# Entropy Approach to 2nd Law for CM

- Start with existence of entropy as a <u>thermodynamic property</u> (measure of microscopic disorder of system, or better, energy states of system)
  - $S=S(U,V)$ function of two indep. variables

- Imagine two systems, A and B, separated by rigid wall (V_A, V_B constant), only exchange is heat transfer, δQ

- Combined system C is isolated
  - no interaction with surroundings
  - total energy U_C fixed
  - 2nd Law, $S_{C,final} - S_{C,initial} = \mathscr{P}_s \geq 0$

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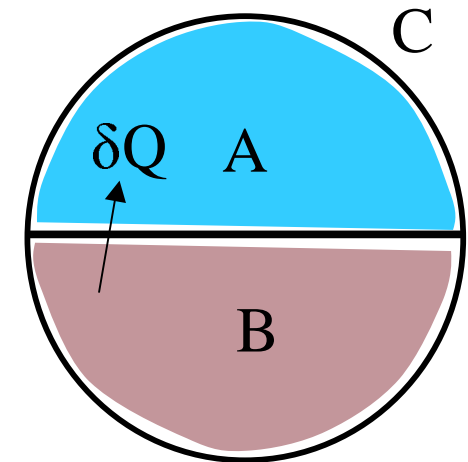
Equilibrium at Maximum Entropy

- Assume A and B not in equilibrium with each other
- Since entropy is extensive property
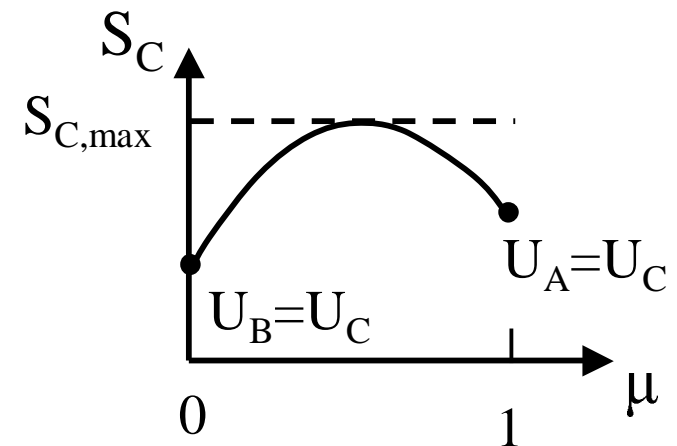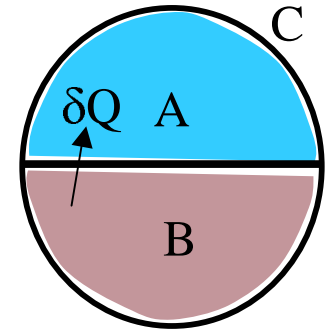
  - $S_C = S_A(U_A, V_A) + S_B(U_B, V_B)$
  - valid if A, B individually in equilibrium
  - also, $U_C = U_A + U_B = \mu U_C + (1-\mu)U_C$

- As interaction occurs, S_C will increase until equilibrium achieved $(S_{C,max})$

- Since V_A, V_B and U_C fixed, only free variable is μ

  - maximize S_C, $dS_C/d\mu = 0$

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Thermodynamic Def'n. of Temperature

- Taking derivative (using chain-rule)

$$\frac{dS_C}{d\mu} = \left(\frac{\partial S_A}{\partial U_A}\right)_{V_A} \frac{dU_A}{d\mu} + \left(\frac{\partial S_B}{\partial U_B}\right)_{V_B} \frac{dU_B}{d\mu}$$

$$= \left(\frac{\partial S_A}{\partial U_A}\right)_{V_A} U_C + \left(\frac{\partial S_B}{\partial U_B}\right)_{V_B} \left(-U_C\right)$$

- Equals zero, when $\left(\dfrac{\partial S_A}{\partial U_A}\right)_{V_A} = \left(\dfrac{\partial S_B}{\partial U_B}\right)_{V_B}$

- So, two systems are in thermal equilibrium when they have same $\left(\dfrac{\partial S}{\partial U}\right)_V$

- But, same T also implies thermal equilibrium

- Therefore, let $\boxed{T \equiv \dfrac{1}{\left(\dfrac{\partial S}{\partial U}\right)_V}}$ (show reason for 1/ next)
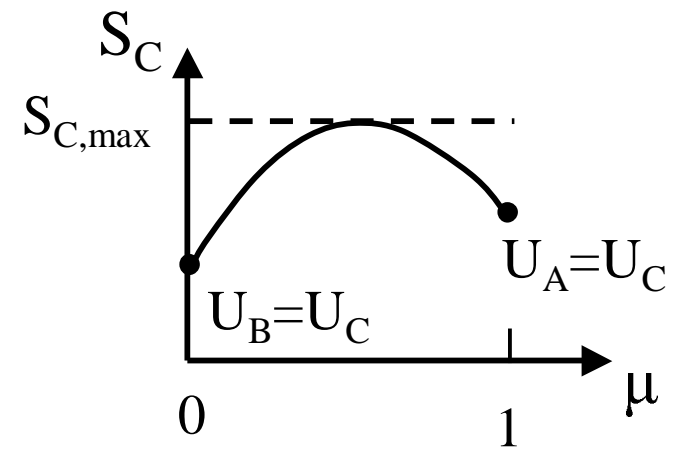
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Thermodynamic Def'n. of T (con't)

- Need to show thermodynamic def'n. of T consistent with 0th Law of Thermo. (Q from high to low T)

$$\frac{dS_C}{d\mu} = \left(\frac{\partial S_A}{\partial U_A}\right)_{V_A} U_C + \left(\frac{\partial S_B}{\partial U_B}\right)_{V_B} (-U_C)$$

$$dS_C = \left(\frac{1}{T_A} - \frac{1}{T_B}\right) U_C d\mu$$

- If $T_B > T_A$, $\left(\dfrac{1}{T_A} - \dfrac{1}{T_B}\right) > 0$

- 2nd Law $\Rightarrow dS_C > 0$, so $d\mu > 0$ energy flowing from B to A

- For $dS_C/d\mu$ to truly be maximum, then $d^2S_C/d\mu^2 < 0$
  - result, $\left(\dfrac{\partial^2 S}{\partial U^2}\right)_V < 0 \Rightarrow \left(\dfrac{\partial T}{\partial U}\right)_V > 0$ U increases with T

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Heat Transfer as Entropy Transfer

- Idealize, **Thermal Energy Reservoir (TER)**
  - CM with fixed volume, only exchanges energy as Q, uniform and (nearly) constant T
  - Since fixed volume, $dS/dU=1/T$
  - From 1st Law, $dU=\delta Q$, so $dS_{TER}= \delta Q/T$

- Now consider two interacting TERs, isolated from surroundings
  - 2nd Law, $\delta \mathcal{P}_s=d(S_A+S_B)$
    $$= \delta Q(1/T_A-1/T_B)>0$$
  - entropy production associated with Q across finite temperature difference

TER
T, dU

↑ δQ

TER
T_A

↑ δQ

TER
T_B

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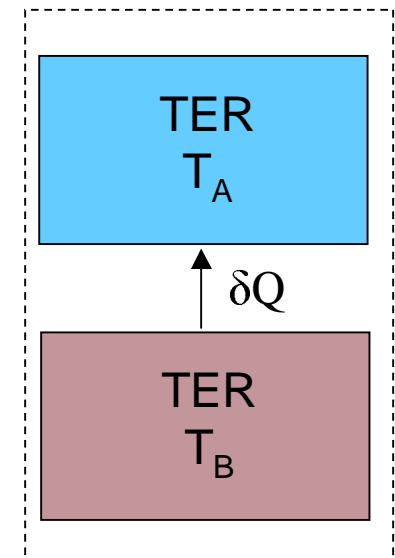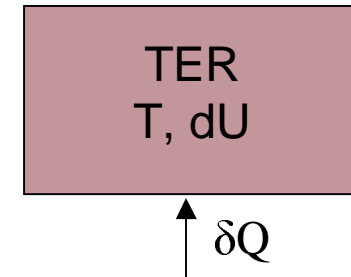
Second Law for Control Mass

- Control mass interacting with TER and **M**echanical **E**nergy **R**eservoir (MER)

  - CM with no microscopic disorder (no entropy), can only exchange energy as reversible work

- Together, form isolated system

- 2nd Law

  - $\delta\mathcal{P}_s = d(S_{TER} + S_{MER}^{0} + S)$

    $= -\delta Q/T + dS$

  $$\boxed{dS = \delta Q/T + \delta\mathcal{P}_s}$$

  - in terms of inequality

  $$\boxed{dS \geq \delta Q/T}$$

MER

δW_{rev}

System
T

δQ

T
TER

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