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Quiz 2 next Tues, Feb 8

Cover all material since Quiz 1, including today's lecture and HW3

Will post list of topics to focus on this Sat

Will provide formulas on future quizzes and exams, you show me you know how to use the formulas

Homeworks: email if > 8 hr

HW3 answers Sat

Mon

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(2)

Chapter 2: The Second Law of Thermodynamics: Equilibrium of An Isolated System Corresponds to Maximum of Entropy

Chapter 1: discussed energy, work, heat
1st law of thermodynamics, conservation of energy
relation of temperature to molecular motion

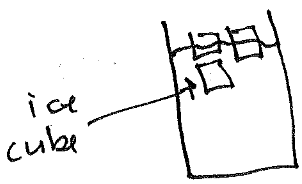
Two big questions:

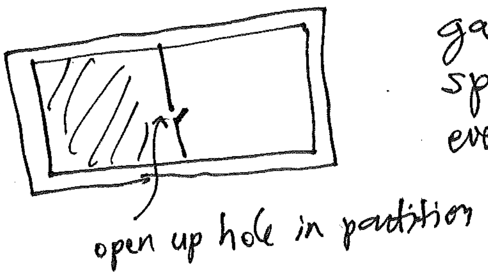
① - how to think of temperature for non-gases?
liquids, solids, magnets
polymers, black holes, metals

② - how to understand <u>spontaneous</u> behavior?

why does heat transfer from hot to cold systems?

$T_1 > T_2$
$\xrightarrow{}$ energy from T_1 to T_2





gas automatically, spontaneously spreads to entire container even though no change in energy (no work done, no heat exchanged)

Also : ω

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(1)

Any Chapter 1 questions before beginning Chapter 2?

heat capacity

$$\begin{tikzcd}
 & C_V = \left(\frac{\partial U}{\partial T}\right)_V \\
C = \frac{Q}{\Delta T} \arrow[ur] \arrow[dr] & \\
 & C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P
\end{tikzcd}$$

upper case C

specific heat

$$\begin{tikzcd}
 & C/M \text{ per mass} \\
c \arrow[ur] \arrow[dr] & \\
 & C/n \text{ per mole}
\end{tikzcd}$$

lower case c

adiabatic exponent γ $\quad V^\gamma P = \text{const}$ adiabatic process

$1 \leq \gamma = \frac{f+2}{f} \leq \frac{5}{3}$ $\quad \underbrace{C_P/C_V = \gamma}$ for ideal gas

$C_P = C_V + Nk$ ideal gas

latent heat $\quad L = \frac{Q}{m}$ constant pressure $\left\{ \begin{array}{ll} \text{sublimation} & s \to g \\ \text{melting} & s \to l \\ \text{vaporization} & l \to g \end{array} \right.$

energy needed to melt amount of mass m

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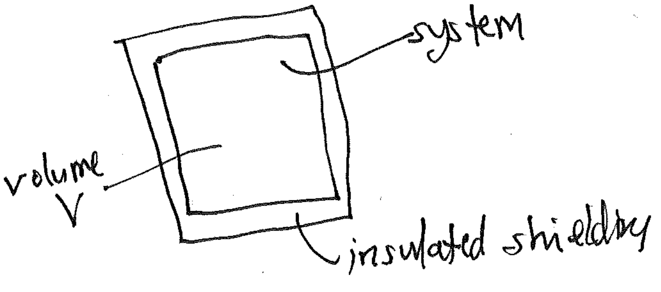
Entropy $S(U,V,N)$ of Macroscopic Isolated System

We will introduce a new concept related to macroscopic systems called the entropy that can explain our key question about temperature. and about spontaneous behavior, and nearly all other questions about equilibrium macroscopic behavior

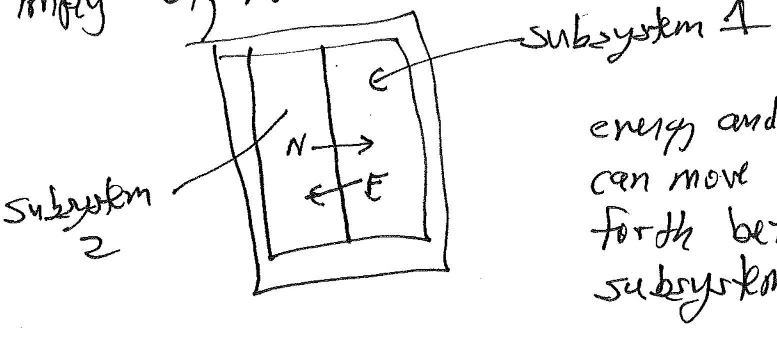
consider isolated macroscopic system like gas, liquid, solid, magnet, etc.

"isolated" is code word for "conserved quantities"



total energy U_{tot} conserved
total number of particles N_{tot} conserved
total volume of system fixed, V

this does not imply U, N conserved for macroscopic subsystems

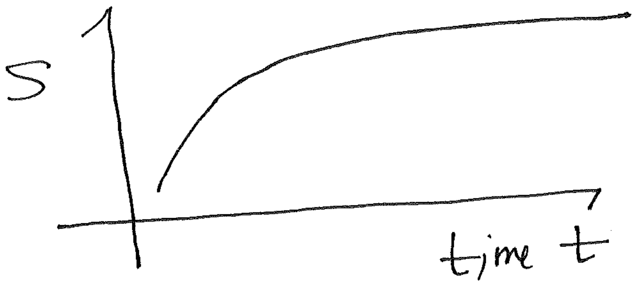


energy and particles can move back and forth between subsystems

Then there is a non-negative number $S = S(\mathcal{U}_{tot}, N_{tot}, V)$ called the entropy of the macroscopic system such that S has a maximum value when system is in thermodynamic equilibrium

monoatomic ideal gas: $S = N\left[\frac{5}{2} + \ln\left(\frac{V}{N}\left(\frac{4\pi m \mathcal{U}}{3h^2 N}\right)^{3/2}\right)\right]$

S not meaningful for small systems or single particles like electron, atom, magnetic spin, photon, etc.



← system in equilibrium when S hits maximum value

S increases its value by system distributing energy and particles between subsystems until temperature, pressure, chemical potential equal everywhere in system.

$$\frac{dS}{dt} \geq 0 \qquad \frac{dS}{dt} > 0 \ \text{nonequilibrium}$$

$$\frac{dS}{dt} = 0 \ \text{equilibrium}$$

Outline of Key Argument

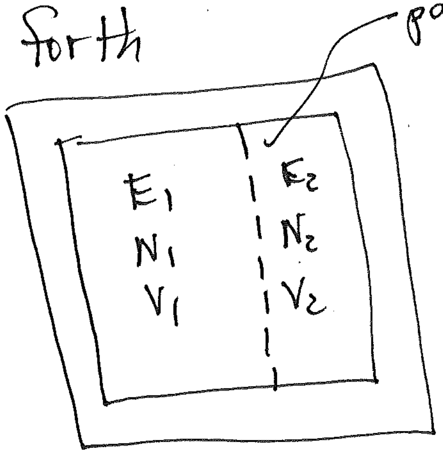
Why Entropy is Important

Following is one of the ~~most~~ important arguments of course, Will take time to appreciate it but let me put it before you so you can quickly see kinds of assumptions and conclusions used.

Make sure you understand assumptions and can reproduce logic of this argument!

Consider macroscopic system that is isolated so total energy, total number of particles is conserved.

consider partition that divides system into two macroscopic subsystems such that only energy can move back and forth



partition (say made of impermeable metal)

$E_1 + E_2 = E$ = constant

$N_1 + N_2 = N$ = constant

$V_1 + V_2 = V$ = constant

partition only allows E_1, E_2 to change

Entropy Argument Cont'd

Turns out that entropy S is an additive quantity just like energy, entropy of two subsystems is sum of their individual entropies

so for our isolated macroscopic system with two subsystems of energy E_1, E_2 we have

$$S(E,N,V) = S_1(E_1,N_1,V_1) + S_2(E_2,N_2,V_2)$$

$$= S_1(E_1) + S_2(E_2)$$

if partition doesn't allow N_1, N_2, V_1, V_2 to change

Let us assume that entropy will have a maximum value when entire system is in equilibrium, will justify this insight later. Since system is isolated and energy conserved

$$E = E_1 + E_2$$

so total entropy is really function of E_1:

$$S = S_1(E_1) + S_2(E_2) = S_1(E_1) + S_2(E - E_1)$$

Entropy Argument Cont'd

Condition for entropy to have maximum value with respect to changes of energy E_1's:

$$0 = \frac{dS}{dE_1} = \frac{d}{dE_1}\left(S_1(E_1) + S_2(E_2)\right)$$

$$= \frac{dS_1}{dE_1} + \frac{dS_2}{dE_2} \cdot \frac{dE_2}{dE_1}$$

$$E_1 + E_2 = 0 \Rightarrow \frac{dE_2}{dE_1} = -1$$

$$= \frac{dS_1}{dE_1} - \frac{dS_2}{dE_2}$$

so we conclude that equilibrium requires that the quantity

$$\frac{dS_1}{dE_1}$$

be same for all subsystems. We will define a temperature T by:

$$\boxed{\frac{1}{T} = \frac{dS_1}{dE_1}}$$

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

since V, N constant

Then $\boxed{T_1 = T_2 \text{ for equilibrium,}}$

Will show later this reduces to our favorite concept of T for an ideal gas so this definition turns out to be reasonable.

Temperature Defined By $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V}$ Indicates Flow of Heat From Hot to Cold

For nonequilibrium system such that $T_1 \neq T_2$, entropy will increase over time: $\frac{dS}{dt} > 0$

But $S = S_1(E_1) + S_2(E_2)$ implies

$$\frac{dS}{dt} = \frac{dS_1}{\partial E_1} \cdot \frac{dE_1}{dt} + \frac{dS_2}{dE_2} \cdot \overbrace{\frac{dE_2}{dE_1}}^{=-1} \cdot \frac{dE_1}{dt}$$

using again conservation of energy $E_1 + E_2 = E$

$$= \frac{dE_1}{dt}\left(\frac{dS_1}{dE_1} - \frac{dS_2}{dE_2}\right)$$

$$\frac{dS}{dt} = \frac{dE_1}{dt}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \underbrace{> 0}_{\text{since entropy increases over time}}$$

assume $T_1 > T_2 > 0 \Rightarrow \frac{1}{T_2} > \frac{1}{T_1}$ so $\frac{1}{T_1} - \frac{1}{T_2} < 0$

then $\frac{dE_1}{dt} < 0$ so product $\frac{dE_1}{dt}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) > 0$

this implies E_1 decreases with time, E_2 increases with time so heat "flows" from high T_1 to low T_2

Fact that $T_1 > T_2$ implies $\frac{dE_1}{dt} < 0$ is key reason to define

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

rather than by $T = \left(\frac{\partial S}{\partial E}\right)_{N,V}$

Note key assumptions:

$\frac{dS}{dt} > 0$ nonequilibrium

S maximum equilibrium

S additive $S = S_1 + S_2$

conserved quantity $E = E_1 + E_2$

Outline of Chapter 2

We are going to define entropy S in terms of another quantity called the multiplicity Ω (upper case Greek omega) of the macroscopic system,

$\Omega(E,V,N)$ is an integer, it counts number of ways that energy, particles, volume can be spread over various subsystems

introduce idea of "macrostate", subsystem characterized by
macroscopic values of E, N, V

introduce idea of microstate, ~~list of all~~ huge list of state of each
microscopic component of system for macroscopic values
E, N, V

then $\Omega(E,V,N)$ is number of microstates consistent with
given macroscopic values of E, V, N

Ω tends to be a very big #, $\sim 10^{N_A} \sim 10^{10^{23}}$

Define $$\boxed{S = k \ln \Omega}$$

Boltzmann's great discovery

$\uparrow$ Boltzmann constant $1.4 \cdot 10^{-23} \frac{J}{K}$

$S = O(N_A)$

Examples of Macrostates and Microstates

consider <u>three coins</u>, these are microscopic pieces

state of coin is heads H or tails T

<u>microstate</u> of 3 coins is specific list of state of each coin

$$\left.\text{TTT}\quad\text{TTH}\quad\text{THT}\quad\text{HTT}\quad\text{THH}\quad\cdots\right\}\text{ microstates}$$

there are $2\times2\times2=2^3=8$ microstates for 3 coins

define macrostate by number of heads, for 3 coins

there are <u>four</u> macrostates: 0, 1, 2, or 3 heads

Define multiplicity $\Omega(N_H, N)$ to be the total number of microstates that have N_H heads, given N coins

macrostate (# heads)	microstate	$\Omega(n_H, 3)$
0	TTT	1
1	TTH THT HTT	3
2	THH HTH HHT	3
3	HHH	1

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Can generalize to "macroscopic" system containing N coins

\# of microstates is 2^N since $\overbrace{2\times 2\times\cdots\times 2}^{N \text{ coins}}$

\# of macrostates is much smaller, $N+1$
no heads, 1 head, …, N heads

what is multiplicity $\Omega(N_H, N)$, number of microstates consistent with total # of heads N_H?

This is classic combinatoric problem: given N slots, in how many ways can I place N_H objects in those slots?

answer is binomial coefficient $\binom{N}{N_H}$ pronounced N take N_H

there are N ways to choose 1st slot
$N-1$ ways " " 2nd slot
⋮
$(N-N_N+1)$ " " N_Hth slot

But if coins are identical, can't distinguish cases where locations of heads are switched. So

$$\Omega(N_H, N) = \binom{N}{N_H} = \frac{N(N-1)\cdots(N-N_H+1)}{1\cdot 2\cdots N_H} = \frac{N!}{N_H!\,(N-N_H)!}$$

where $N! = 1\cdot 2\cdot 3\cdots N$

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Properties of Binomial Coefficients

$0! = 1 \quad 1! = 1 \quad 2! = 2 \quad 3! = 6 \quad 4! = 24$

$\binom{n}{k} = \binom{n}{n-k}$ kind of symmetry

$\binom{n}{0} = 1 \quad \binom{n}{1} = n$

$$(a+b)^n = \cancel{a}\binom{n}{0}a^n + \binom{n}{1}a^{n-1}b + \binom{n}{2}a^{n-2}b^2 + \cdots + \binom{n}{n-1}ab^{n-1} + \binom{n}{n}b^n$$

setting $a=b=1$, we conclude

$$\boxed{2^n = \binom{n}{0} + \binom{n}{1} + \cdots + \binom{n}{n}}$$

Mathematica f^n is Binomial[n, k] $= \binom{n}{k}$

watch out! for most cases, use decimal point not integer to avoid expensive exact integer arithmetic

type Binomial[10., 5.] not Binomial[10, 5]

Factorial[n] is $n!$, defined through Gamma f^n

Probability of Macrostate

For N coins, probability of observing macrostate with N_H heads is

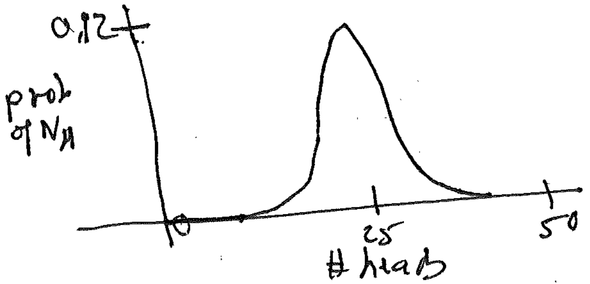
$$p(N_H, N) = \frac{\binom{N}{N_H}}{2^N}$$

provided all microstates are equally likely

if we flip 100 coins many times, will see macrostates that have ~ 50% heads, some macrostates much more probable than other microstates

Exactly the same situation for macroscopic thermodynamic systems, only most likely macrostates are observed, these are the ones with the most microstates, i.e. Ω is a max

Problem 2.37 of Schroeder



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prob = Table[ Binomial [50,n] / 2^50, {n, 0, 50}]
ListLinePlot [prob]
```