

- move  $\Delta x$
- wait time  $\tilde{T}$  to equilibrate
- repeat

If we push too fast, pressure can't equalize

We must push against a slightly higher pressure than avg

In this case,  $PdV$  is an underestimate for work so

$$dU = Q + W$$

$$dU = TdS - PdV$$

$$TdS = dU + PdV$$

$$Q = dU - W$$

$$TdS - Q = PdV + W$$

$$= PdV + -(P + \Delta P)dV$$

remember,  $dV < 0$

$$TdS - Q \underset{-}{>} 0$$

$$Q \leq TdS \quad \text{in general}$$

$$Q = TdS, \text{ quasistatic}$$

So far, we have considered how entropy changes with  $U$ , &  $V$ .

What about  $N$ ?

We would expect adding more particles to increase the entropy

$$S = S(U, V, N)$$

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

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

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

$\uparrow$   
Energy added  
by increasing  
entropy at  
const  $V, N$

(Heat)

$\uparrow$   
Energy added  
by increasing  
volume

(work)

$\uparrow$   
Energy added  
by increasing  
# of particles

$$-\tau \left(\frac{\partial S}{\partial N}\right)_{U,V} = \mu \quad \text{Chemical Potential}$$

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

Energy added by  
adding more particles  
to the system

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

$$U = U(S, V, N)$$

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

if increasing entropy  
doesn't change  $U$ ,  
we are in thermal  
equilibrium

$T dS$   
↑  
the same in equilibrium      what changes when we're not

$\left(\frac{\partial U}{\partial V}\right)_{S,N} = -P$   
Normally, increasing  $V$  will decrease  $U$ ,  
hence the  $-$  sign

$P dV$   
↑  
the same in equilibrium      changes if we aren't

$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$   
 $\mu$  is the energy  
added by adding  
 $dN$  many particles  
w/o changing  
 $S$  or  $V$

$\mu dN$   
↑  
the same in equilibrium      changes if not

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

thermal

- if two systems are not in equilibrium,  
that means we are not at max entropy
  - Overall entropy is increased if energy flows from  
lower  $\frac{\partial S}{\partial U}$  to higher  $\frac{\partial S}{\partial U}$  low  $\frac{\partial S}{\partial U} \rightarrow$  high T
- $\Delta U$  leaving the low  $\frac{\partial S}{\partial U}$  system causes a small decrease in entropy
  - $\Delta U$  entering the high  $\frac{\partial S}{\partial U}$  system causes a large increase in entropy
  - Results in net gain of entropy

- Entropy increased if particles move from  
a low  $\frac{\partial S}{\partial N}$  to high  $\frac{\partial S}{\partial N}$

Since  $M \propto -\frac{\partial S}{\partial N}$

Particles move from higher to lower

M

Ex: a small Einstein solid

$$N = 3$$

$$q = 3$$

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

What is  $\mu$  for this system?

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

Add another oscillator while keeping entropy constant (+ volume)

$$N = 4$$

$$q = 3$$

$$\Omega = 20 \quad \text{Entropy increased}$$

To keep entropy the same

remove a "q"

$$N = 4 \quad \left( \frac{\Delta U}{\Delta N} \right)_S = -\frac{q}{1} = -\hbar\omega$$
$$q = 2 \quad \Omega = 10$$

Be careful!

$\mu$  for ideal gas

$$\mu = \frac{\partial U}{\partial N} = \frac{\partial}{\partial N} \left( \frac{3}{2} N k T \right) = \frac{3}{2} k T \quad \checkmark$$

Wrong! We have changed entropy!

$$N \rightarrow N + \Delta N$$

$$U(N) = \frac{3}{2} N k T$$

$$U(N + \Delta N) = \frac{3}{2} (N + \Delta N) k T$$

$$S(U, V, N) = N k \left[ \ln \left( V \left( \frac{4 \pi m U}{3 k^2} \right)^{3/2} \frac{1}{N^{5/2}} \right) + \frac{5}{2} \right]$$

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

Add  $\Delta N$  then remove energy until  $S$  is the same as before

or: solve the above for  $U$  + take  $\left( \frac{\partial U}{\partial N} \right)_{S, V}$

Easier:

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

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