

Thermal Physics

PHYS/BMME 441

Gökçe Başar

Lectures 7 - 9

When & Where: Mon. / Wed. 8:00- 9:45 PM, Phillips 247

Textbook: *An Introduction to Thermal Physics*, Daniel V. Schroeder

Website: sakai.unc.edu

Gibbs Entropy

Microcanonical ensemble: all microstates are equally probable

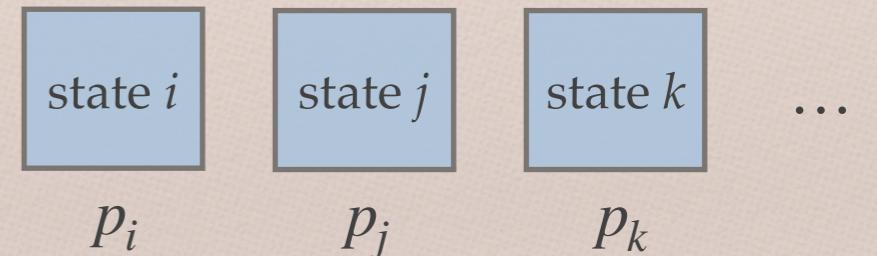
Relax this condition: Each microstate i occurs with a probability p_i

$$\text{Gibbs entropy} \quad S = -k \sum_i p_i \log p_i$$

microcanonical ensemble

``Replica trick'': Take W copies of the system

On average there are $p_i W$ copies of the system in state i



$$\text{Total number of configurations: } \Omega_{tot} = \frac{W!}{(p_1 W)!(p_2 W)!(p_3 W)! \dots}$$

$$\text{entropy for a single copy of the system: } S = \frac{1}{W} \times (k \log \Omega_{tot}) \sim -k \sum_i p_i \log p_i$$

Microcanonical Ensemble Revisited

microcanonical ensemble: all p_i s are constant

$$S = -k \sum_i p_i \log p_i \quad p_i = \frac{1}{N_{total}} = \frac{1}{\Omega} \Rightarrow S = -k \sum_{i=1}^{\Omega} \frac{1}{\Omega} \log \frac{1}{\Omega} = k \log \Omega$$

Which probability distribution for the microstates maximizes the entropy?

For which set $\{p_1, p_2, \dots, p_n\}$ the Gibbs entropy, $S = -k \sum_i p_i \log p_i$, is maximum?

$$\frac{\delta}{\delta p_i} \left[-k \sum_i p_i \log p_i + \Lambda \left(\sum_i p_i - 1 \right) \right] = 0 \Rightarrow p_i = \text{constant}$$

Lagrange multiplier *Total prob.=1*

Microcanonical ensemble: the ensemble that maximizes the Gibbs entropy!
(with the constraint that all states have the same energy)

Information (Shannon) Entropy

- A thermodynamic system has an absurdly large number of microstates.
- Yet we disregard all that information and quantify it with a few number of macroscopic quantities (*energy, volume, etc..*).
- Entropy is a measure of the information we disregard.

entropy  *information*

Encode a message as a sequence of symbols and reproduce it elsewhere

What is the most economical way of doing that for a generic message?

e.g. an outcome of a game of coin toss with 100 fair coins

Heads: 0, Tails: 1

Outcome for each coin=one symbol

00001001001110101010....

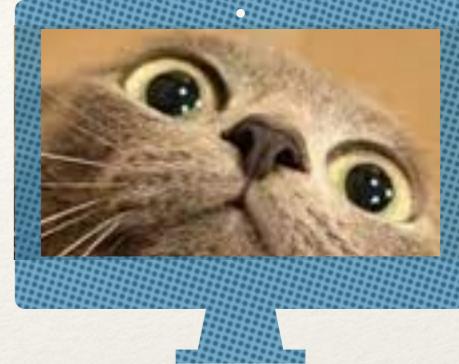
Most economical encoding: 1 bit/ symbol

Information Entropy



Message: a sequence of symbols sampled from the set $\{s_1, s_2, s_3, \dots, s_n\}$

each symbol s_i appears with a probability p_i



Information Entropy:

Minimum number of bits / symbol on average needed to encode a message

$$S = - \sum_i p_i \log_2 p_i$$

[Shannon, 1948]

e.g. coin toss: $S = - \sum_{i \in \{H,T\}} p_i \log_2 p_i = -2 \frac{1}{2} \log_2 \frac{1}{2} = 1$ (1 bit/symbol)

Information Entropy

e.g. draw a card from a deck: ♠ or ♣: 2 points , ♥: 1 point , ♦: 0 points
p: 1/2 1/4 1/4

$$S = - (1/2)\log_2(1/2) - 2 \times (1/4)\log_2(1/4) = 3/2$$

Information Entropy

e.g. draw a card from a deck: ♠ or ♣: 2 points , ♥: 1 point , ♦: 0 points

p: 1/2 1/4 1/4

$$S = - (1/2)\log_2(1/2) - 2 \times (1/4)\log_2(1/4) = 3/2$$

Information Entropy

e.g. draw a card from a deck: ♠ or ♣: 2 points , ♥: 1 point , ♦: 0 points

p: 1/2 1/4 1/4

$$S = - (1/2)\log_2(1/2) - 2 \times (1/4)\log_2(1/4) = 3/2$$

♠ or ♣ = 0, ♥=10, ♦=01
1 bit 2 bits

e.g. English language: 27 characters (space= 1 character)
[Shannon, 1951]

- Assume each letter appears equally frequent $S_0 = \log_2(27) \approx 4.75$

Information Entropy

e.g. draw a card from a deck: ♠ or ♣: 2 points , ♥: 1 point , ♦: 0 points

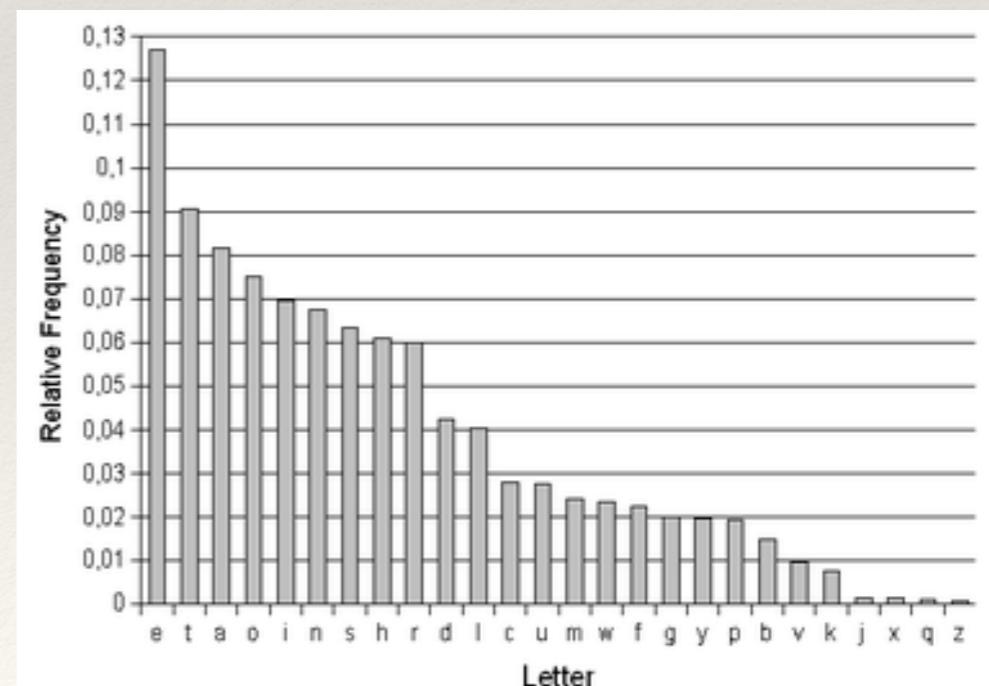
$$p: \quad \begin{matrix} 1/2 \\ 1/4 \\ 1/4 \end{matrix}$$

$$S = - (1/2)\log_2(1/2) - 2 \times (1/4)\log_2(1/4) = 3/2$$

$$\begin{matrix} \spadesuit \text{ or } \clubsuit & =0, \\ 1 \text{ bit} & \end{matrix} \quad \begin{matrix} \heartsuit & =10, \\ 2 \text{ bits} & \end{matrix} \quad \begin{matrix} \diamondsuit & =01 \end{matrix}$$

e.g. English language: 27 characters (space= 1 character)
[Shannon, 1951]

- Assume each letter appears equally frequent $S_0 = \log_2(27) \approx 4.75$
- 1st order approximation: (letter frequency) $S_1 \approx 4.03$



Information Entropy

e.g. draw a card from a deck: ♠ or ♣: 2 points , ♥: 1 point , ♦: 0 points

p: 1/2 1/4 1/4

$$S = - (1/2)\log_2(1/2) - 2 \times (1/4)\log_2(1/4) = 3/2$$

e.g. English language: 27 characters (space= 1 character)
[Shannon, 1951]

- Assume each letter appears equally frequent $S_0 = \log_2(27) \approx 4.75$
 - 1st order approximation: (letter frequency) $S_1 \approx 4.03$

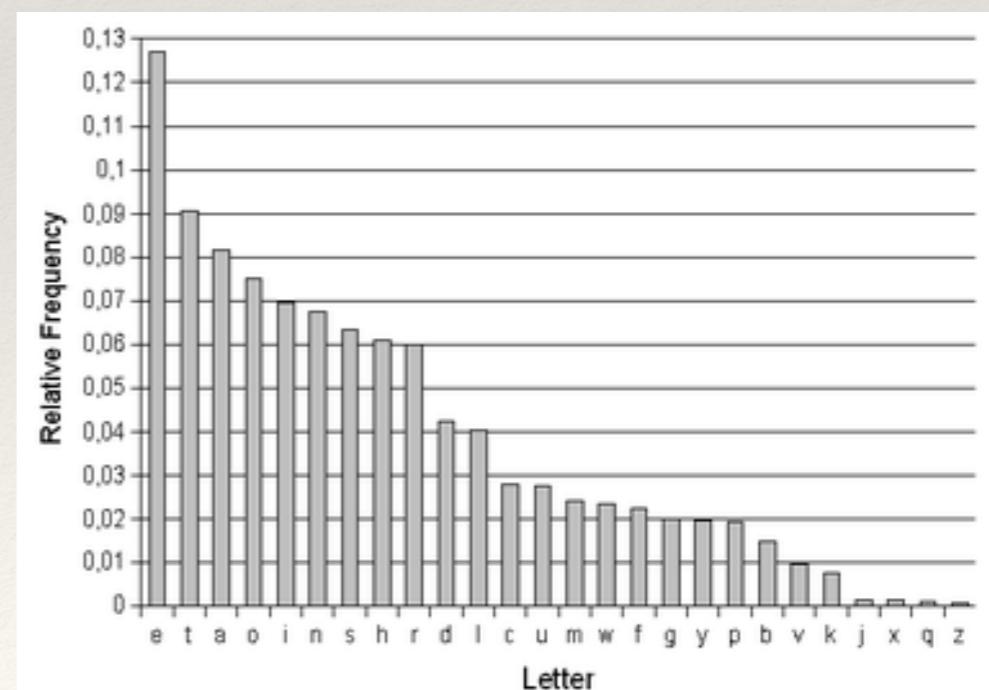
Correlations between letters:

- 2nd order approximation: (“*bigrams*”) $S_2 \approx 3.32$

e.g. TH is more common than TW

三

$$S_{English} \approx 2.14$$



Information Entropy



Claude Shannon

$$S = - \sum_i p_i \log_2 p_i$$

not sure what to call this....
maybe uncertainty?

“You should call it entropy, for two reasons:

In the first place your uncertainty function has been used in statistical mechanics under that name, so it already has a name.

In the second place, and more important, nobody knows what entropy really is, so in a debate you will always have the advantage.”



John von Neumann

Outlook for this week

Chapter 3: Interactions and Implications (chapters 3.1 to 3.5)

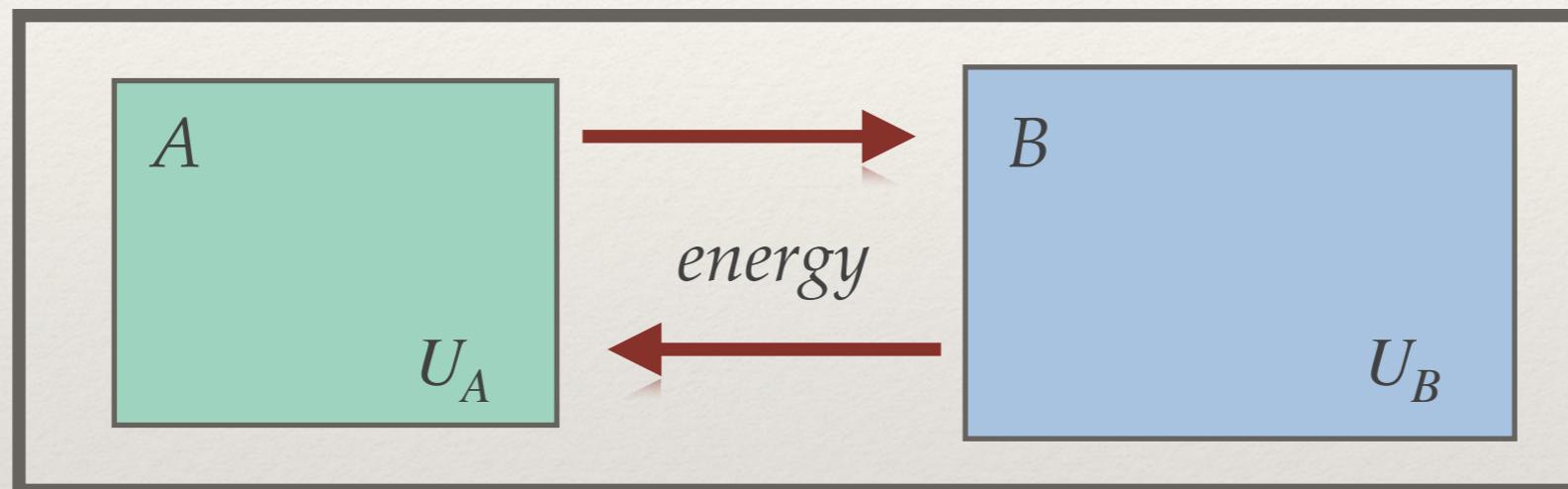
read chapters:

- 3.1 Temperature
- 3.2 Entropy and Heat
- 3.3 Paramagnetism
- 3.4 Mechanical Equilibrium and Pressure
- 3.5 Diffusive Equilibrium and Chemical Potential

Temperature

Recall: Zeroth law \Rightarrow the notion of temperature

Today: *entropy \Leftrightarrow temperature*

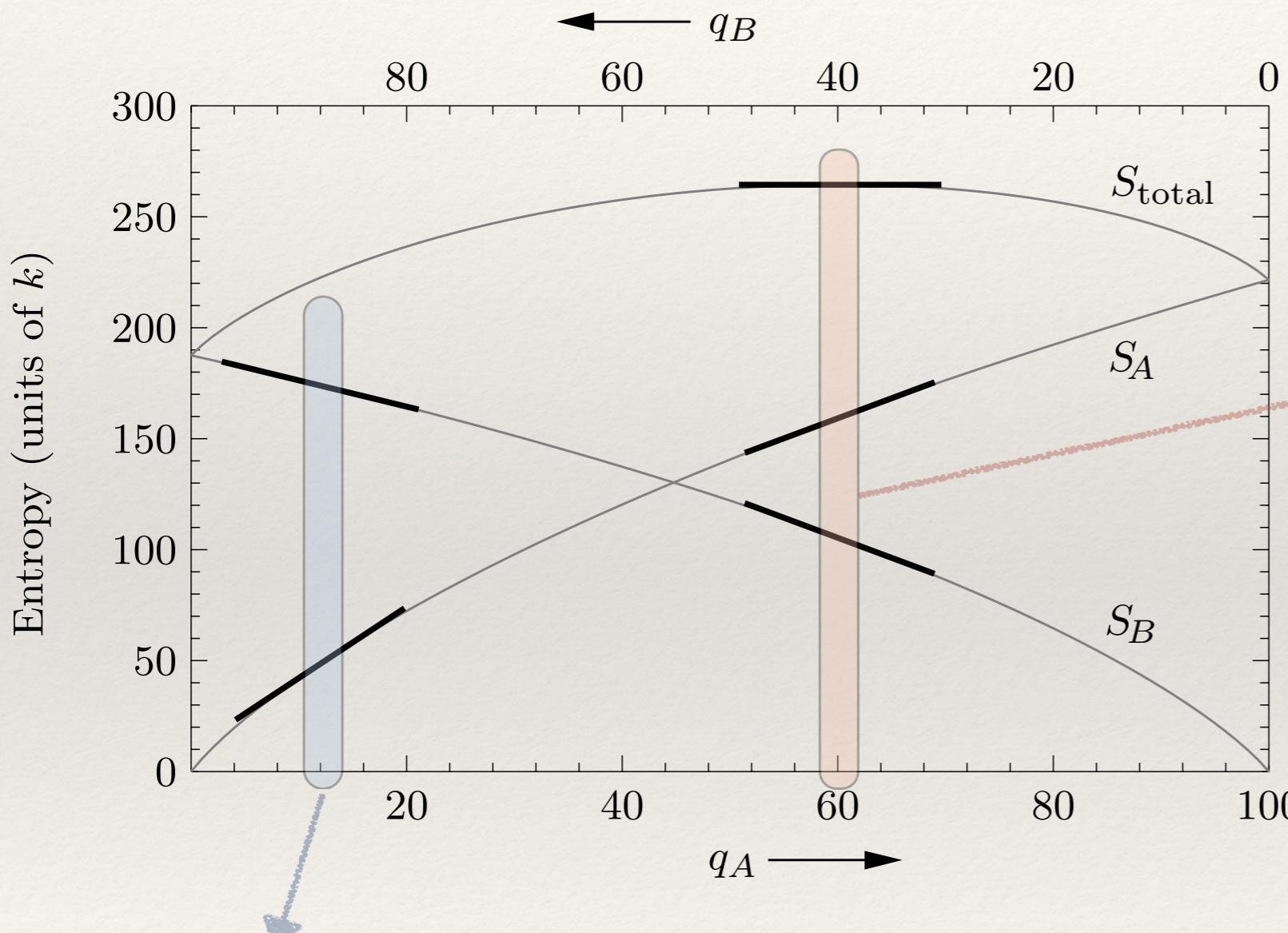


Thermal Equilibrium: $\frac{\partial S_{total}}{\partial U_A} = 0 \rightarrow \frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A} = 0 \rightarrow \frac{\partial S_A}{\partial U_A} = - \frac{\partial S_B}{\partial U_B}$

At thermal equilibrium the slopes of entropy vs energy graphs are equal

Temperature

e.g. Einstein solid $N_A = 300$, $N_B = 200$, $q_{total} = 100$, recall: $U \propto q$



$|\text{slope of } S_B| < |\text{slope of } S_A|$ energy flows from B to A

$$\text{temperature} = \frac{1}{\text{slope}}$$

$|\text{slope of } S_{total}| = 0$

$|\text{slope of } S_B| = |\text{slope of } S_A|$

Thermodynamic equilibrium

Temperature

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

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

Everything else
kept constant

Dimensional analysis: $S = k \log \Omega, [k] = J/K \Rightarrow [\partial S / \partial U] = 1/K$

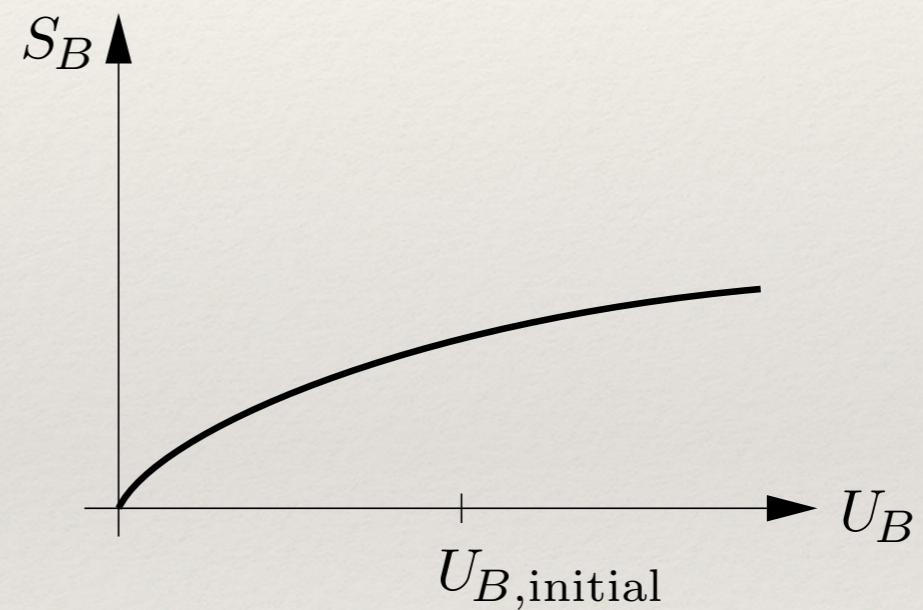
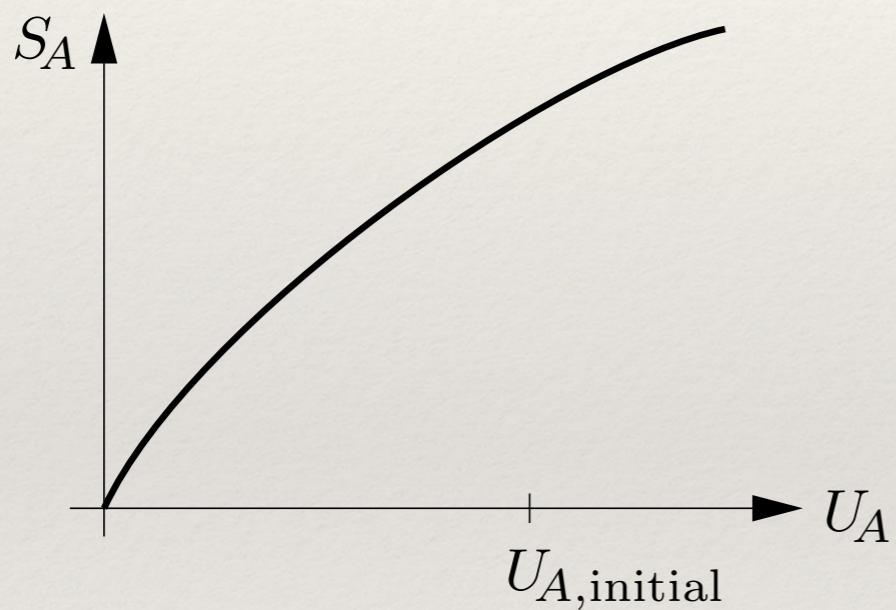
Remark: This definition of temperature starts from the *microscopic* definition of entropy (in terms of microstates, likelihood of possible arrangements etc..).

Historically entropy and the second law was defined entirely *macroscopically* in terms of heat and temperature without a detailed understanding of the underlying microscopic physics.

It was Boltzmann who made the connection for the first time between the second law and microscopic order/disorder. This was a revolutionary idea at the time (a time where the existence of atoms has not even been widely accepted).

Temperature

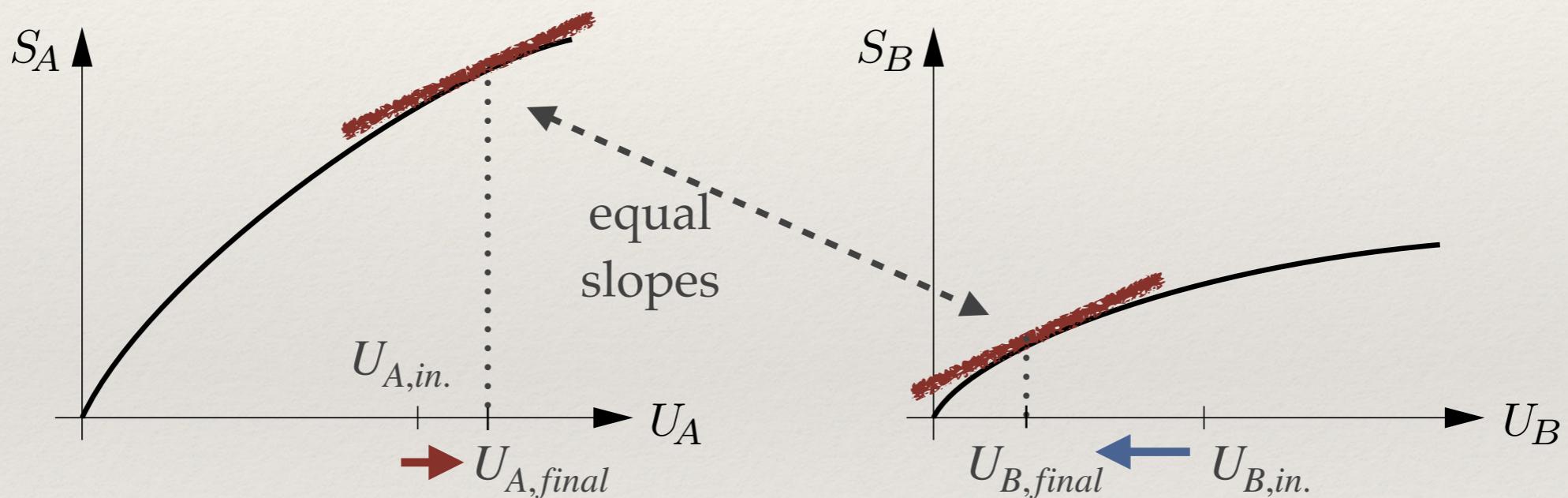
$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{N,V,\dots}$$



What will happen?

Temperature

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



Temperature

e.g. Einstein solid at high temperature ($q \gg N$)

$$S = Nk \left[\log\left(\frac{q}{N}\right) + 1 \right], \quad U = \epsilon q \quad \Rightarrow \quad T = \left(\frac{\partial S}{\partial U} \right)^{-1} = \left(\frac{Nk}{U} \right)^{-1}$$

$U = NkT$ as expected from *equipartition theorem* ($N_{dof} = 2$) why?

e.g. Monoatomic ideal gas

$S = Nk \log(U^{3/2}) + \text{terms independent of } U$

$$U = \frac{3}{2}NkT$$

Entropy and Heat

How to calculate heat capacities:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

Now we know how
to *calculate* T

e.g. Einstein solid at low temperature ($q \ll N$)

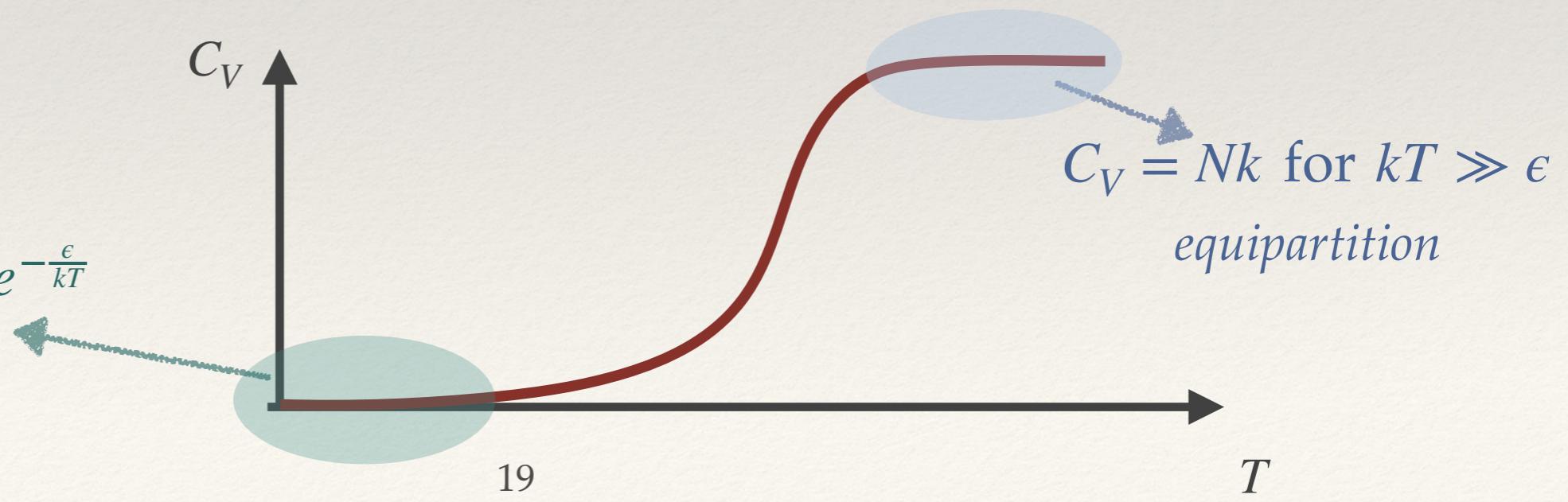
Equipartition theorem does not hold at low T . But *quantum mechanics does!*

$$\Omega = \frac{(N+q-1)!}{(N-1)!q!} \sim \left(\frac{eN}{q} \right)^q \Rightarrow S = k \log \Omega = kq \left[\log \left(\frac{N}{q} \right) + 1 \right] \Rightarrow \frac{1}{T} = \frac{k}{\epsilon} \log \left(\frac{N\epsilon}{U} \right)$$

$$U = N\epsilon e^{-\frac{\epsilon}{kT}}$$

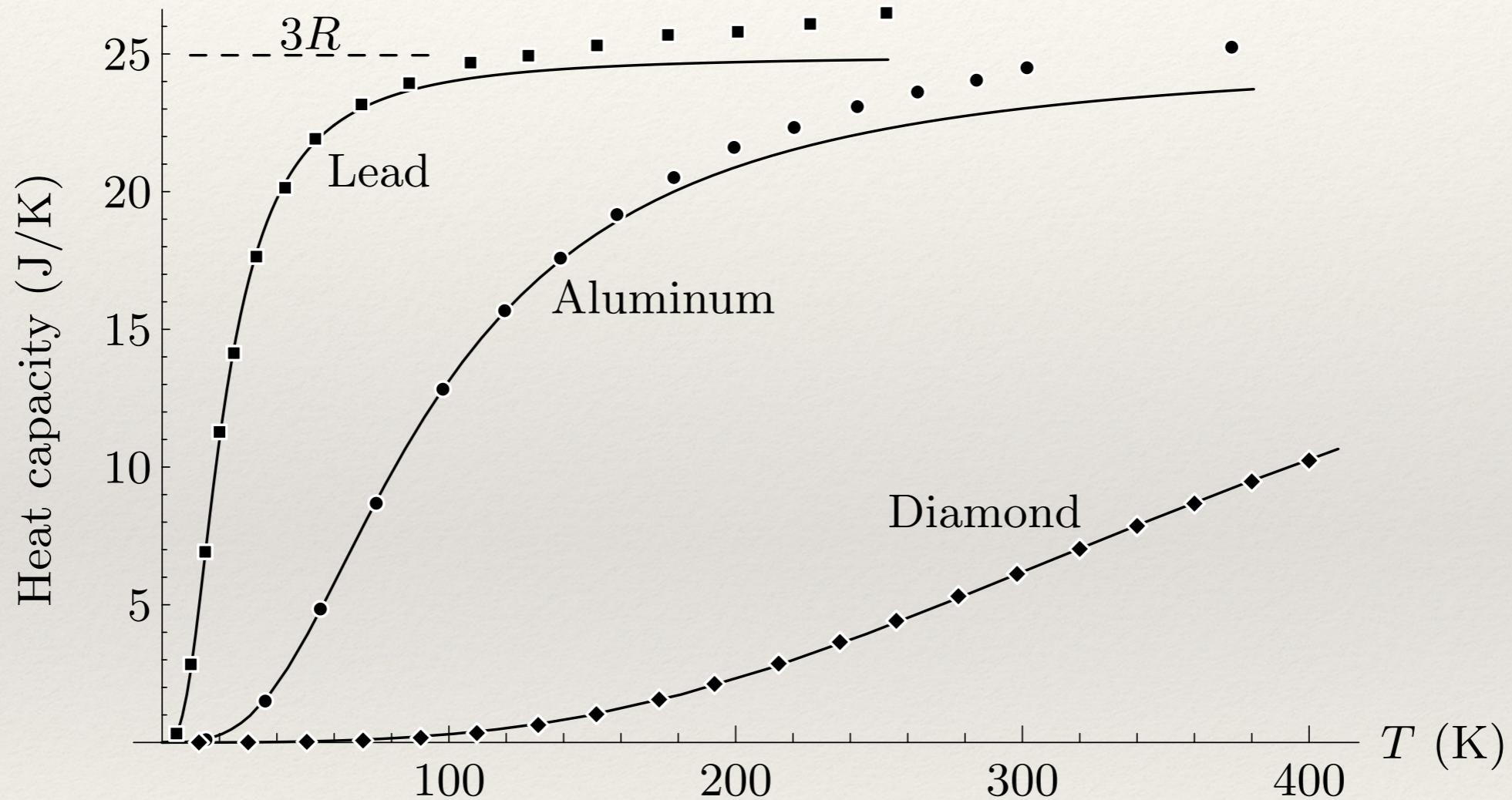
$$C_V = Nk \left(\frac{\epsilon}{kT} \right)^2 e^{-\frac{\epsilon}{kT}}$$

$$\lim_{T \rightarrow 0} C_V = 0$$



Entropy and Heat

Recall...



Measuring Entropy

For complicated systems, calculating C_V from first principles is typically not possible.

One can always measure it though... 

with N , V , etc. fixed:

incoming heat increases the thermal energy hence the entropy

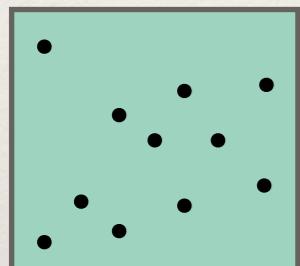
$$dS = \frac{dU}{T} = \frac{dQ}{T}$$

recall: dQ is not an exact differential

As we heat up the system the temperature increases
(with the exception of certain phase transitions)

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

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



Measuring Entropy

e.g. warming up a cup of water



200g, 20°C → 100°C

Recall: heat required to warm up water by 1K: 1 cal ≈ 4.2 J

$$C_V = 840 \text{ J/K} \quad (\text{approximately constant})$$



$$\Delta S = C_V \int_{293 \text{ K}}^{373 \text{ K}} \frac{dT}{T} \approx 200 \text{ J/K}$$

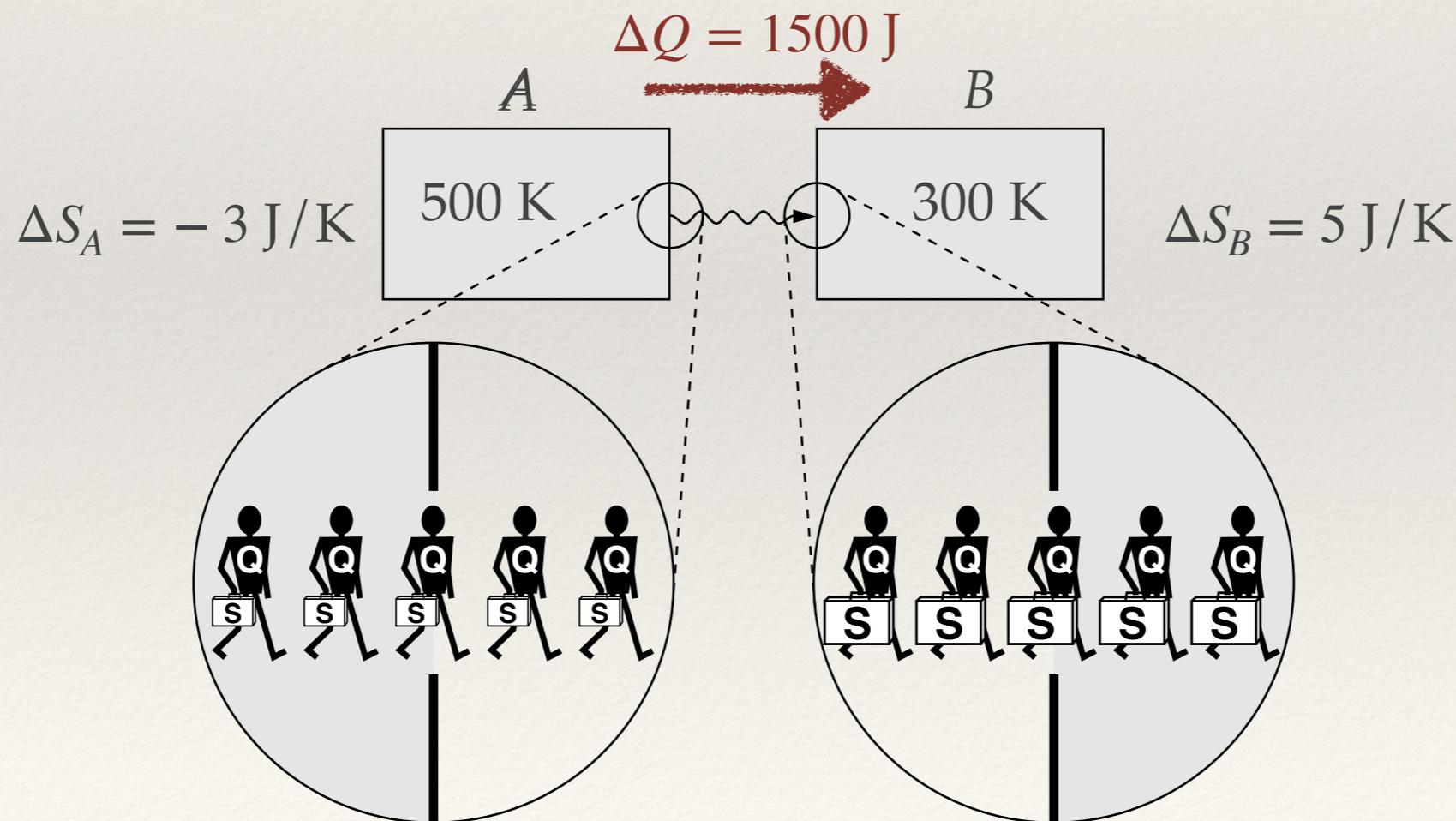
$$\frac{\Delta S}{K} = 1.5 \times 10^{25} \Rightarrow \text{the multiplicity increases by } e^{1.5 \times 10^{25}}$$

A Small Historical Detour

Clausius, 1865: *entropy*: ``the thing that changes by $\Delta Q/T$ when heat enters into a system at temperature T '' $\Delta S = \frac{\Delta Q}{T}$

Coined the name *entropy* and humbly introduced the unit ``Clausius'' (Cl= 1cal/ $^{\circ}\text{C}$). The name stuck, the unit didn't...

e.g.



Third Law

The measurement of entropy is defined with respect to a reference state.

Third Law (``Nernst theorem''): $\lim_{T \rightarrow 0} S(T) = 0$

$$\int_0^T \frac{C_V}{T} dT = S(T) - S(0) = S(T) \quad \Rightarrow \quad \textit{absolute scale for entropy}$$

Third Law

The measurement of entropy is defined with respect to a reference state.

Third Law (``Nernst theorem''): $\lim_{T \rightarrow 0} S(T) = 0$

$$\int_0^T \frac{C_V}{T} dT = S(T) - S(0) = S(T) \quad \Rightarrow \quad \text{absolute scale for entropy}$$

At $T=0$, the system settles in a unique ground (lowest energy) state.

More precisely: The degeneracy of ground state (if present) does not grow extensively

For the integral to be convergent $\lim_{T \rightarrow 0} C_V \sim T^n$ with $n \geq 1 \Rightarrow \lim_{T \rightarrow 0} C_V = 0$

At $T=0$ all the degrees of freedom ``freeze-out'' quantum mechanically.
Classical results (such as Dulong and Petit) are not valid. Third law in this
sense is essentially implies that world at $T=0$ is quantum mechanical.

A Model of Paramagnetism

Two-state paramagnet: • One dimensional lattice of spin-1/2 particles

- Each particle has a magnetic moment $\vec{\mu}$



- number of up spins : N_\uparrow $N_\uparrow + N_\downarrow = N$: fixed
- number of down spins : N_\downarrow

- Energy per particle: $U_i = -\vec{B} \cdot \vec{\mu}_i = \mp B\mu$ $U_{total} = B\mu(N_\downarrow - N_\uparrow) = B\mu(N - 2N_\uparrow)$

- Magnetization: $M = \mu(N_\uparrow - N_\downarrow) = -U/B$

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

A Model of Paramagnetism

Two-state paramagnet: • One dimensional lattice of spin-1/2 particles

- Each particle has a magnetic moment $\vec{\mu}$



- number of up spins : N_\uparrow $N_\uparrow + N_\downarrow = N$: fixed
- number of down spins : N_\downarrow

- Energy per particle: $U_i = -\vec{B} \cdot \vec{\mu}_i = \mp B\mu$ $U_{total} = B\mu(N_\downarrow - N_\uparrow) = B\mu(N - 2N_\uparrow)$

- Magnetization: $M = \mu(N_\uparrow - N_\downarrow) = -U/B$

Multiplicity:

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

Entropy:

$$\frac{S}{k} = N \log \frac{N}{(N - N_\uparrow)} - N_\uparrow \log \frac{N_\uparrow}{(N - N_\uparrow)}$$

A Model of Paramagnetism

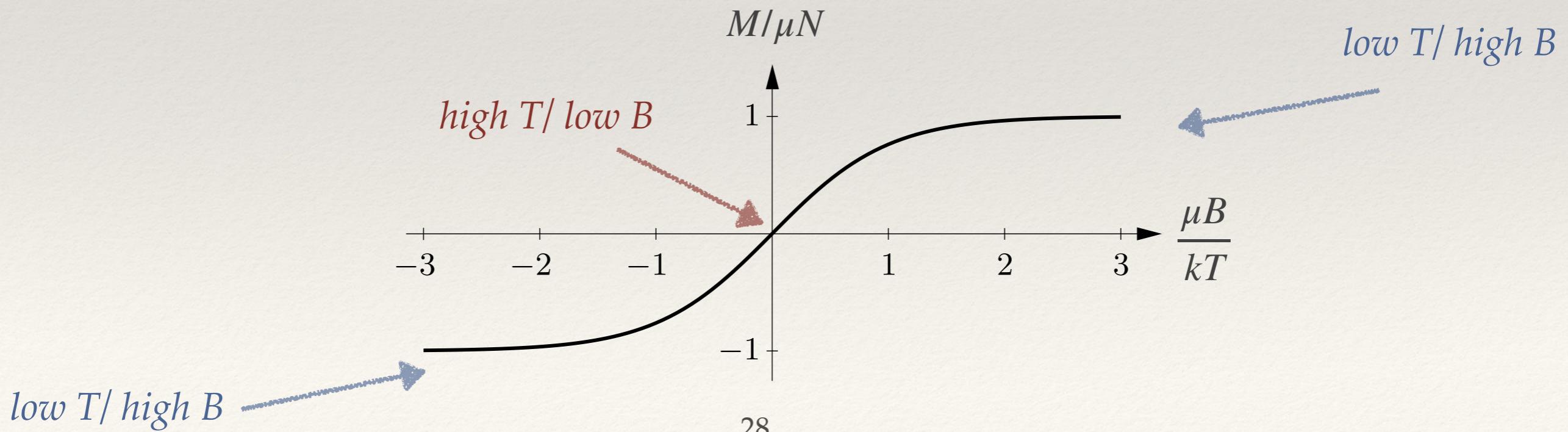
after some tedious algebra...

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{N,B} = \frac{k}{2\mu B} \log \left(\frac{N - U/\mu B}{N + U/\mu B} \right)$$

invert it to get:

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

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

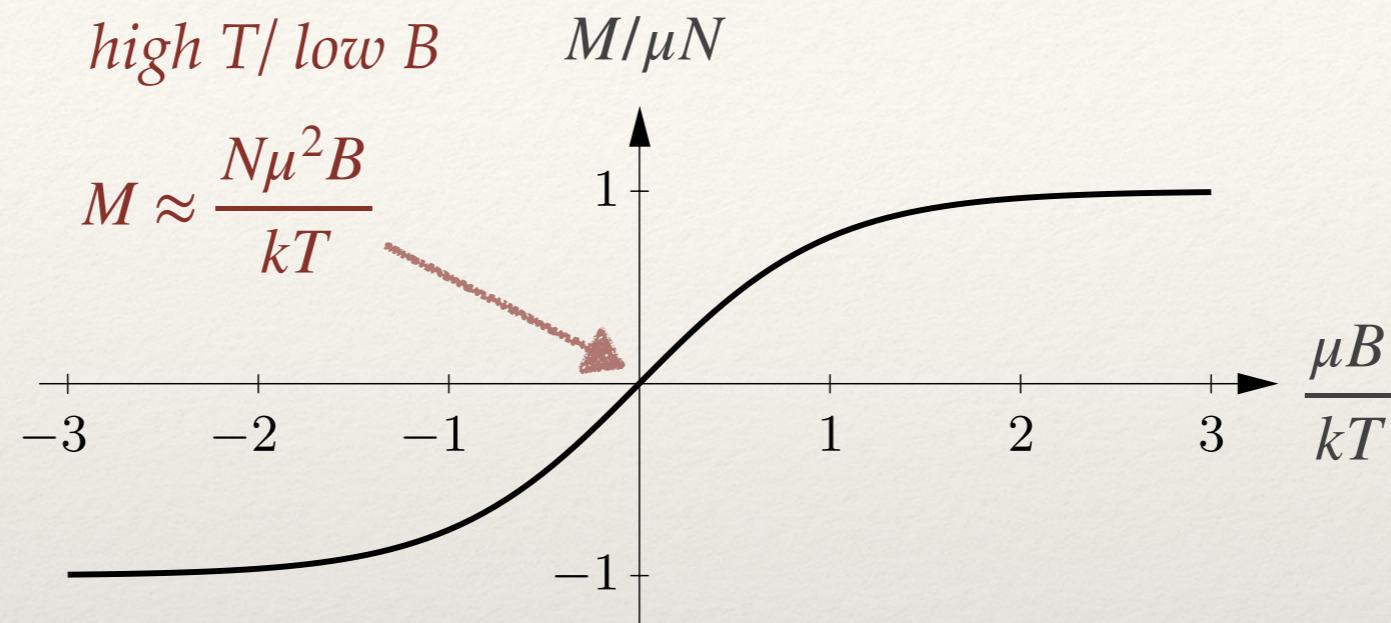


A Model of Paramagnetism

Curie's Law

high T/ low B

$$M \approx \frac{N\mu^2 B}{kT}$$



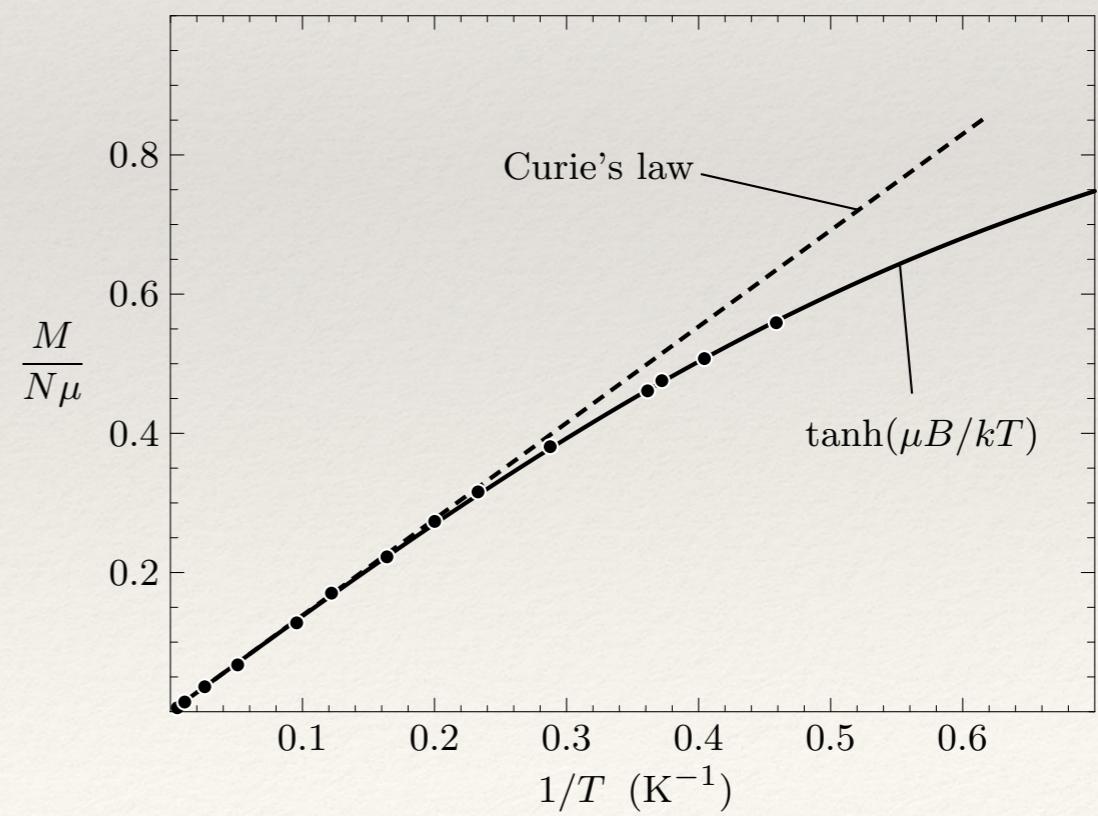
For electrons

$$\mu_B = \frac{e\hbar}{2m} \approx 5.8 \times 10^{-5} \text{ eV/T}$$

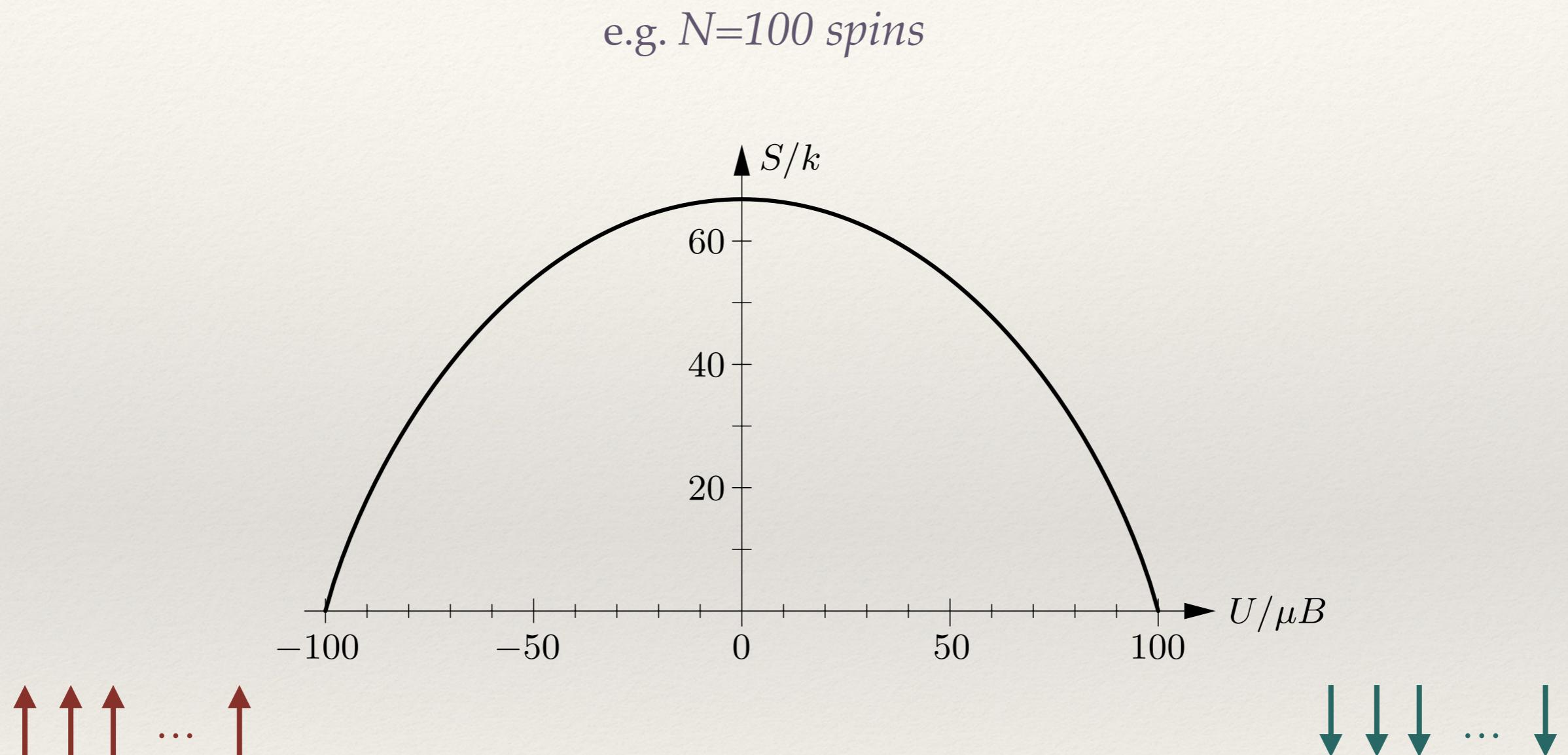
Bohr magneton

$$kT_{room} \approx 1/40 \text{ eV}$$

$$\frac{\mu_B \times (1T)}{kT_{room}} \ll 1$$

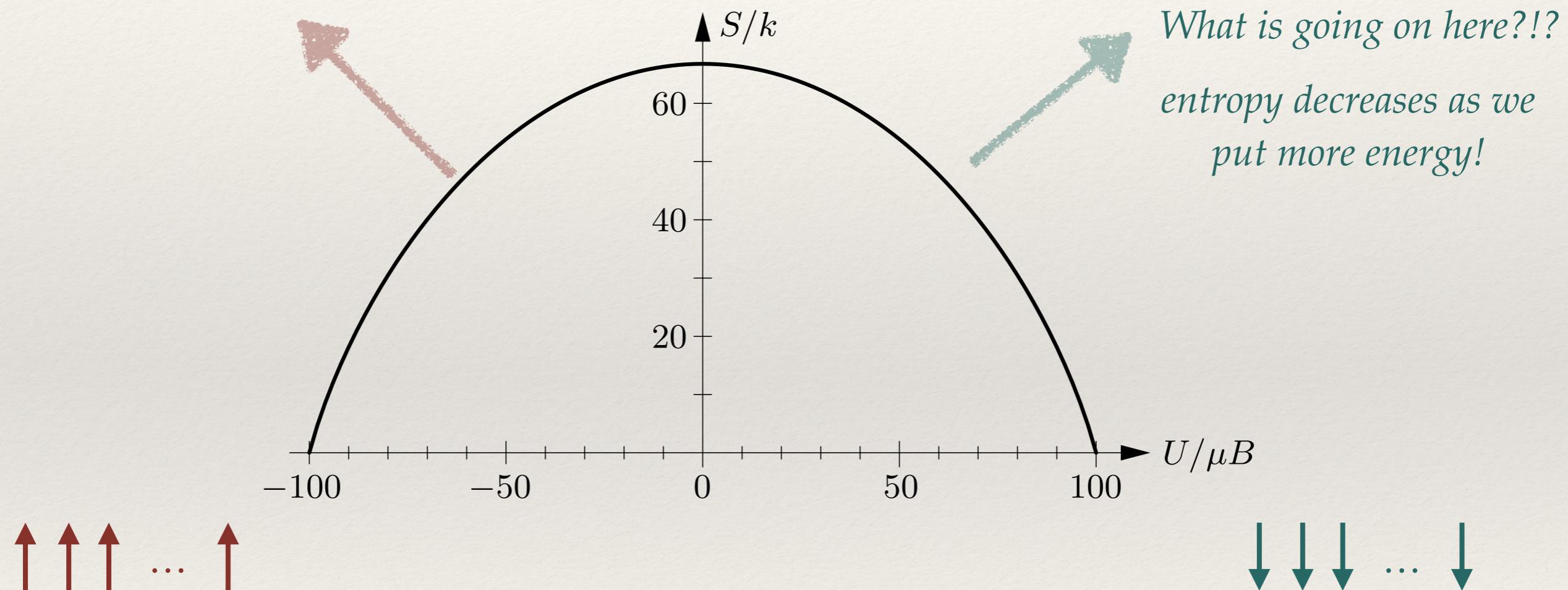


A Model of Paramagnetism



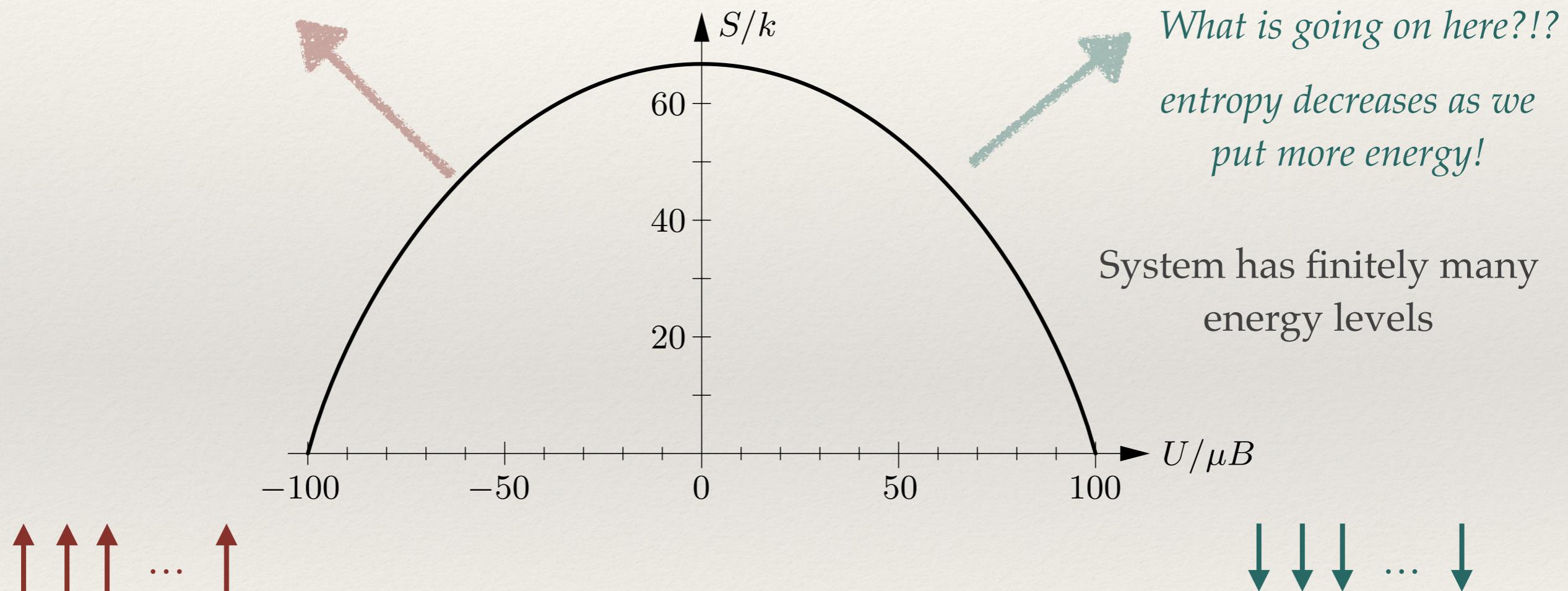
A Model of Paramagnetism

*entropy increases just like
an Einstein solid*



A Model of Paramagnetism

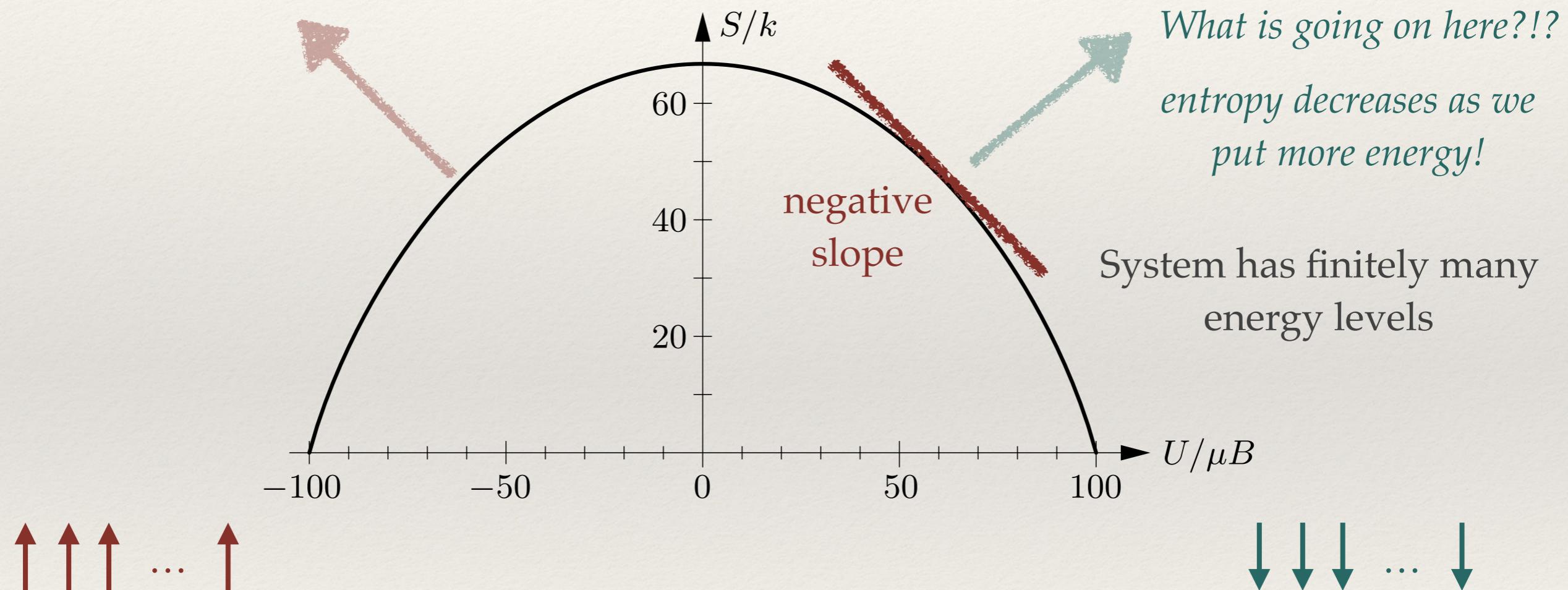
*entropy increases just like
an Einstein solid*



For $U>0$ the system *gains* entropy by giving energy away!

A Model of Paramagnetism

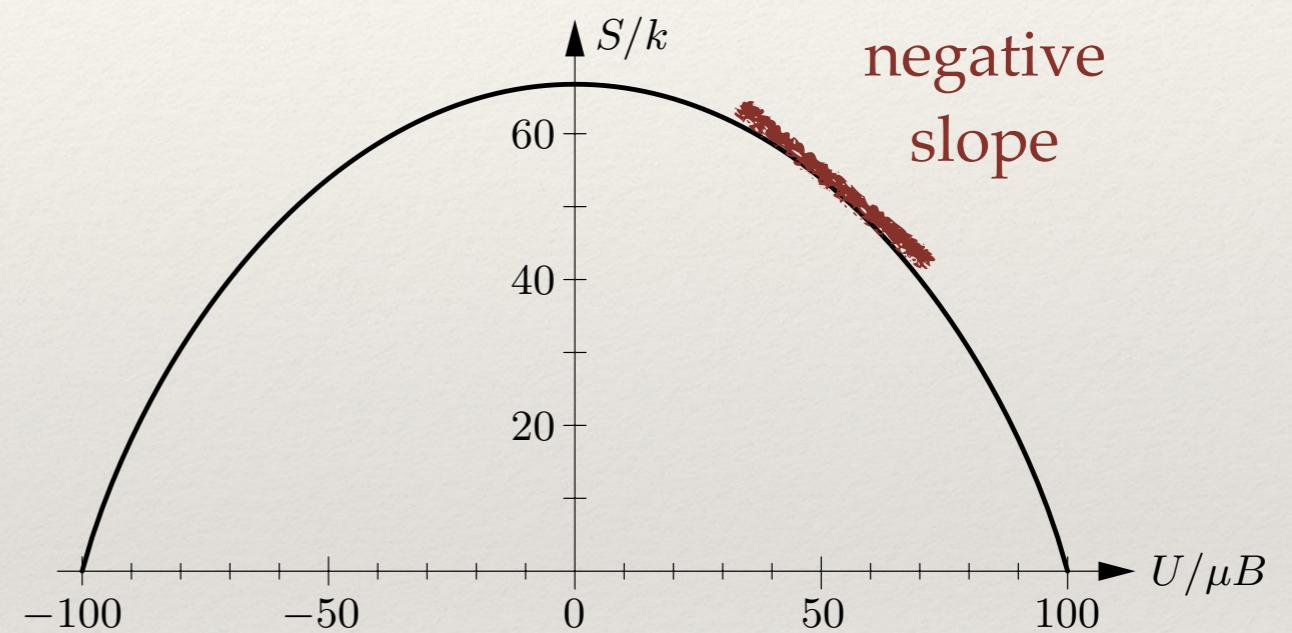
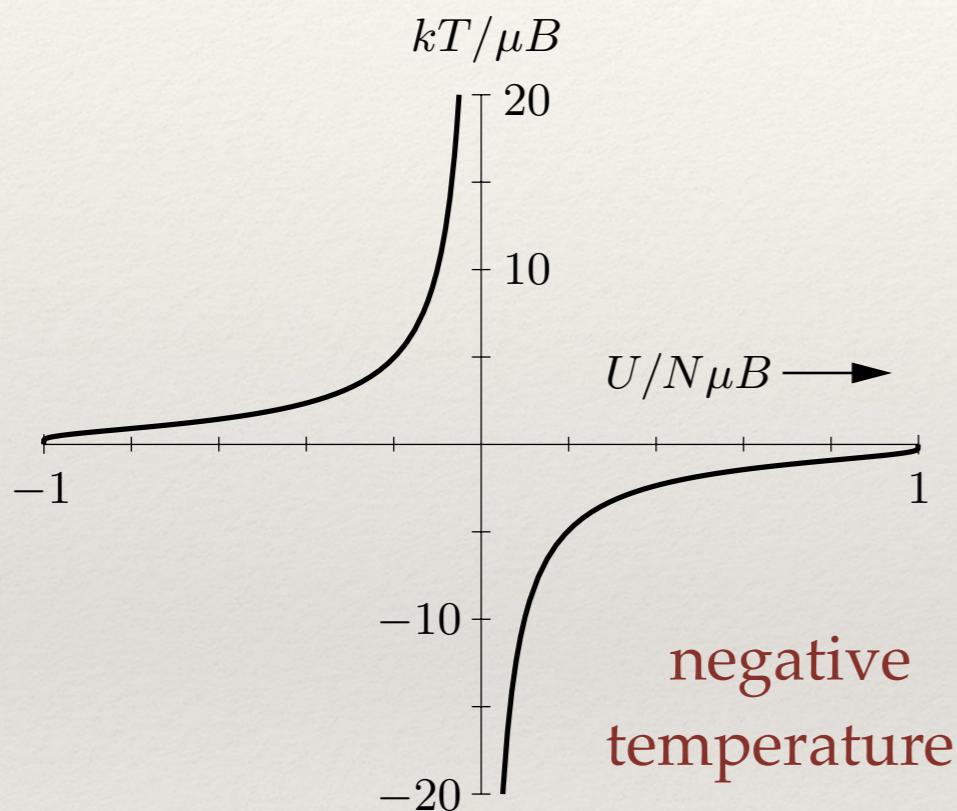
*entropy increases just like
an Einstein solid*



For $U>0$ the system *gains* entropy by giving energy away!

A Model of Paramagnetism

e.g. $N=100$ spins

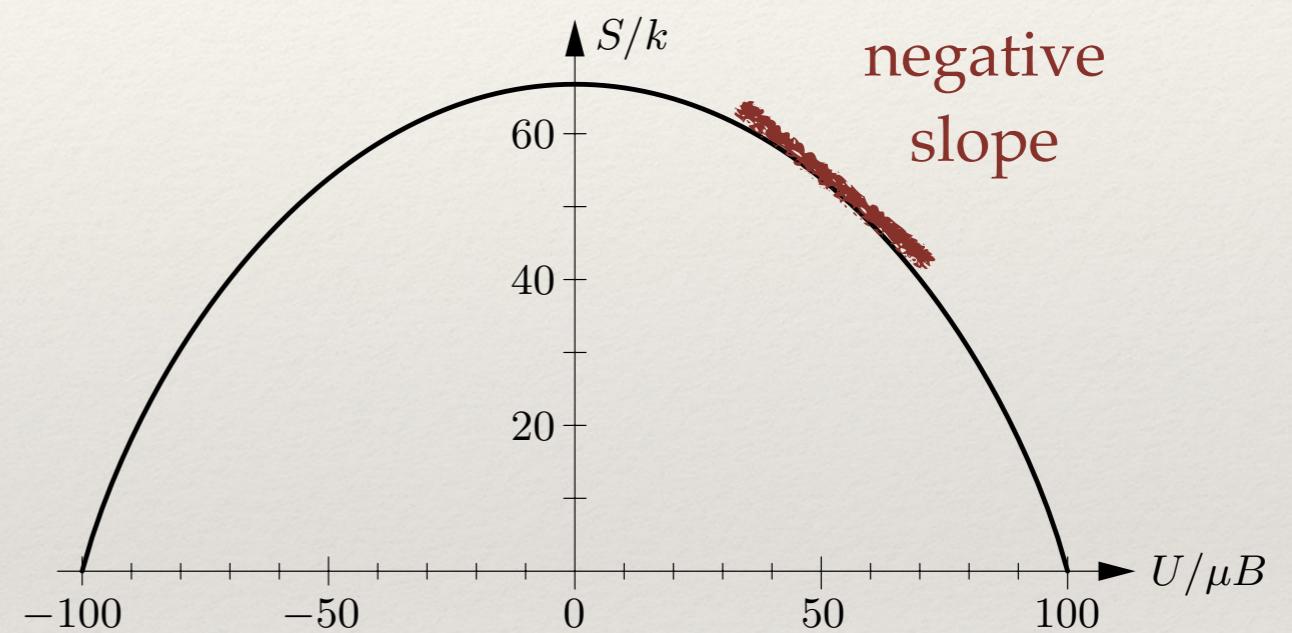
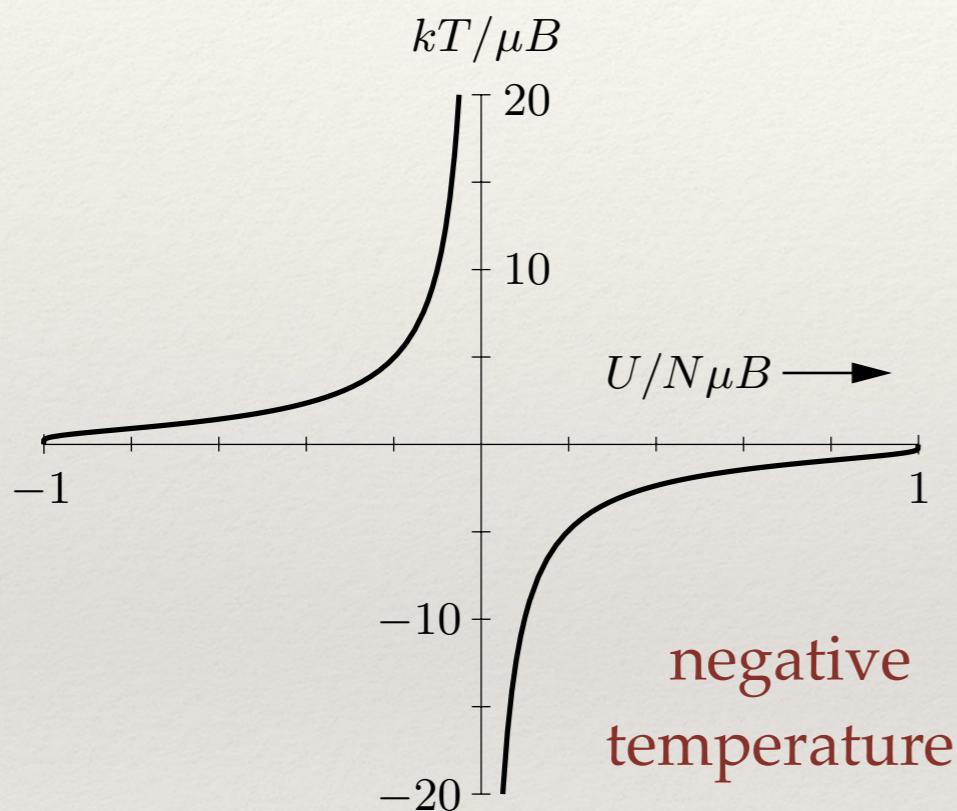


For $U>0$ the system *gains* entropy by *giving energy away!*

Temperature is ``greater than infinity'' since the system will give energy to any system with $U<0$ (positive temperature)

A Model of Paramagnetism

e.g. $N=100$ spins



For $U>0$ the system *gains* entropy by *giving energy away!*

Temperature is ``greater than infinity'' since the system will give energy to any system with $U<0$ (positive temperature)

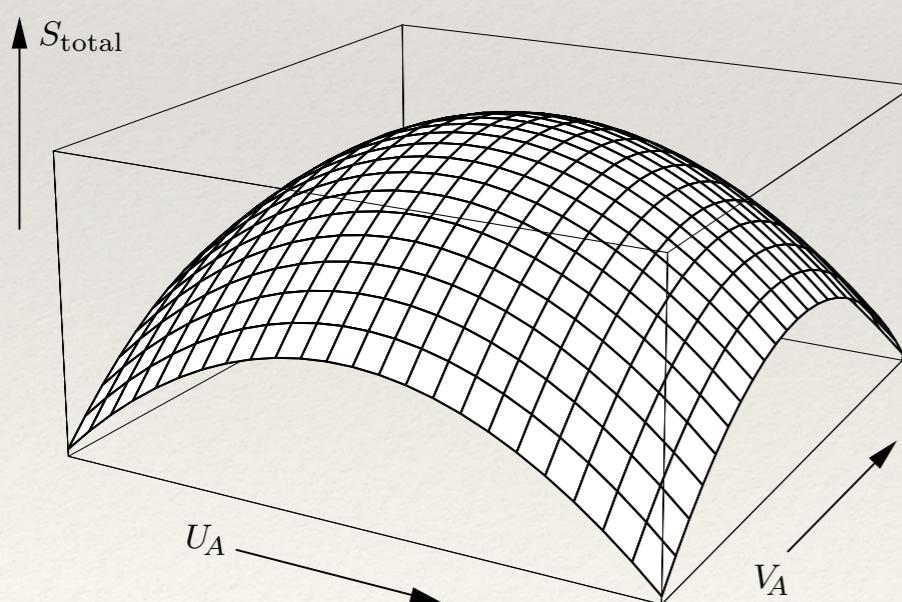
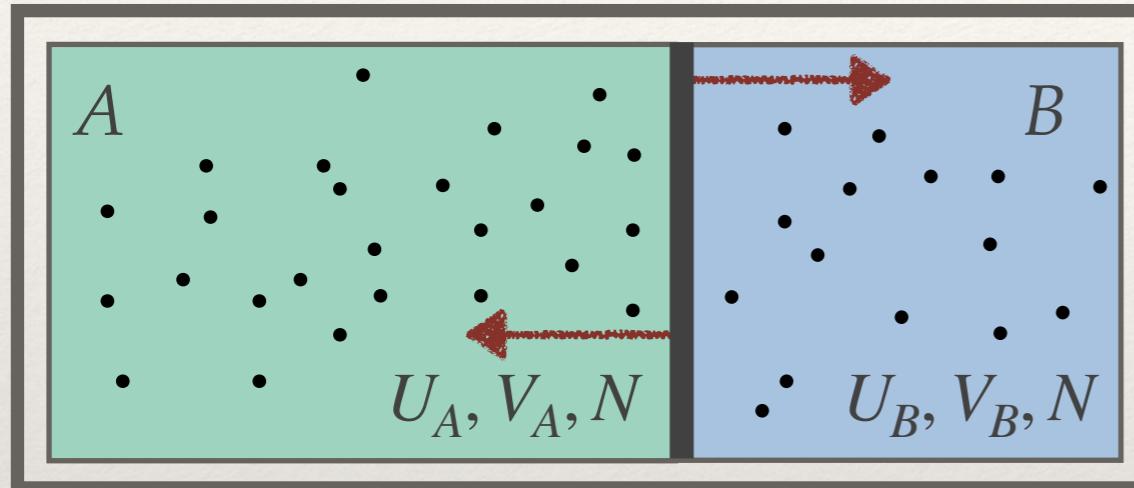
Mechanical Equilibrium and Pressure

Temperature



Spontaneous exchange of energy

$$T_A = T_B \Leftrightarrow \frac{\partial S_{tot}}{\partial U} = 0$$



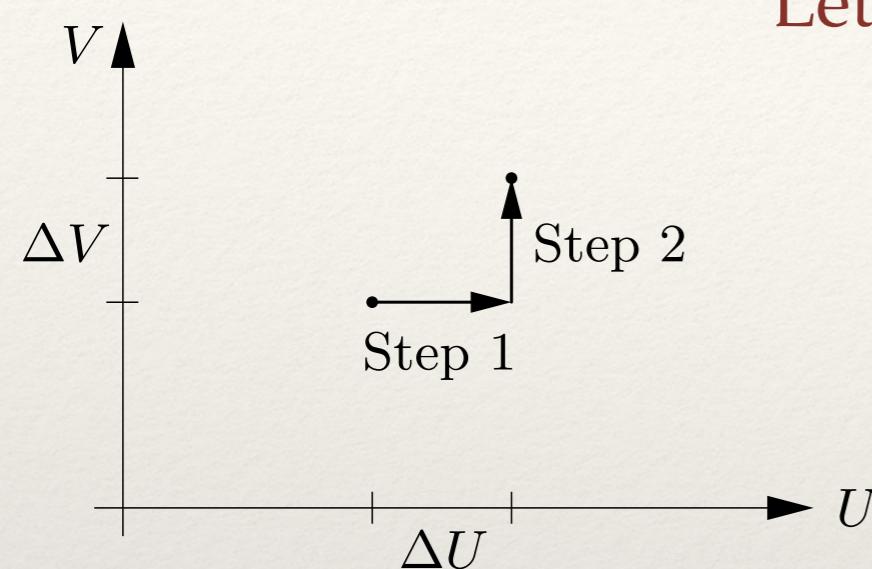
When the gases are allowed to exchange *volume* the equilibrium will be reached when

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

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

*the partial derivatives are evaluated at fixed N_A , U_A . We further assumed that they are in thermal equilibrium.

Pressure and Temperature Revisited



Let U and V vary by small amounts

$$\Delta S = (\Delta S)_{\text{step1}} + (\Delta S)_{\text{step2}}$$

$$\Delta S = \left(\frac{\Delta S}{\Delta U} \right)_V \Delta U + \left(\frac{\Delta S}{\Delta V} \right)_U \Delta V$$

Infinitesimally:

$$dS = \left(\frac{\partial S}{\partial U} \right)_V dU + \left(\frac{\partial S}{\partial V} \right)_U dV = \frac{1}{T} dU + \frac{p}{T} dV$$

$$dU = TdS - pdV$$

``thermodynamic identity''

The First Law Revisited

First Law

$$dU = dQ + dW$$

For a *quasi-static* change in volume
(p =uniform throughout the change)
and no other work is done:

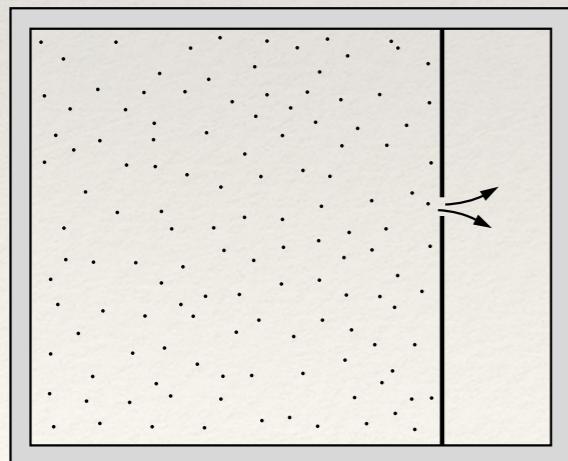
Thermodynamic Identity

$$dU = TdS - pdV$$

$$dQ = TdS, \quad dW = -pdV \quad (\text{quasi-static})$$

First Law = Thermodynamic Identity

e.g. not a quasi-static change: free expansion



- no change in energy
- no heat exchange with the environment
- no work done on the system

$$\Delta U = T\Delta S - p\Delta V = 0$$

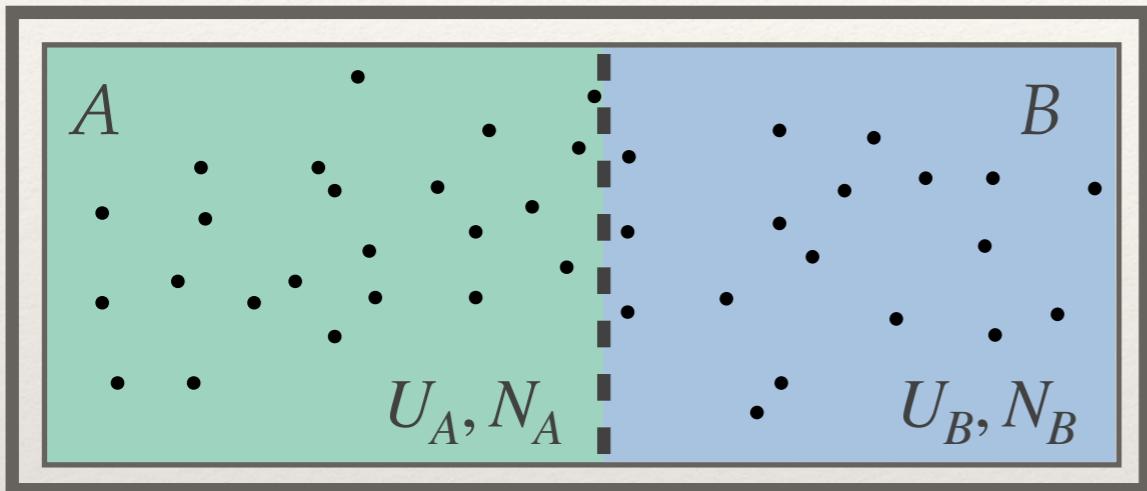
$$\Delta S = \frac{p}{T} \Delta V$$

entropy is created during the process

Diffusive Equilibrium and Chemical Potential

The gases are able to exchange particles

Thermal equilibrium: $T_A = T_B$



Mechanical equilibrium: $p_A = p_B$

Diffusive equilibrium: $?_A=?_B$

When gases no longer
exchange particles

$$dN_A = - dN_B$$

$$\frac{\partial S_{tot}}{\partial N_A} = 0 \quad \Rightarrow \quad \frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}$$

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

chemical potential

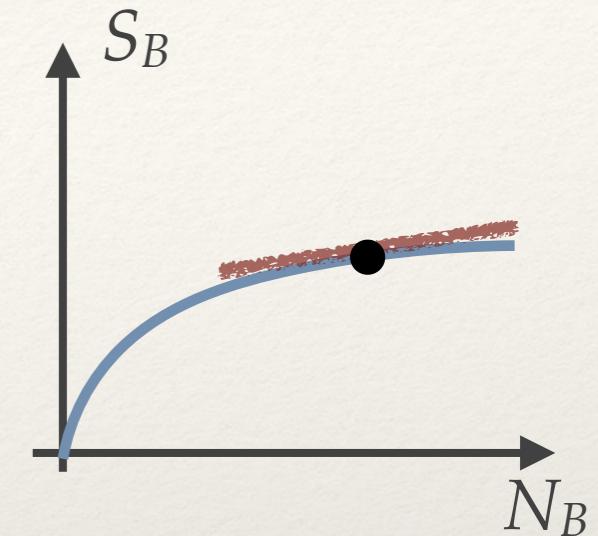
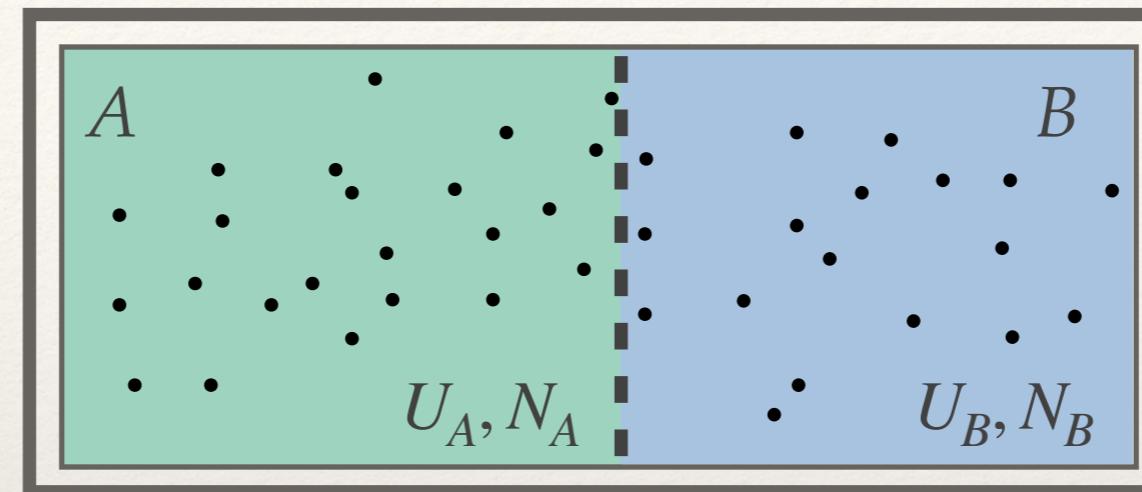
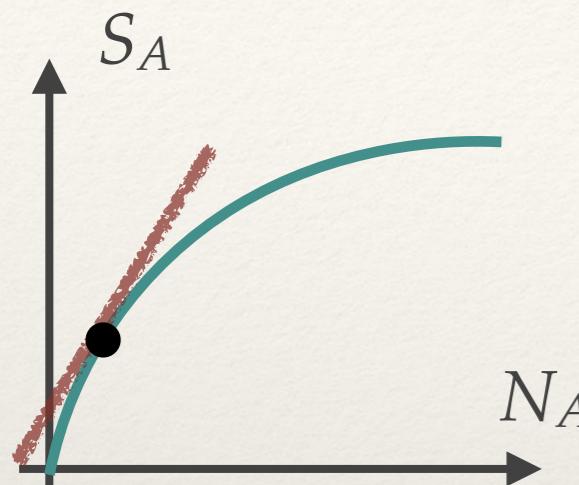
factor of (-T) for
convention

μ has

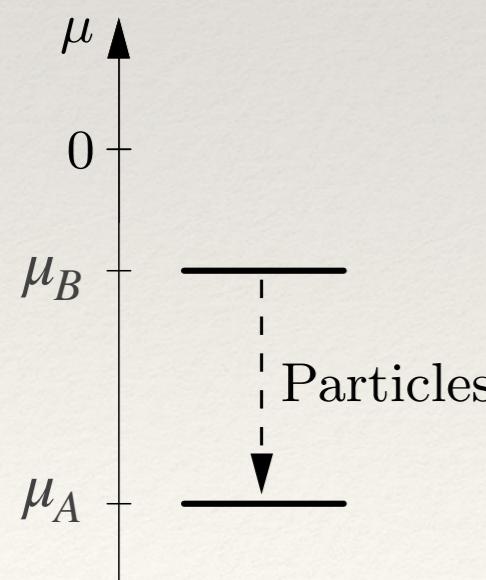
dimensions of
energy

Diffusive equilibrium: $\mu_A = \mu_B$

Diffusive Equilibrium and Chemical Potential



Larger slope: increase N_A , gain entropy



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

- sign: particles tend to flow from a system of higher μ (smaller slope) to lower μ (larger slope)

Thermodynamic Identity

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

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

e.g. constant S

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

Change in energy of the system when we add a particle.

Generally negative since we have to remove energy to keep the entropy constant

For more than one species:

$$dU = TdS - pdV + \sum_i \mu_i dN_i \quad i=1,2,\dots : over species$$

Chemical Potential

e.g. Einstein solid with $N=3, q=3$ ($E = \epsilon q$) *each oscillator = ``particle''*

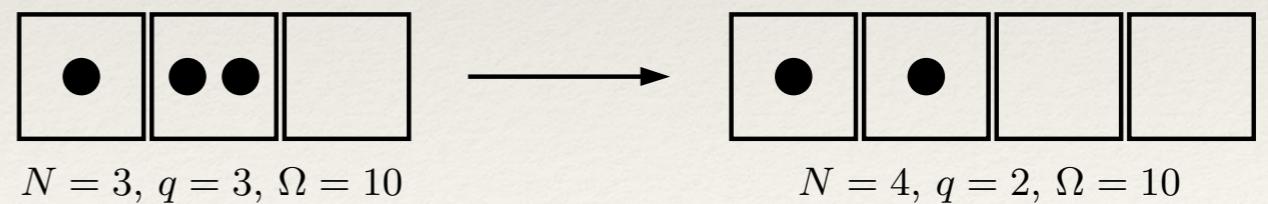
$$\text{Multiplicity} \quad \Omega = \frac{(N+q-1)!}{(N-1)!q!} = \frac{5!}{3!2!} = 10 \quad \text{Entropy } S=k \log 10$$

Add one more oscillator (``particle'') $\Omega = \frac{6!}{3!3!} = 20, \quad S = k \log 20$

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

To keep entropy fixed ($k \log 10$) we need to subtract one unit of energy ($N=4, q=2$)

$$\mu = \left(\frac{\Delta U}{\Delta N} \right)_S = \frac{-\epsilon}{1} = -\epsilon$$



Chemical Potential

e.g. ideal gas $S = Nk \left[\log \left(\frac{V}{N} \left(\frac{mU}{3N\pi\hbar^2} \right)^{3/2} \right) + \frac{5}{2} \right]$ Sackur-Tetrode

$$U = \frac{3}{2}kT \quad S = Nk \left[\log \left(V \left(\frac{mU}{3\pi\hbar^2} \right)^{3/2} \right) - \log N^{5/2} + \frac{5}{2} \right]$$

$$\mu = - T \left(\frac{\partial S}{\partial N} \right)_{U,V} = - kT \log \left(\frac{V}{N} \left(\frac{mU}{3\pi\hbar^2} \right)^{3/2} \right) = - kT \log \left(\frac{V}{\lambda^3 N} \right) \quad \lambda = \left(\frac{mkT}{2\pi\hbar^2} \right)^{-1/2}$$

Typical gas: (H at room temperature and atmospheric pressure)

Typical volume of H $\lambda^3 \approx 1.3 \times 10^{-31} \text{m}^3$ $\mu \approx -0.32 \text{eV}$

*Volume of per particle
1/density* $\frac{V}{N} \approx 4.2 \times 10^{-26} \text{m}^3$

When compressed, μ increases: system
is more willing to give up particles

Putting it Altogether

For any macroscopic system described by energy, volume and number of particles:

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN$$

Type of interaction	Exchanged quantity	Governing variable	Formula
thermal	energy	temperature	$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$
mechanical	volume	pressure	$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}$
diffusive	particles	chemical potential	$\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{U,V}$

Outlook

Chapters 4 & 5: Classical Thermodynamics

Applications of laws of thermodynamics for practical systems

4) Engines, Refrigerators

5) Free Energies, Phase transitions

Chapters 6, 7 & 8: Statistical Mechanics

Using microscopic models to derive the thermodynamic properties

6) Boltzmann Statistics: Matter at high temperatures

7) Quantum Statistics: Matter at low temperatures, Quantum effects,
bosons, fermions

8) Interacting Particles, Ising Model

Thank you!