Diffusive Equilibrium & Chemical Potential

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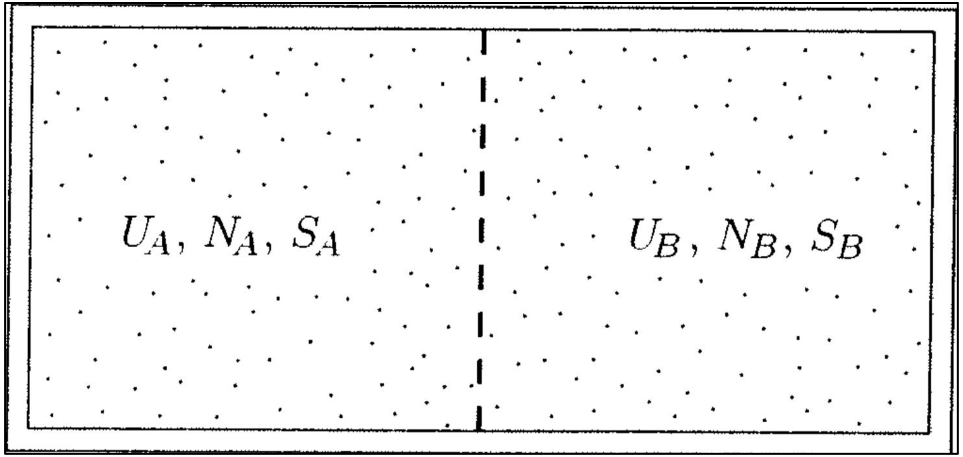
Given a System as Such:

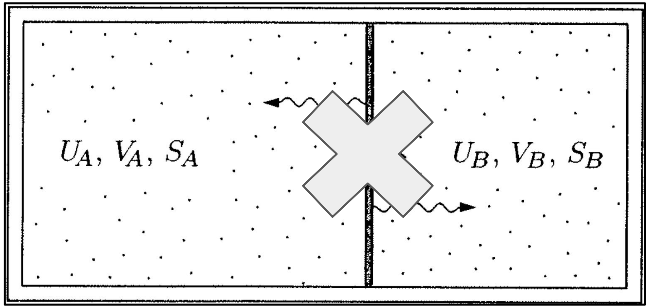


Given the slotted divider in the container A & B can exchange:

- Energy (U)
- Number of Particles (N)
- Entropy (S)

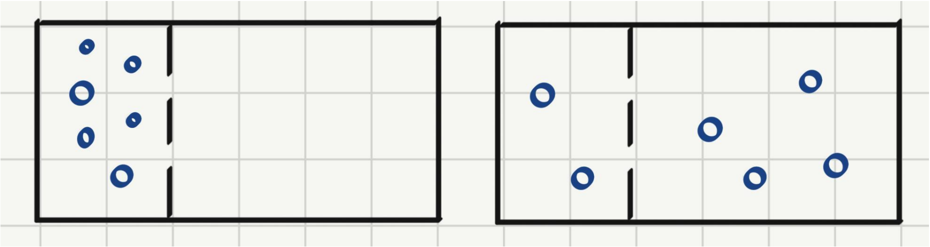
(Volume can also vary but I will keep it constant)

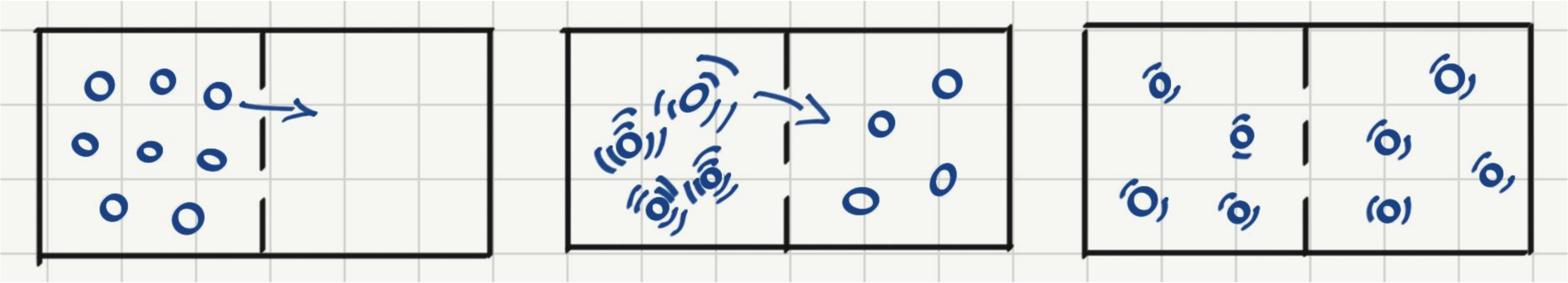
The two figures differ in what the systems can exchange. (We don't want the bottom right one)



What does approaching Diffusive Equilibrium look like?

- What's the most likely behavior given initial conditions?
  - How do I relate that to a variable I know?
- How does particle distribution relate to volume distribution?





Within the System:

- Energy is conserved
- Number of particles is conserved

*Had volume varied, we would know the partial change in entropy with respect to volume to be zero at equilibrium as well.

At Equilibrium (Max Entropy):

We actually want to find the largest $\Omega_A+\Omega_B$ but we can't derive the omega function so we try the next best thing.

$$\left(\frac{\partial S_{\text{total}}}{\partial U_A}\right)_{N_A,V_A} = 0 \qquad \text{and} \qquad \left(\frac{\partial S_{\text{total}}}{\partial N_A}\right)_{U_A,V_A} = 0.$$

Since we can write total U in terms of U_a, and likewise for N_a, we can differentiate total entropy in terms of U_a & N_a

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}$$

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}$$

Multiply by -T for convention

$$-T\,\frac{\partial S_A}{\partial N_A} = -T\,\frac{\partial S_B}{\partial N_B}$$

The negative factor is for making this into a potential.

Checking units we can see this is an energy.

Notice in this last equation we have an *External* variable being divided by another *External* variable.

We want to identify the resulting *Internal* variable.

Chemical Potential

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

Units of Energy

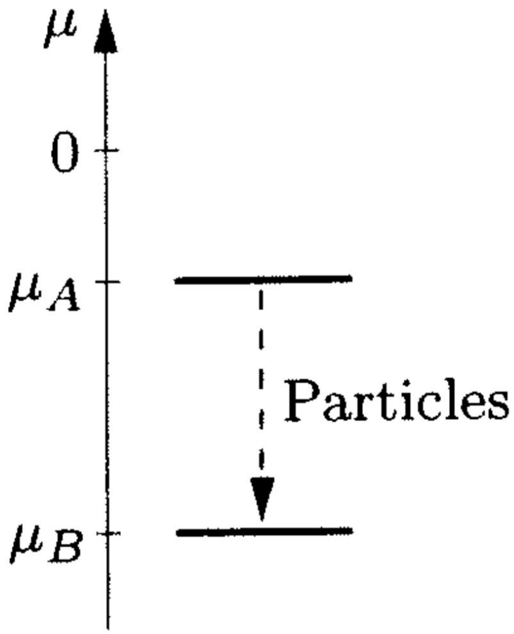
Intensive

Diffusive Equilibrium

$$\mu_A = \mu_B$$

When the system is out of Diffusive Equilibrium:

- System with largest partial differential dS/dN gains particles since it gains more entropy than the other system loses. (Neglecting -1, so opposite of μ)
- The same system will have the lowest chemical potential due to the negative.



New Look at Thermodynamic Identity!!!

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

$$= \frac{1}{T}\, dU + \frac{P}{T}\, dV - \frac{\mu}{T}\, dN.$$

Solving for dU

$$dU = T\, dS - P\, dV + \mu\, dN.$$

- The last term in the last line is known as the <u>*Chemical Work*</u>

Getting Familiar with Chemical Potential

$$dU = T\,dS - P\,dV + \mu\,dN.$$

Treating Entropy and Volume as constant:

$$dU = \mu\,dN, \qquad \text{that is,} \qquad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}.$$

This definition for *Chemical Potential* makes the units much clearer. (eV)