Lecture 19

Last time: Postulates of SM

P1: Laws of motion apply to an isolated system as $N \to \infty$ (N = # of particles)

$\Rightarrow$ E is conserved (1st law of thermodynamics)

P2: In an isolated system, all microstates in a macrostate are equally likely "the ensemble"

$$\rho_j = \frac{1}{W} \qquad j = 1, 2, \ldots$$

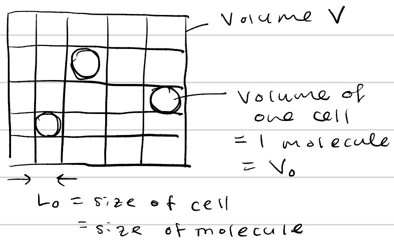
W = number of accessible microstates = "partition function"

P2: (strong) time average = ensemble average

Today: W and S

But first: why P2 (strong) can never be strictly true.

Ex: gas in box



Lets do

$M = 25 = \frac{V}{V_0}$

$N = 3$ identical

$$W = \frac{25 \cdot 24 \cdot 23}{3!} = \frac{M!}{(M-N)!\,N!}$$

$$N! = N(N-1)\ldots 2 \cdot 1$$

Sterling's formula (good approx): $N! \approx N^N e^{-N}$

$$\Rightarrow W = \frac{M!}{(M-N)!\,N!} \approx \frac{M^M e^{-M}}{(M-N)^{M-N} e^{-M+N} \; N^N e^{-N}} = \frac{M^M}{(M-N)^{M-N} N^N}$$

$M >> N$

$$\approx \frac{M^M}{M^{M-N} N^N}$$

$$\Rightarrow W = \frac{1}{M^{-N} N^N} = \left(\frac{M}{N}\right)^N \quad \text{(true if } M >> N >> 1)$$

Let's plug in more realistic numbers

$V = 1\ cm^3$ of gas at 1 atm and room T has approximately $N = 10^{19}$ molecules in it, of molecular volume $V_0 \approx 10\ \text{Å}^3$ moving $v_{gas} = 300$ m/s.

$$M = V/V_0 = 1\ cm^3 / 10\ \text{Å}^3 = 10^{23}$$ ($1\ \text{Å} = 10^{-8}$ cm)

$$N = 10^{19}$$

$$\Rightarrow \frac{M}{N} = \frac{10^{23}}{10^{19}} = 10^4 \Rightarrow W = (10^4)^{10^{19}}$$

How many of these microstates have been visited in the $1\ cm^3$ of gas since the beginning of the universe?

$$L_0 \approx V_0^{1/3}, \quad v_{gas} = 300\ m/s$$

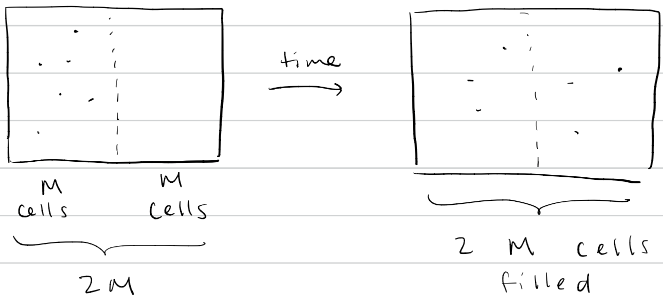
$$\Rightarrow \Delta t = \frac{L_0}{v_{gas}} = 10^{-12}\ s = 1\ ps$$

Lifetime of the universe ≈ 14 by $= 10^{18}$ s

The actual # of microstates explored by the gas since the beginning of the universe is:

$$\frac{10^{18}\ s}{10^{-12}\ s} = 10^{30} << W = (10^4)^{10^{19}}$$

Ex: A calculation w/ W:



$$W_{left} \approx \left(\frac{M}{N}\right)^N$$

$$W_{\substack{whole\\box}} \approx \left(\frac{2M}{N}\right)^N$$

$$P_{left} = \frac{W_{left}}{W_{box}}$$ by P2 $\Rightarrow$ $P_{left} = \left(\frac{1}{2}\right)^N$

For 6 particles: $P_{left} = \left(\frac{1}{2}\right)^6 = 0.015 = 1.5\%$

For 1 cm^3 of gas, $N \simeq 10^{19}$, $P_{left} = \left(\frac{1}{2}\right)^{10^{19}} \approx 0$

(immesurably small)

For any large N, it will always be true that

$$W(t>0) \geq W(t=0)$$

W and S

While $E_1 + E_2 = E$,

but $W_1 \cdot W_2 = W_{TOT}$

ex: $W_1 = 3$ $W_2 = 3$

$W_{TOT} = W_1 \cdot W_2$

Define S to be $\ln W$ $\Rightarrow$ $S_{TOT} = \ln W_1 + \ln W_2$

$= S_1 + S_2$

extensive variable.