

Entropy & molecular statistics

Always hear that Entropy = disorder

What does this mean?

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

He found that

$$S = k_B \ln W$$

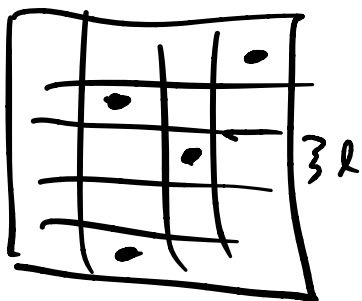
Where W is the number of "microstates" of the system

What is a microstate? It is a ^{single} configuration having the same thermodynamic properties

In particular applies for same N, V, E

(will talk more about z temp later)

Best example is lattice gas:



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

$E = 0$ no overlap
 ∞ overlap

What is W ? Learned

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

Key feature of Boltzmann entropy is extensive

Two copies of system

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

$$S(2 \text{ systems}) = S_1 + S_2 \quad \text{b/c}$$

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

What is entropy for the lattice gas?

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

not needed
for big N
↓

Stirling's approx! $\ln N! \approx N \log N - N + \frac{1}{2} \ln(2\pi N)$

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

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

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

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 * $dE=0$

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

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

$$\approx k \left[N_f \ln N_f - N_f + (N_i-M) \ln (N_i-M) - (N_i-M) \right. \\ \left. - N_i \ln N_i + N_i - (N_f-M) \ln (N_f-M) + (N_f-M) \right]$$

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

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

$$= n R \ln V_f/V_i$$

Same as classical isothermal expansion
ideal gas

Previously, we discussed how Entropy acts as a potential in a closed system, where $dS \geq 0$ Ch 5

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 Mc 's can exchange with the system too

Energy as a potential: combining 1st & second law

First law

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

Clausius Ineq, $dS \geq dq/T$

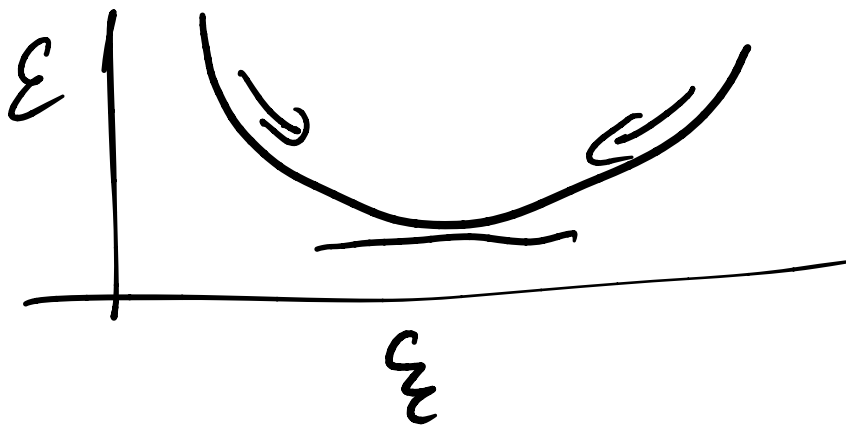
$$\Rightarrow dq \leq TdS$$

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



$\frac{dE}{d\xi} < 0$ 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 , changes in volume make a bigger change to U

at large T , this relationship is a bit less obvious, but the

converse makes some sense,

At large T a small change in U makes a smaller change in S

Example for ideal gas!

Skipped

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

\uparrow T $-P$

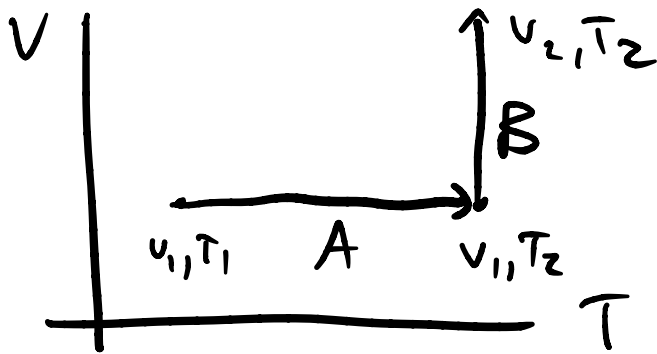
can rearrange to find S

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

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

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

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



$$\Delta S = \Delta S_A + \Delta S_B$$

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

$$\Delta S_B = \int_{v_1}^{v_2} \frac{nR}{V} dV = nR \ln(v_2/v_1)$$

$$\Delta S = C_V \ln(T_2/T_1) + nR \ln(v_2/v_1)$$

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

What if we want energy as function of

$$S, \text{ for ideal gas } C_V = \frac{3}{2} nR$$

$$\text{and } E = \frac{3}{2} nRT \Rightarrow T = \frac{2}{3} \frac{E}{nR}$$

$$\Delta S = \frac{3}{2} \left[nR \ln(T_2/T_1) + \frac{2}{3} nR \ln(v_2/v_1) \right]$$

$$\Rightarrow \Delta S = \frac{3}{2} nR \ln \left(T_2/T_1 \cdot (v_2/v_1)^{2/3} \right)$$

$$\Rightarrow T_2/T_1 = e^{\Delta S/c_v} (v_1/v_2)^{2/3} \quad \rightarrow \text{Typo!}$$

$$E = \frac{3}{2} nRT_r e^{(S-S_r)/c_v} (v_r/v)^{2/3}$$

if @ S_r, v_r, T_r , $E = \frac{3}{2} nRT_r$

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

$$dH = dE + p dV + V dp$$
$$\uparrow \quad dE = T dS - p dV$$

$$\Rightarrow dH = T dS + V dp$$

Enthalpy is potential for constant S & p
Adding pV made a new thermo potential
that swapped $-p$ & V

How can we get rid of $T dS$ (for $S \downarrow T$?)

$$G \equiv H - TS$$

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

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

For completion (and for statmech)

$$A = E - TS$$

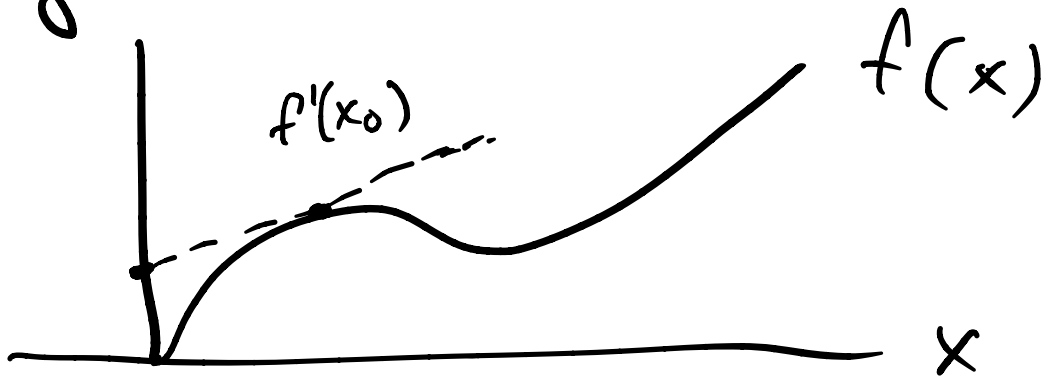
$$\begin{aligned}
 dA &= dE - Tds - SdT \\
 &\leq (Tds - pdV) - Tds - SdT \\
 &\leq -SdT - pdV
 \end{aligned}$$

Potential for const T, V (simulations)

$$\begin{array}{ccc}
 E & \xrightarrow{-TS} & A \\
 +pV \downarrow & & \downarrow +pV \\
 H & \xrightarrow{-TS} & G
 \end{array}$$

← There is a unifying principle here

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 net S ,

$$A \equiv \mathcal{E}(S, V) - S \left(\frac{\partial \mathcal{E}}{\partial S} \right)_V \leftarrow \text{already shared} = T$$

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

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