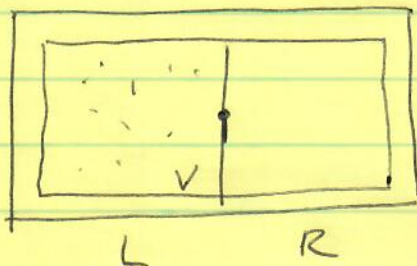


SECOND LAW OF THERMODYNAMICS

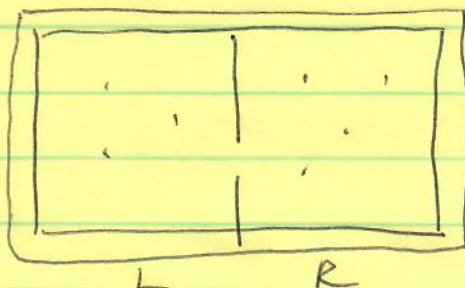
(irreversibility, entropy, arrow of time...)

Now we will apply probabilistic modeling to macroscopic systems of many particles.



N, E, V

* open valve & wait *



After equilibrium achieved, each molecule has independent probability $p_L = 1/2$ to be in region L
& $p_R = 1/2$ to be in region R.

What is the probability to find N_L molecules on the left?

BINOMIAL DISTRIBUTION

(N indep draws from $\{L, R\}$)

$$\begin{aligned}
 p(N_L; N) &= W_{N, 1/2}^{N \text{ total molecules}}(N_L) \\
 &= \binom{N}{N_L} p^{N_L} q^{N-N_L} \quad p=q=1/2 \\
 &= \binom{N}{N_L} \frac{1}{2^N}
 \end{aligned}$$

Stat mech jargon: $p(N_L; N) = \Omega(N_L, N) 2^{-N}$

Ω is called statistical weight or multiplicity

$$\text{In this example, } \Omega(N_L, N) = \binom{N}{N_L} = \frac{N!}{N_L! (N-N_L)!}$$

is the # of ways to distribute N distinguishable molecules so that there are N_L on the left.

Each such configuration is called a "microstate"

In this example, a microstate can be specified by

molecule	side
1	L
2	R
3	R
\vdots	\vdots
\vdots	\vdots
N	L

Each microstate is equally probable.

The macrostate is a few quantities that can be obtained from the microstate and measured macroscopically, at least approximately. In this example, the macrostate is N, N_L .

Associated with a macrostate A is a multiplicity:

$$\Omega(A) = \# \text{ of } \underline{\text{microstates}} \text{ consistent with macrostate } A.$$

Returning to the example. Since N is large (and p is fixed), we can approximate binomial \rightarrow gaussian

$$p(N_L, N) \rightarrow \frac{1}{\sqrt{2\pi} \sigma} e^{-(N_L - \bar{N}_L)^2 / 2\sigma^2}$$

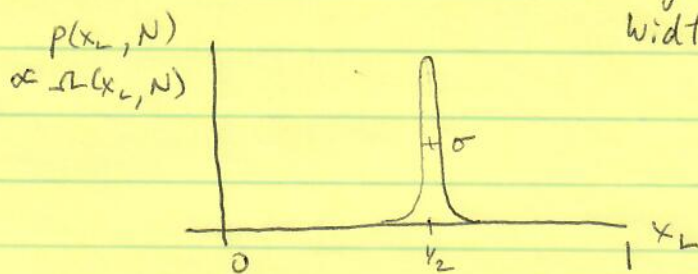
$$\sigma^2 = Npq = N/4 \quad \bar{N}_L = pN = N/2$$

expressing as a fraction $x_L \equiv N_L/N$,

Here used
 $p(x_L) dx_L = p(N_L) dN_L$
 $\Rightarrow p(x_L) = p(N_L) \cdot N$

$$p(x_L, N) = \sqrt{\frac{2N}{\pi}} e^{-2N(x_L - 1/2)^2}$$

extremely peaked @ $1/2$!
width $\sigma \sim 1/\sqrt{N}$



if $N \sim 10^{20}$, x_L never deviates from $1/2$ by much more than $\frac{1}{\sqrt{N}} \sim 10^{-10}$

Any value of x_L between $0 \leq x_L \leq 1$ is possible. But values near $x_L = 1/2$ are overwhelmingly likely, because their multiplicities Ω are so much larger.

This is a simple consequence of introducing a probabilistic description in which each microstate is equally likely.

FUNDAMENTAL POSTULATE OF STAT MECH:

For an isolated system in equilibrium, every possible microstate is equally likely.

⇒ MOST PROBABLE MACROSTATE = MACROSTATE w/ LARGEST Ω ★

The entropy is defined to be the logarithm of the multiplicity for an isolated system.

Boltzmann's
Formula

$$\text{entropy } S = k_B \log \Omega$$

natural log

for a given macrostate

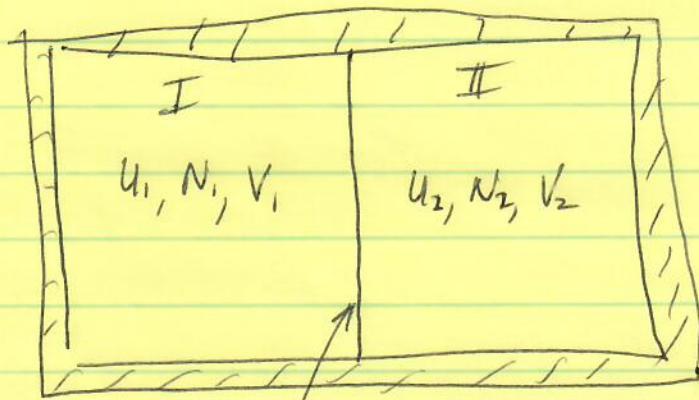
Thus, statement ★ may be restated as

Any large isolated system in equilibrium will be found in the macrostate with the largest entropy.

This is called the Second Law of Thermodynamics

This definition of entropy involves microstates. However, entropy can still be measured experimentally by relating it to temperature. In fact, it is a state function.

Isolated system
w/ two subsystems.



rigid, impermeable, heat-conducting wall

The macrostate is $(U_1, U_2, V_1, V_2, N_1, N_2)$

Rigid & Impermeable $\Rightarrow N_{1,2} \neq V_{1,2}$ fixed

But, only $U_1 + U_2 = U$ fixed, not $U_{1,2}$ individually.
(total energy)

How does energy distribute between I & II?

The second law tells us that the total entropy S is maximized.

$$\Omega(U_1, N_1, V_1; U_2, N_2, V_2) = \Omega_I(U_1, N_1, V_1) \Omega_{II}(U_2, N_2, V_2)$$

↑ multiplicity of macrostate of whole sys

For brevity, suppress dependence on fixed vars N_i, V_i
And substitute $U_2 = U - U_1$

$$\Rightarrow \Omega(u, u_1) = \Omega_I(u_1) \Omega_{II}(u - u_1)$$

$$S = k \ln \Omega$$

$$\Rightarrow S(u, u_1) = S_I(u_1) + S_{II}(u - u_1)$$

$$\text{Maximize } S! \quad 0 = \frac{\partial S}{\partial u_1} = \frac{\partial S_I(u_1)}{\partial u_1} + \frac{\partial S_{II}(u - u_1)}{\partial u_1}$$

$$= \frac{\partial S_I(u_1)}{\partial u_1} - \frac{\partial S_{II}(u_2)}{\partial u_2}$$

So, in equilibrium, energy is distributed s. th.

$$\left. \frac{\partial S_I}{\partial u} \right|_{u=u_1} = \left. \frac{\partial S_{II}}{\partial u} \right|_{u=u_2}$$

What else is the same between two systems in thermodynamic equilibrium? Temperature.

$$\text{CLAIM: } \boxed{\frac{1}{T} = \frac{\partial S}{\partial u}}$$

Where T is the absolute temperature, as appears in the Ideal Gas Law.

To check this, we will compute S for the ideal gas.

First, a digression about the size of numbers.

"Small numbers" $n \lesssim 100$

"Large numbers" $N \approx 10^n$. e.g. $N_A = 6 \times 10^{23}$

Small + Large \approx Large $n + N \approx N$

"Very Large numbers" $n \approx 10^N$ eg $n = 10^{(10^{23})}$

(Large) \times (Very Large) \approx (Very Large)

$$10^{10^{23}} \times 10^{23} = 10^{(10^{23} + 23)} \approx 10^{10^{23}}$$

VLN's are counterintuitive and only appear in statistical mechanics. Usually we take their logarithm, so that they are merely large.

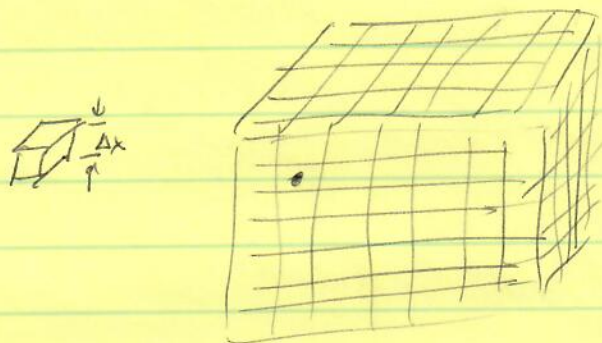
of microstates of the universe
 $\approx 10^{10^{120}}$

Back to the Ideal Gas: Ω for a mono-atomic gas

Microstates? \vec{r}_1, \vec{p}_1 ; \vec{r}_2, \vec{p}_2 ; ...; \vec{r}_N, \vec{p}_N positions
& momenta

How do we count the number of values for continuous variables?

Pos. Hous: divide the volume into boxes of size $(\Delta x)^3$



Each particle in
one of $(V/\Delta x^3)$ boxes

Therefore $\Omega \propto \left(\frac{V}{\Delta x^3}\right)^N$

What about momenta? Constraint set by conservation of energy: $\frac{1}{2}mv^2 = p^2/2m$

$$\underbrace{p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + \dots + p_{Nx}^2 + p_{Ny}^2 + p_{Nz}^2}_{3N \text{ terms}} = 2mU$$

if $x^2 + y^2 = r^2$ defines a circle, and $x^2 + y^2 + z^2 = r^2$ a sphere, this equation defines a $3N$ -dimensional hypersphere in momentum space.

(Schroeder appx): $\text{Area}_d(r) = \frac{2\pi^{d/2}}{(\frac{d}{2}-1)!} r^{d-1}$

To get a number of states, again need to divide momentum space into boxes of size $(\Delta p)^3$ for each particle

$$\Omega \approx \frac{2\pi^{3N/2}}{(\frac{3N}{2})!} \frac{(2mU)^{3N/2}}{(\Delta p)^{3N}}$$

Since $\vec{p} \nparallel \vec{x}$ independent, Ω is the product of these multiplicities:

$$\Omega \approx \frac{2\pi^{3N/2}}{(\frac{3N}{2})!} \frac{V^N (2mU)^{3N/2}}{(\Delta p \Delta x)^{3N}}$$

QUANTUM THEORY tells us two more things.

I. We need another factor of $1/N!$

(Every atom is indistinguishable, so a permutation of the atoms does not give a distinct state.)

* ASSUMES ALL OCCUPIED STATES DISTINCT, EXCELLENT APPROX UNLESS DENSITY IS VERY HIGH

II The uncertainty principle sets the box size.

$$\Delta p \Delta x \approx h$$

finer distinctions in $\vec{p} \nparallel \vec{x}$ cannot be measured.

FINAL RESULT:
$$\Omega \approx \frac{1}{N!} \left(\frac{2\pi m}{h^2} \right)^{3N/2} \frac{V^N U^{3N/2}}{(\frac{3N}{2})!}$$

This is approximate, but OK because Ω is a V.L.N., $10^N \sim 10^{10^{23}}$

Using Stirling approx. $\nparallel S = k \ln \Omega$,

"Sackur-Tetrode equation"

$$S = Nk \left[\log \left(\frac{V}{N} \left(\frac{4\pi m U}{3h^2 N} \right)^{3/2} \right) + \frac{5}{2} \right]$$

S is just a "large number". Ω is a V.L.N...

What is $\partial S / \partial U|_{V,N}$?

$$S = \frac{3}{2} Nk \ln U + (\text{terms indep of } U)$$

$$\text{So } \partial S / \partial U|_{V,N} = \frac{3}{2} \frac{Nk}{U}$$

$$\text{Equipartition} \Rightarrow U = \frac{3}{2} NkT$$

$$\text{So } \partial S / \partial U|_{V,N} = \frac{1}{T} \quad \checkmark$$

We can also write this as $TdS = dU$ for infinitesimal changes at fixed V, N near equilibrium.

But at fixed volume, $dU = dQ$ (quasistatic)

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

quasistatic, fixed volume
(we will soon see we can drop the fixed volume requirement.)

$$dQ = C_V dT, \text{ so } \boxed{dS = \frac{C_V}{T} dT}$$

example: How much does the entropy of an ideal gas increase if the temperature is raised from T_i to T_f at fixed volume?

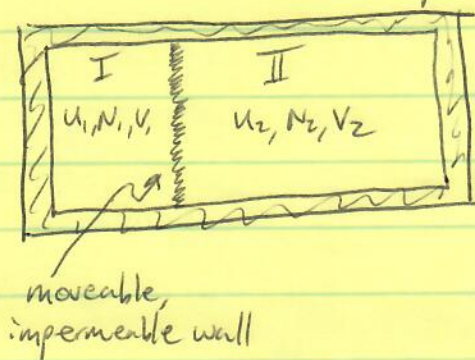
$$C_V = \frac{3}{2} Nk \quad (\text{monatomic I.G.})$$

$$\Delta S = \int_{T_i}^{T_f} C_V \frac{dT}{T} = C_V \log(T_f/T_i)$$

$$\Delta S = \frac{3}{2} Nk \log(T_f/T_i)$$

INTUITIVE UNDERSTANDING: volume accessible in momentum space increases with the temperature. ($\sum p_i^2 = 2mU \sim mT$)

What about pressure? Thought experiment!



$$U_1 + U_2 = U \quad V_1 + V_2 = V \quad \text{but now } V_{1,2} \text{ can change}$$

$$(N = N_1 + N_2, \quad N_{1,2} \text{ fixed})$$

Wall moves to maximize entropy.

$$S(U, V; u_1, v_1) = S_I(u_1, v_1) + S_{II}(U - u_1, V - v_1)$$

$$\text{Maximize } S: \quad 0 = \left. \frac{\partial S}{\partial u_1} \right|_V \Rightarrow \left. \frac{\partial S_I}{\partial u_1} \right|_V = \left. \frac{\partial S_{II}}{\partial u_2} \right|_V \quad \text{as before}$$

$$\underline{\text{AND}} \quad 0 = \left. \frac{\partial S}{\partial V_1} \right|_U \Rightarrow \left. \frac{\partial S_I}{\partial V_1} \right|_U = \left. \frac{\partial S_{II}}{\partial V_2} \right|_U$$

Intuitively, the forces on the LHS & RHS of the wall should match: $P_I = P_{II}$ $\left. \frac{\partial S_I}{\partial V_1} \right|_U$ related to P ?

$$\text{CLAIM:} \quad \frac{\partial S}{\partial V} = \frac{P}{T}$$

Check with ideal gas:

$$S_{\text{ideal gas}}(U, V, N) = Nk \ln V + \text{terms indep of } V$$

$$\frac{\partial S}{\partial V} = \frac{Nk}{V} = \frac{P}{T} \quad \checkmark$$

\uparrow
Ideal gas law

Now we know how entropy changes for quasi-static, equilibrium processes:

$$\begin{aligned} dS &= \left. \frac{\partial S}{\partial U} \right|_V dU + \left. \frac{\partial S}{\partial V} \right|_U dV \\ &= \frac{1}{T} dU + \frac{P}{T} dV \end{aligned}$$

More commonly written

**** MEMORIZE!** $\boxed{TdS = dU + PdV}$

This is called the thermodynamic identity

Rearrange: $dU = TdS - PdV$

the quasi-static first law of thermodynamics
with $dS = dQ/T$

Away from Quasistatic: $TdS \geq dQ$
 $-PdV \leq dW$

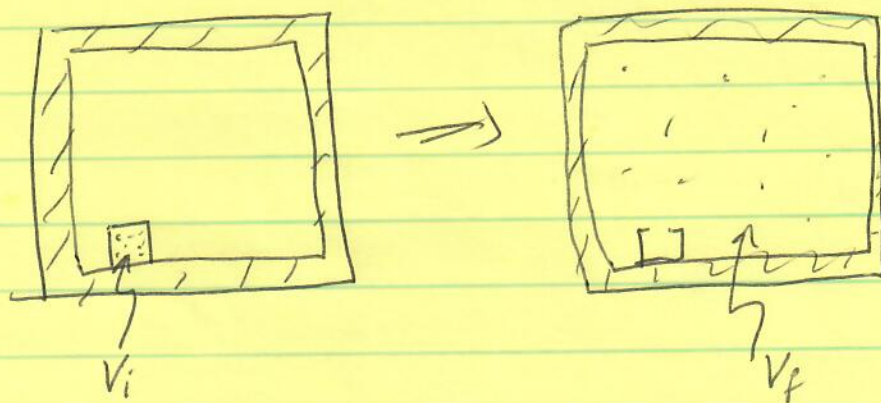
At constant pressure, $dQ = C_p dT$

$$\text{So } dS = C_p \frac{dT}{T}$$

$$\Delta S = \int_{T_i}^{T_f} C_p \frac{dT}{T} = C_p \ln(T_f/T_i)$$

An example where $\Delta S \neq 0$, but $dQ = 0$:

Free expansion of ideal gas



No heat is added, but the entropy still goes up.

$$S = Nk \ln V + (\text{terms indep of } V)$$

$$\Rightarrow \Delta S = Nk \ln(V_f/V_i)$$