

# Entropy & molecular statistics

Always hear that Entropy = disorder  
What does this mean?

Boltzmann wanted to construct a function of molecular states that had some properties as thermodynamic entropy

He found that

$$S = k_B \ln W$$

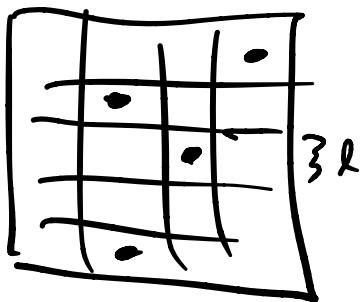
Where  $W$  is the number of "microstates" of the system

What is a microstate? It is a configuration having the same thermodynamic properties

In particular applies for same  $N, V, E$

(will talk more about  $\equiv$

Best example is lattice gas: (temp later)



$N$  gas molecules in  $N_{cells} = N_c$   
 $V = \ell^2 N_c$  so  $N_c$  is like volume

$E = \begin{cases} 0 & \text{no overlap} \\ \infty & \text{overlap} \end{cases}$

What is  $\omega$ ? Learned

$$\omega = \binom{N_c}{M} , \text{ number of ways to pick } N \text{ spots from } N_c \text{ to fill}$$

Key feature of Boltzmann entropy is extensive

Two copies of system

$$\# \text{ states} = \omega^2$$

$$S(2 \text{ systems}) = S_1 + S_2 \quad k$$

$$S = k \ln(\#) = 2k \ln \omega$$

What is entropy for the lattice gas?

$$S = k \ln \frac{N_c!}{M!(N_c-M)!}$$

↓  
not needed  
for big  $N$

Stirlings approx:  $\ln N! \approx N \log N - N + \frac{1}{2} \ln(2\pi N)$

$$N! \approx N^N e^{-N} \cdot \sqrt{2\pi N}$$

$$S \approx k \left[ N_c \ln N_c - N_c - M \ln M + M - (N_c - M) \ln(N_c - M) + (N_c - M) \right]$$

$$S \approx k \ln \frac{N_c^{N_c}}{M^M (N_c - M)^{N_c - M}}$$

maximized for  
 $M = N_c/2$

How can we apply this? What is

entropy of expansion from  $N_i \rightarrow N_f$  sites  
Isothermal Expansion\*  $\Delta E = 0$

$$\Delta S = k \ln \frac{N_f!}{M! (N_f - M)!} - k \ln \frac{N_i!}{M! (N_i - M)!}$$

$$= k \ln \left[ \frac{N_f!}{N_i!} \cdot \frac{(N_i - m)!}{(N_f - m)!} \right]$$

$$\approx k \left[ N_f \ln \frac{N_f}{N_f - m} + (N_i - m) \ln \frac{N_i}{N_i - m} - (N_i - m) \right. \\ \left. - N_i \ln \frac{N_i}{N_i + N_f - m} - (N_f - m) \ln \frac{N_f}{N_f - m} + (N_f - m) \right]$$

$$= k \left[ N_f \ln \frac{N_f}{N_f - m} - N_i \ln \frac{N_i}{N_i - m} + m \ln \frac{N_f - m}{N_i - m} \right]$$

$$\underset{m/N_f \rightarrow 0}{\approx} k m \ln \frac{N_f}{N_i} = m k_B \ln \frac{V_f}{V_i}$$

$$= n R \ln \frac{V_f}{V_i}$$

Same as classical isothermal expansion  
ideal gas

Previously, we discussed how entropy acts as a potential in a closed system, where  $dS \geq 0$

such that entropy increases for a spontaneous process until maximized

But what about non-closed systems?

Most reactions done where  $q$  can be exchanged w/ surroundings & open to a pressure reservoir. Sometimes  $M$ 's can exchange with the system too

Energy as a potential: combining 1st & second law

First law

$$dE = dq + dw = dq - pdV$$

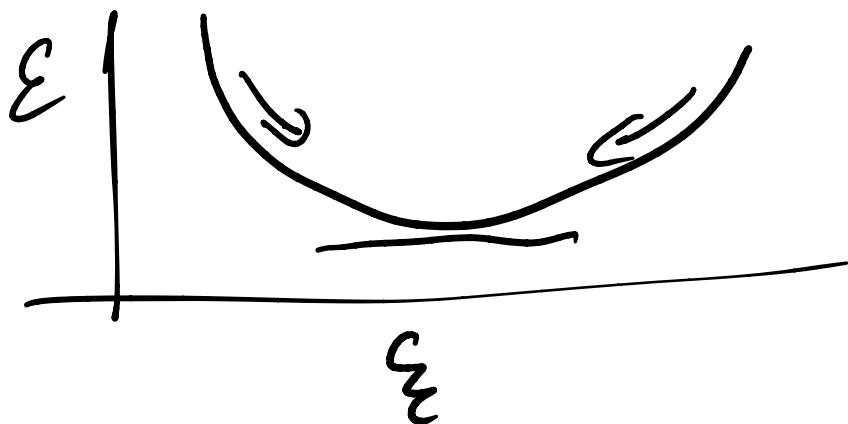
Clausius Ineq,  $dS \geq dq/T$

$$\Rightarrow dq \leq TdS$$

$$\text{So } dE \leq TdS - pdV$$

Equality is still equilibrium

① if  $S$  &  $V$  constant,  
then  $U$  acts as a potential  
 $dE \leq 0$ , so energy is minimized



$\frac{dE}{dS} < 0$  moves right  
etc

$$E(S, V) \Rightarrow dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV$$

also know (first law)

$$dE = dq - pdV = TdS - pdV$$

This means  $T = \left(\frac{\partial E}{\partial S}\right)_V$  and  $-p = \left(\frac{\partial E}{\partial V}\right)_S$

$P$  and  $T$  are sensitivity  
coefficients (more later)

so at large  $P$ , change in volume  
makes a bigger change to  $U$

at large  $T$ , this relationship is  
a bit less obvious, b.t the  
converse makes some sense,  
At large  $T$  a small change in  $U$   
makes a smaller change in  $S$

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Example for ideal gas:

Skipped

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV$$

$\underbrace{T}_{-P}$

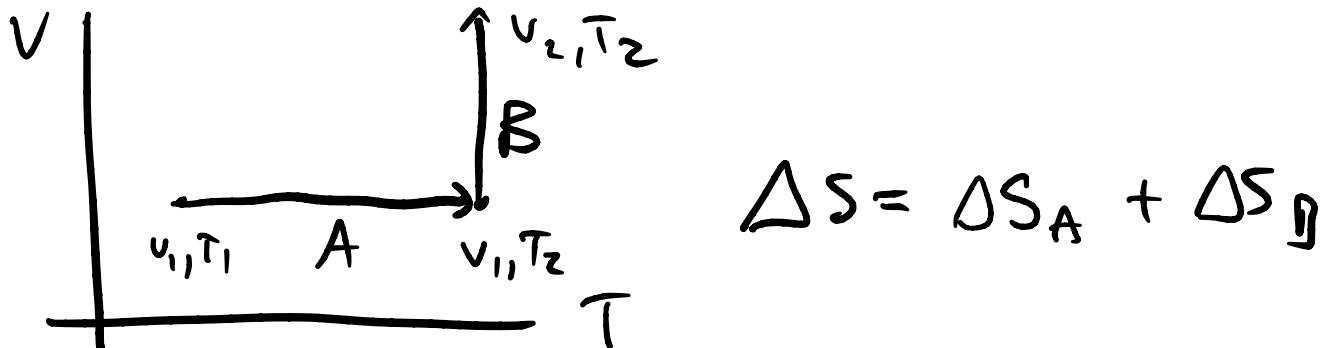
can rearrange to find  $S$

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

$$\text{now } dE (\text{const } V) \approx dq = C_V dT$$

$$\Rightarrow dS = \frac{C_V}{T} dT + \frac{P}{T} dV$$

$$= C_V/T dT + \frac{nR}{V} dV \quad (\text{ideal gas})$$



$$\Delta S_A = \int_{T_1}^{T_2} \frac{C_V}{T} dT = C_V \ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta S_B = \int_{V_1}^{V_2} \frac{nR}{V} dV = nR \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S = C_V \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right)$$

$$\uparrow S - S_{\text{ref}} \quad S_{\text{ref}} = S(T, V)$$

What if we want energy as function of

$S$ , for ideal gas  $C_V = \frac{3}{2}nR$   
and  $E = \frac{3}{2}nRT \Rightarrow T = \frac{2}{3}\frac{E}{nR}$

$$\Delta S = \frac{3}{2} \left[ nR \ln \left( \frac{T_2}{T_1} \right) + \frac{2}{3} nR \ln \left( \frac{V_2}{V_1} \right) \right]$$

$$\Rightarrow \Delta S = \underbrace{\frac{3}{2} n R}_{C_V} \ln \left( \frac{T_2}{T_1} \cdot \left( \frac{V_2}{V_1} \right)^{2/3} \right)$$

$$\Rightarrow \frac{T_2}{T_1} = e^{\Delta S / C_V} \left( \frac{V_1}{V_2} \right)^{2/3} \xrightarrow{\text{Typo?}}$$

$$E = \frac{3}{2} n R T_r e^{(S - S_r) / C_V} \left( \frac{V_r}{V} \right)^{2/3}$$

if @  $S_r, V_r, T_r$ ,  $E = \frac{3}{2} n R T_r$

increases for increasing entropy

steeply, decreases for increasing  $V$

- Increase in entropy from increasing heat flow const  $V$
- decrease w/  $V$  from the adiabatic expansion

why bother w/ this derivation?

key is  $E(S, V)$  is not potential minimized  
each value is fixed point @ eq

A system cannot be below  
this surface, can be out of  
equilibrium above it

- Constant S & V are weird conditions  
need to be able to understand  
const T & V

Consider  $H = U + PV$  presented before

$$dH = dU + PdV + Vdp$$

$\overbrace{dU}^{dE} \leq TdS - PdV$

$$\Rightarrow dH \leq TdS + Vdp$$

Enthalpy is potential for constant S & P

Adding PV made a new thermo potential  
that swapped  $-P$  &  $V$

How can we get rid of  $TdS$  (for SIT?)

$$G \equiv H - TS$$

$$\begin{aligned}
 dF &= dH - TdS + SdT \\
 &\leq (TdS + VdP) + SdT - TdS \\
 &\leq SdT + VdP
 \end{aligned}$$

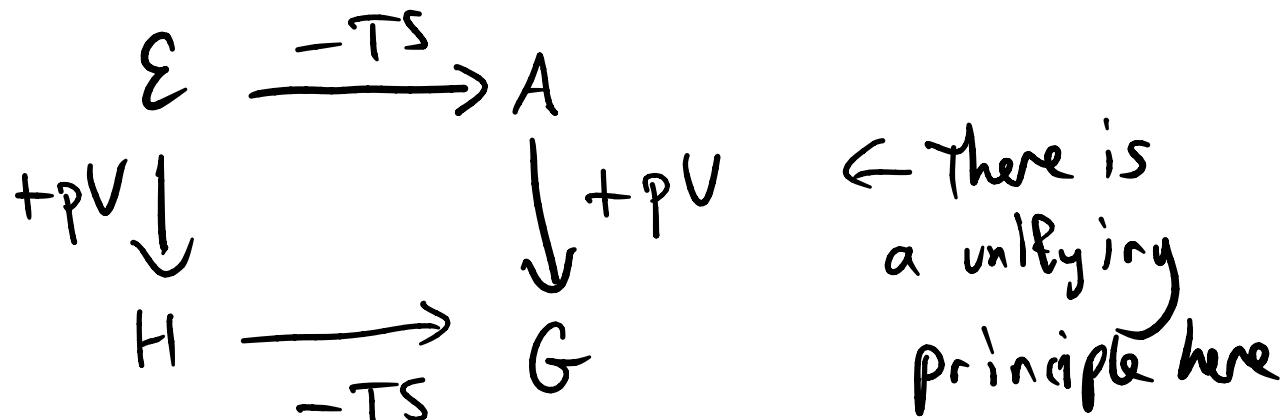
So Gibbs Free Energy is potential that is minimized at constant  $T$  &  $P$  ( $dG \leq 0$ )

For completion (and for statmech)

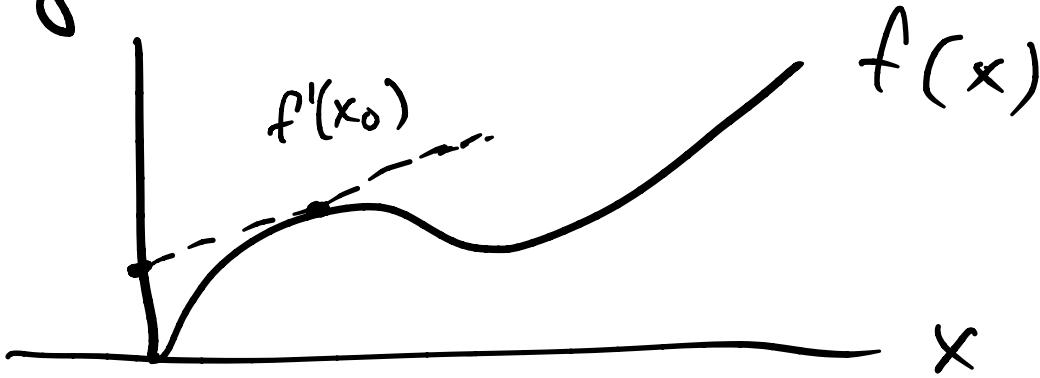
$$A = E - TS$$

$$\begin{aligned}
 dA &= dE - TdS - SdT \\
 &\leq (TdS - pdV) - TdS - SdT \\
 &\leq -SdT - pdV
 \end{aligned}$$

Potential for const  $\bar{T}, \bar{V}$  (simulations)



# Legendre transformations



$$y = f'(x_0)x + b(x_0)$$

$$b(x_0) = y - f'(x_0)x$$

New function with same information

Start with  $\mathcal{E}(S, V)$

To get to a function of  $S$  &  $T$ ,

$$A \equiv \mathcal{E}(S, V) - S \left( \frac{\partial \mathcal{E}}{\partial S} \right)_V V \quad \begin{matrix} \swarrow \\ \text{already shown} \end{matrix} = T$$

$$\text{so } A = \mathcal{E} - TS$$

Can explicitly get  $H$  &  $G$   
for ideal gas (book & HW)