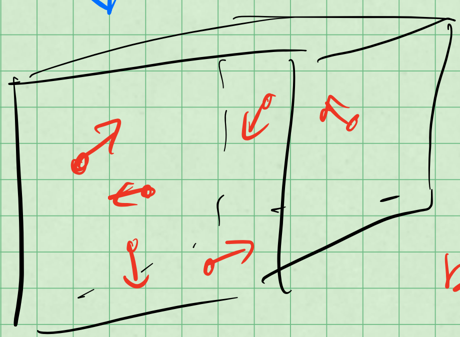
So we have seen some random behavior with spontaneous decays of particles. But here we modeled the average behavior with DiffyQ's.

$$dN = -\lambda dt \Rightarrow N(t) = N_0 e^{-\lambda t}$$

But randomness takes many forms.

Consider a gas at room temp. $\approx 300K$



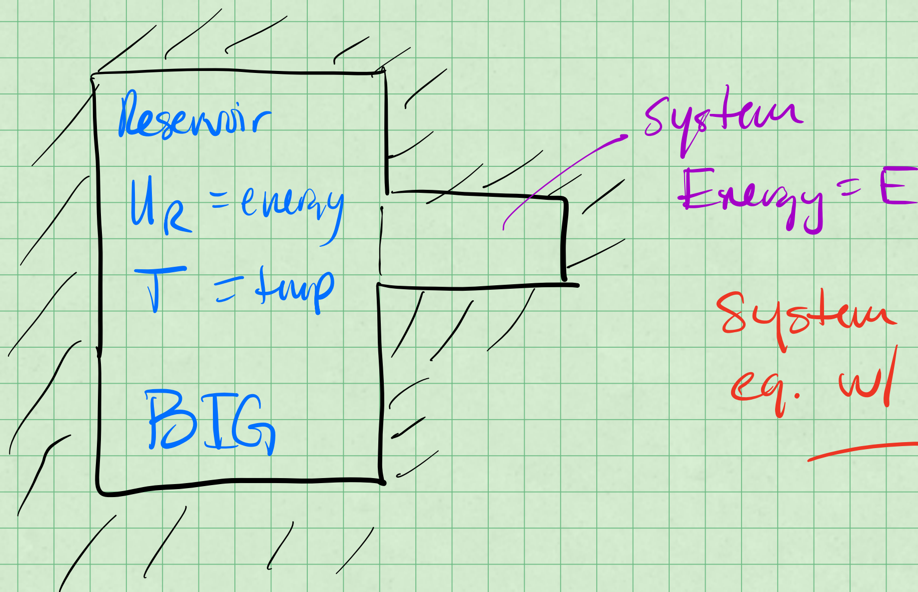
gas molecules randomly moving in a container bouncing of walls

How do we model these behaviors?

You might recall $PV = nRT$ for an ideal gas. This is at thermodynamic equilibrium, but the molecules are still moving!

We can develop $PV = nRT$ from a statistical model of an ideal gas.

First, Some Architecture



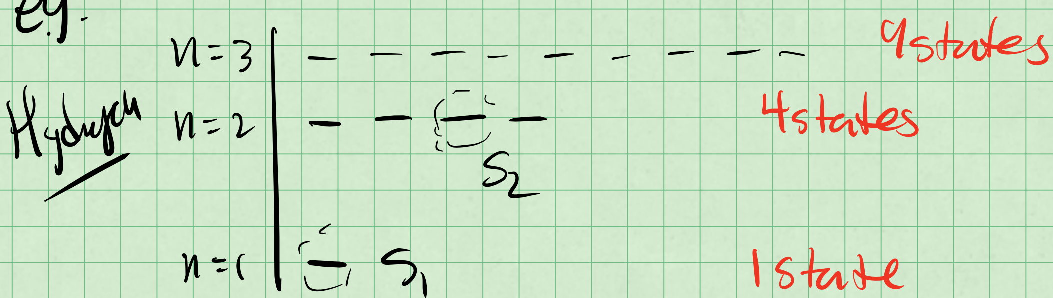
system in thermal eq. w/ reservoir

Focus on one atom:

can take on states s_i with energies $E(s_i)$

+ Probability of occupation depends on $E(s_i)$
also how many states have $E(s_i)$

eg.



If the atom is in S_1, then the reservoir can be considered in some energy state where that 1 atom is in S_1 and the remaining 10^{23} atoms are in states giving rise to U_R energy of reservoir

there's

$\Omega_R(S_1)$ ways the reservoir could have U_R with our atom in S_1

→ total number of configurations.

if in S_2 then $\Omega_R(S_2)$ ways to have U_R.

Probability Ratio

we can't yet calculate probabilities but we can form ratios b/c they are prop. to total ways,

$$\frac{P(S_2)}{P(S_1)} = \frac{\text{probability of atom in } S_2}{\text{probability of atom in } S_1} = \frac{\Omega_R(S_2)}{\Omega_R(S_1)} = \frac{\#\text{ of ways for } S_2}{\#\text{ of ways for } S_1}$$

Enter Ludwig Von!

$$S = k_B \ln(\Omega)$$

entropy $\propto$ log (ways of config)

$$S_R(s_1) = k_B \ln(\Omega_R(s_1))$$

$$S_R(s_2) = k_B \ln(\Omega_R(s_2))$$

$$\frac{P(s_2)}{P(s_1)} = e^{S_R(s_2)/k_B} \Big/ e^{S_R(s_1)/k_B}$$

$$= e^{\overbrace{[S_R(s_2) - S_R(s_1)]}/k_B}$$

Entropy change in reservoir!

$$T dS_R = \underbrace{dU_R}_{\text{change of internal energy (more fast particles)}} + \underbrace{P dV_R}_{\text{change of space (bigger volume)}} - \underbrace{\mu dN_R}_{\text{change of particle (smaller \# of particles)}}$$

Toss out PdV_R & μdN_R

$$S_R(s_2) - S_R(s_1) = \frac{1}{T}\left[U_R(s_2) - U_R(s_1)\right]$$

$$\Delta U_{R\ s_2 \leftarrow s_1} = -\Delta E_{s_2 - s_1} = -\left(E(s_2) - E(s_1)\right)$$

so,

$$P_2/P_1 = e^{-[E(s_2)-E(s_1)]/kT}$$

Boltzmann factor $= e^{-E(s)/kT}$

Can we make this a real probability?

Yes! <u>normalize it!</u>

$$\frac{P(s_2)}{e^{-E(s_2)/kT}} = \frac{P(s_1)}{e^{-E(s_1)/kT}} = \text{const!} = \frac{1}{Z}$$

$$\boxed{P(s) = \frac{1}{Z} e^{-E(s)/kT}}$$

Probability of a state with $E(s)$

Normalization

$$\sum P(s) = 1 = \sum_s \frac{1}{Z} e^{-E(s)/kT}$$

$$1 = \frac{1}{Z} \sum_s e^{-E(s)/kT}$$ but!

$$\boxed{Z = \sum_s e^{-E(s)/kT}}$$

partition function!

constant that depends on T