

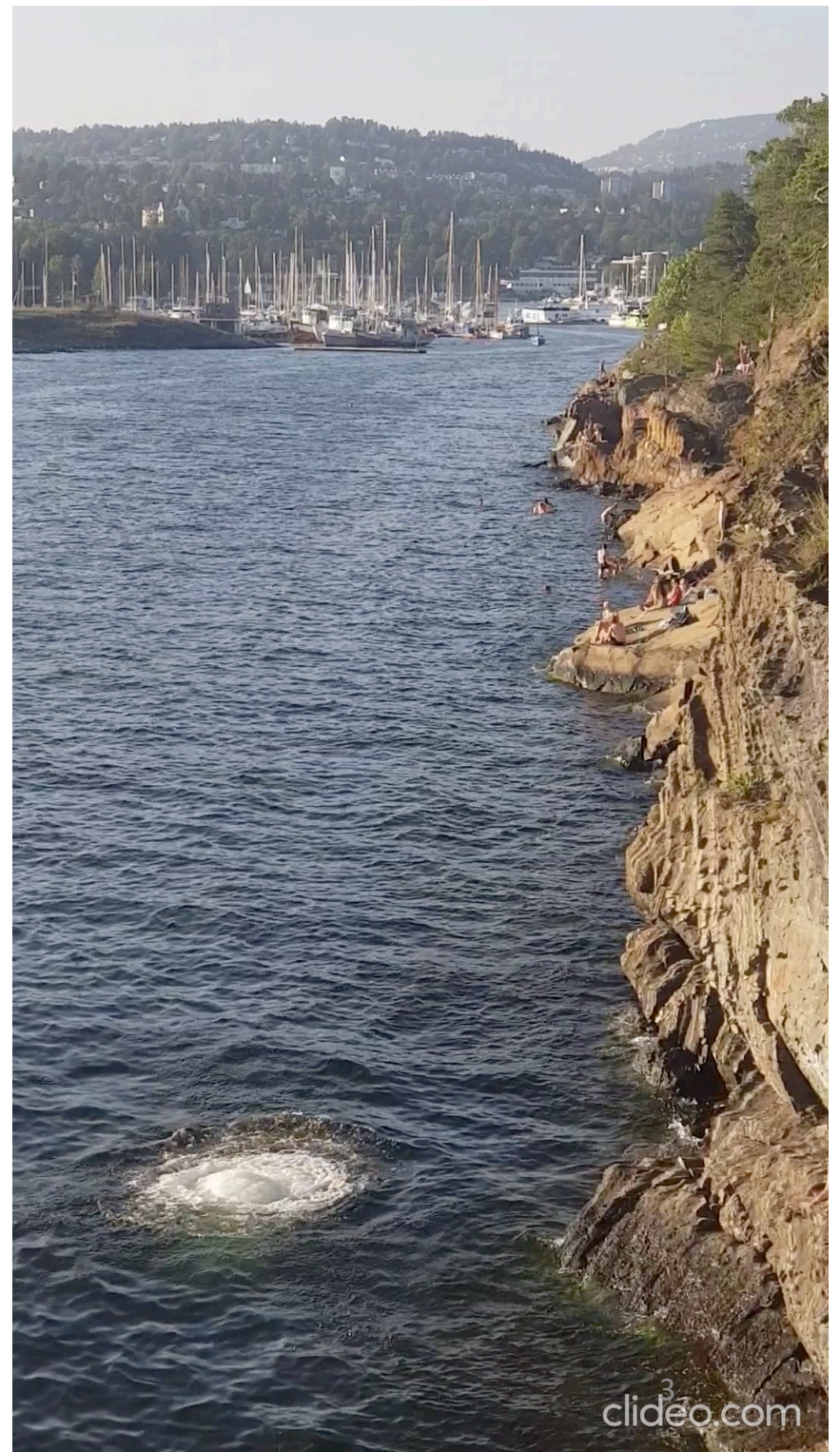
Week 4

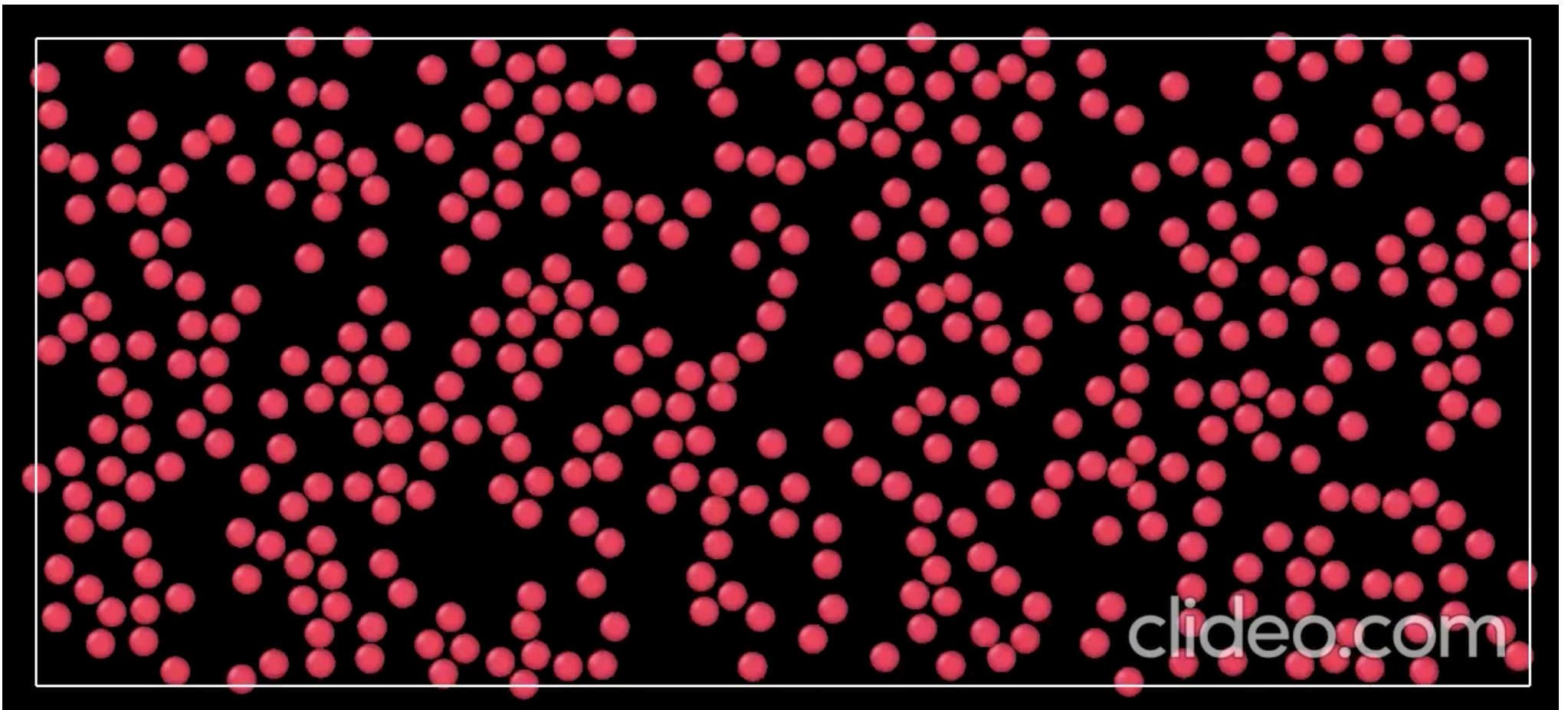
Entropy and entropic forces

Focus question

- Biological question: if energy is always conserved, how can some devices be more efficient than others?
- Physical idea: Order controls when energy can do useful work. Order is not conserved.

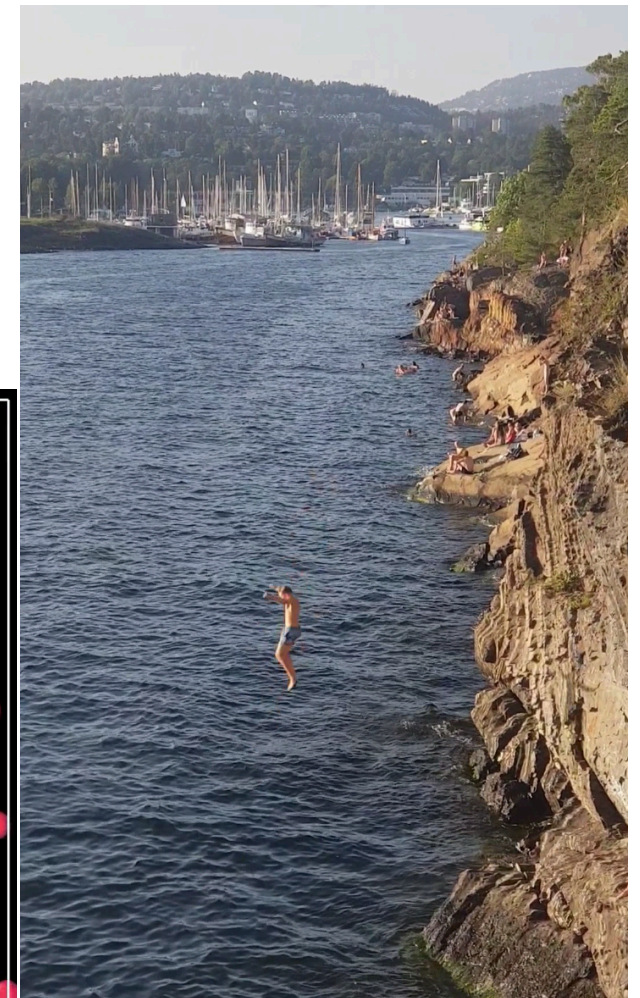
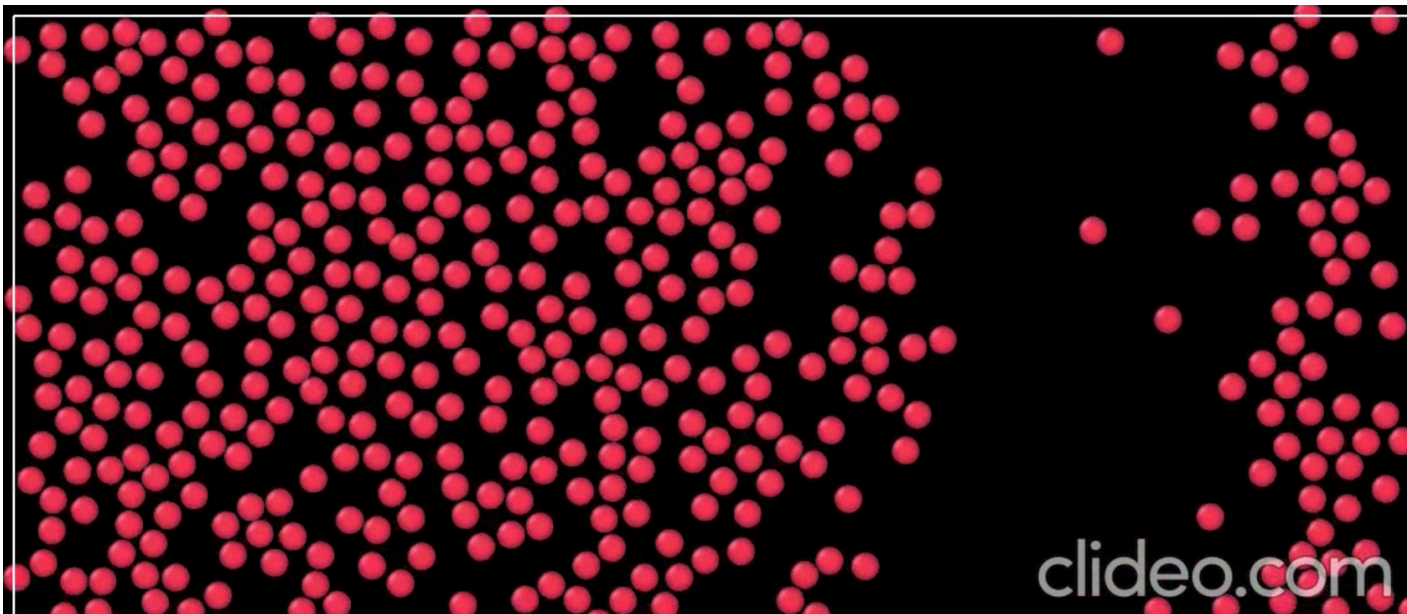
Reversible
or
irreversible





- Particle dynamics:
 - Newtons law of motion
 - Reversible
 - Possible evolution
- Why does it never happen?

- One body: reversible motion (My son can be shot from the water up to Pantern)
- Multibody systems:
 - reversible laws of motion (beads CAN move all to one side)
 - irreversible collective dynamics (it will never happen)
- **M**acro defenition of equilibrium:
 - Homogeneous particle distribution
- **M**icro definition of equilibrium?





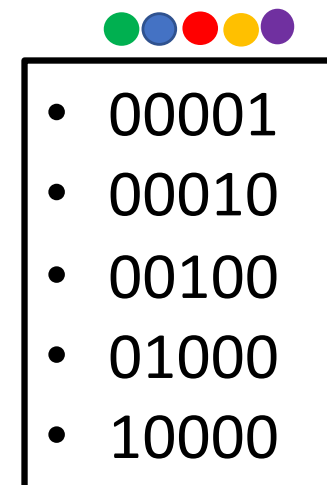
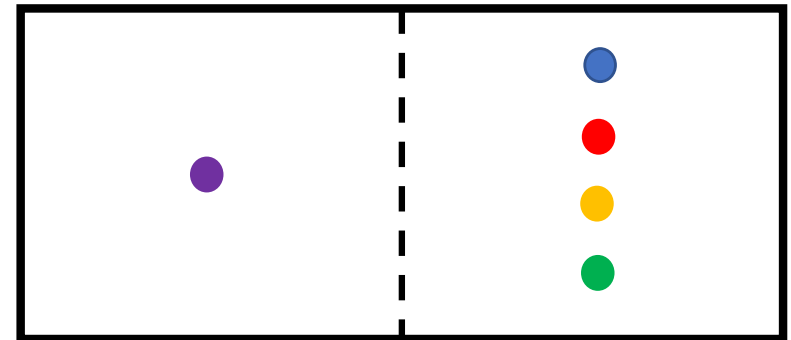
New concept: Microstates and macrostates

- What is the most likely outcome of tossing 3 coins?
- **M**icrostates: state of all coins
 - heads: $s_i=1$, tails: $s_i=0$
 - all microstates are equally likely
- **M**acrostate: sum of states
 - $n = \sum_i s_i (= 0, 1, 2, 3)$
- Which is the most likely **m**acrostate
 - $8 = 2^3$ possible **m**icrostates
 - Probabilities: $n=0: P=1/8$
 $n=1: P=4/8$
 $n=2: P=4/8$
 $n=3: P=1/8$

i:	1	2	3	n
	0	0	0	0
	1	0	0	1
	0	1	0	1
	0	0	1	1
	1	1	0	2
	1	0	1	2
	0	1	1	2
	1	1	1	3

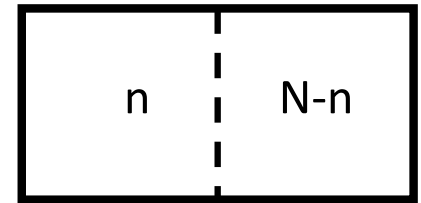
Microstates and macrostates

- Box with left and right side
- Example: $N = 5$
- Particles can be distinguished ($i=1, 2, \dots, 5$)
- Particle state s_i :
 - left: $s_i=1$
 - right: $s_i=0$
- Macrostates $n = \sum_i s_i (= 0, 1, 2, \dots, 5)$
- List the possible microstates of $n=1$



5 microstates => **multiplicity $\Omega(n, N)$** of macrostate $n=1$ is **$\Omega(1, 5) = 5$**

Multiplicity of macrostates



n=0	n=1	n=2	n=3	n=4	n=5
00000	00001	00011	11100	11110	11111
	00010	00101	11010	11101	
	00100	01001	10110	11011	
	01000	10001	01110	10111	
	10000	00110	11001	01111	
		01010	10101		
		01100	10011		
		10010	01101		
		10100	01011		
		11000	00111		

$\Omega(0,5)=1$ $\Omega(1,5)=5$ $\Omega(2,5)=10$ $\Omega(3,5)=10$ $\Omega(4,5)=5$ $\Omega(5,5)=1$

General formula for multiplicity: $\Omega(n, N) = \frac{N!}{(N-n)!n!}$ $\Omega(2,5) = \frac{5!}{3!2!} = 10$

Number of possible microstates: $\Omega_t = \sum_{n=0}^5 \Omega(n) = 32 (= 2^5)$

Probability of macrostates: $P(n, N) = \Omega(n, N)/2^N = \frac{2^{-N}N!}{(N-n)!n!}$

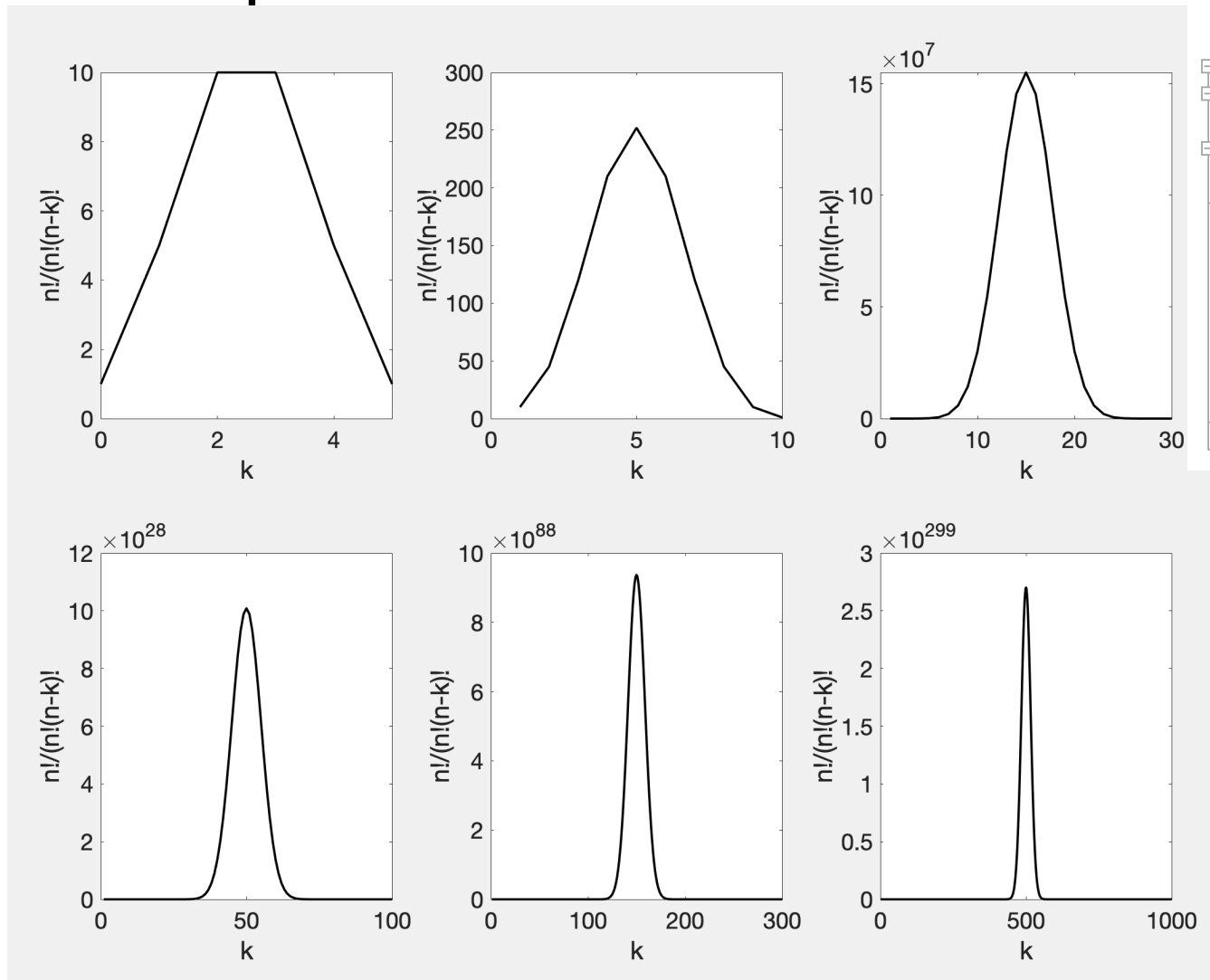
Fundament of statistical mechanics

Fundamental assumption of statistical mechanics:

In an isolated system in thermal equilibrium, all accessible microstates are equally probable.

An isolated system will evolve towards the most probable state = macrostate with the highest multiplicity. We call this the equilibrium state.

Sharpness of distribution



```

n=[5 10 30 100 300 1000];
l=1;
for i=1:2
    for j=1:3
        nk=1;
        for k=1:n(l)
            nk(k)=nchoosek(n(l),k);
        end
        subplot(2,3,l)
        plot(nk, 'k', 'LineWidth',2)
        xlabel('k', 'FontSize',20)
        ylabel('n!/(n!(n-k)!', 'FontSize',20)
        ax1 = gca; % current axes
        ax1.FontSize = 20;
        l=l+1;
    end
end
    
```

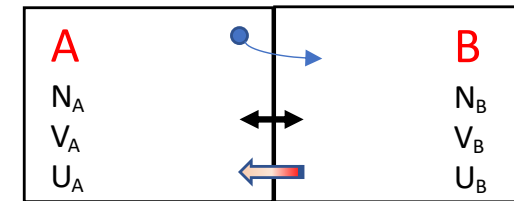
What happens when $q \rightarrow 10^{23}$?

$$\Omega(N, n) = \frac{N!}{n!(N-n)!}$$

We need an approximation for $N!$ when $N \gg 1$

Equilibrium between two systems

- $N=N_A+N_B$, $V=V_A+V_B$, $U=U_A+U_B$, all (N,V,U) constant
- Can vary one of the three $\alpha \in (N, V, U)$,
 - keeping the other 2 constant
 - keep total constant: $\alpha = \alpha_A + \alpha_B = \text{const.}$
- Multiplicity $\Omega_{tot} = \Omega_A \Omega_B$ is maximum
 - = most likely state
 - = equilibrium state



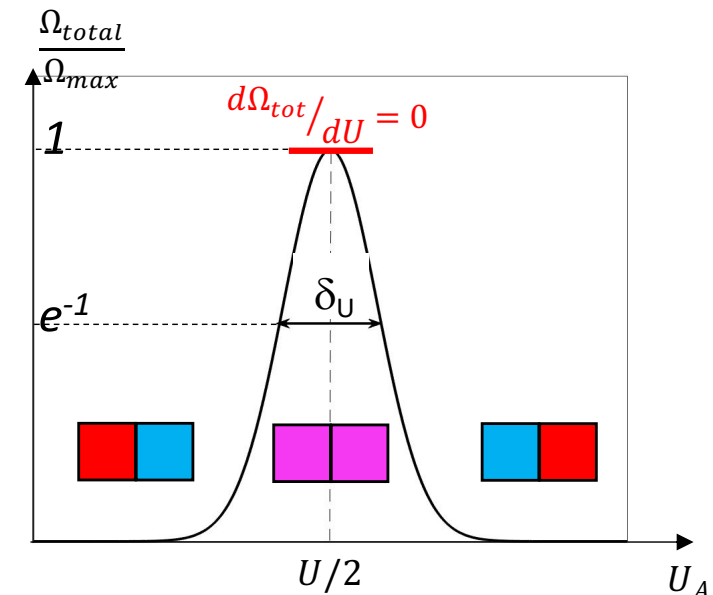
System: can contain "anything"

maximum when $\frac{\partial \Omega_{tot}}{\partial \alpha_A} = 0$

$$\frac{\partial(\Omega_A \Omega_B)}{\partial \alpha_A} = \Omega_A \frac{\partial \Omega_B}{\partial \alpha_A} + \Omega_B \frac{\partial \Omega_A}{\partial \alpha_A} = 0$$

$$d\alpha_A = -d\alpha_B \quad \frac{-1}{\Omega_B} \frac{\partial \Omega_B}{\partial \alpha_B} + \frac{1}{\Omega_A} \frac{\partial \Omega_A}{\partial \alpha_A} = 0$$

Equilibrium condition: $\frac{\partial \ln \Omega_B}{\partial \alpha_B} = \frac{\partial \ln \Omega_A}{\partial \alpha_A}$



Boltzmann's Entropy

$$S = k \ln \Omega$$

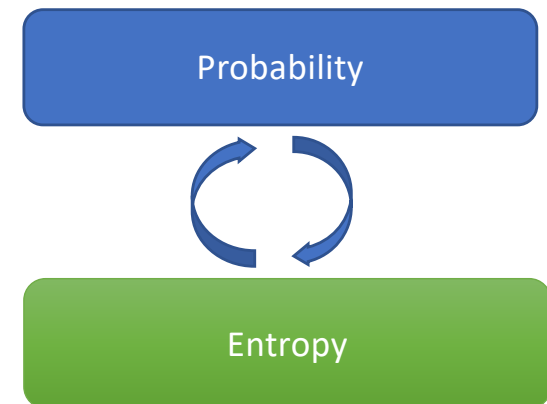


Relates the number of **microstates** (multiplicity) with the thermodynamic (**macroscopic**) state of the system

$$k = 1.381 \times 10^{-23} \text{ J K}^{-1}$$

$$[S] = \text{J K}^{-1}$$

Relates the thermodynamic state of the system with the **probability** to be in a given macrostate



Boltzmann's Entropy and equilibrium

At equilibrium, the multiplicity is maximized. This means that the equilibrium state has maximum entropy

Example:

Thermal equilibrium of two interacting ideal gases through energy exchange



$$\frac{\partial \Omega_{total}}{\partial U_A} = 0 \rightarrow \frac{\partial S_{total}}{\partial U_A} = 0$$

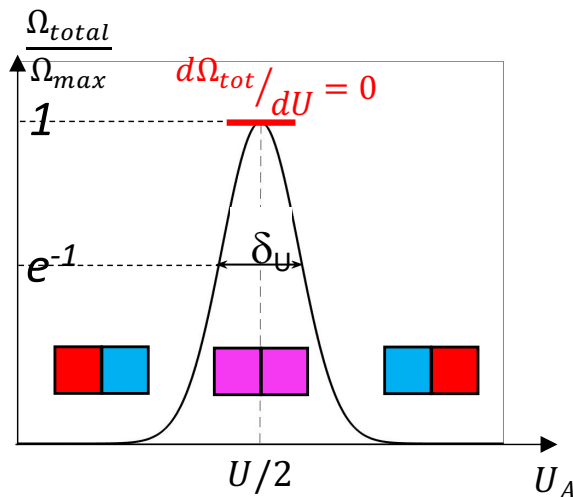
$$\frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_B} = 0 \rightarrow \frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_B} \frac{dU_B}{dU_A} = 0 \rightarrow \frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$$

System A and system B have the same temperature: $T_A = T_B$

Most likely macrostate

Maximum total Entropy
Thermodynamic equilibrium

Interacting systems have the same temperature at equilibrium



$$\frac{[S]}{[U]} = \frac{J K^{-1}}{J}$$

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \equiv \frac{1}{T}$$

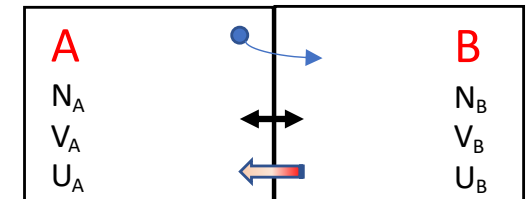
$$T = \left(\frac{\partial S}{\partial U} \right)^{-1}$$

Equilibrium between two systems

- $N=N_A+N_B$, $V=V_A+V_B$, $U=U_A+U_B$, all (N,V,U) constant
- Can vary one of the three $\alpha \in (N, V, U)$,
 - keeping the other 2 constant
 - keep total constant: $\alpha = \alpha_A + \alpha_B = \text{const.}$
- $S_{tot} = S_A + S_B$ is maximum in equilibrium

Equilibrium criterium:

$$\frac{\partial S_B}{\partial \alpha_B} = \frac{\partial S_A}{\partial \alpha_A}$$



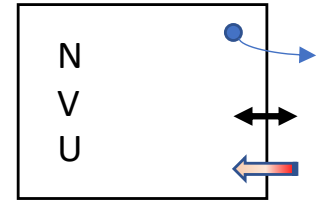
Entropy: $S = k \ln \Omega(N, V, U)$

Thermal equilibrium: $\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$, $\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_{N,V}$, $\frac{[S]}{[U]} = \frac{J K^{-1}}{J}$

Mechanical equilibrium: $\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}$, $P \equiv T \left(\frac{\partial S}{\partial V}\right)_{N,U}$, $\frac{[P]}{[T]} = \frac{J}{m^3 K}$

Chemical equilibrium: $\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}$, $\mu \equiv -T \left(\frac{\partial S}{\partial N}\right)_{U,V}$, $\frac{[\mu]}{[T]} = \frac{J}{K}$

Thermodynamic identity



- Change in entropy due to *energy, volume, particle number* has a total differential:

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

- Use definitions: $\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_{N,V}$, $P \equiv T \left(\frac{\partial S}{\partial V}\right)_{N,U}$, $\mu \equiv -T \left(\frac{\partial S}{\partial N}\right)_{U,V}$

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

- => Thermodynamic identity for $U(S, V, N)$

$$dU = TdS - PdV + \mu dN$$

- The *thermodynamic identity* holds *true* for any infinitesimal change in a system

Ideal gas: entropy S and temperature T

- Sackur-Tetrode Entropy:

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

- Temperature:

$$T = \left(\frac{\partial S}{\partial U} \right)^{-1} = \left(kN \frac{d}{dU} \ln U^{\frac{3}{2}} \right)^{-1} = \left(\frac{3kN}{2} \frac{1}{U} \right)^{-1} \rightarrow U = \frac{3NkT}{2}$$

- Equipartition of energy: $\frac{3kT}{2}$ for the kinetic energy per particle in 3D
- Heat capacity C_V :

$$C_V = \frac{dU}{dT} \rightarrow C_V = \frac{3Nk}{2}$$

Pressure P in the ideal gas:

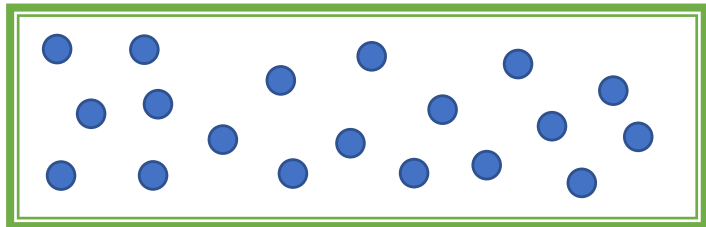
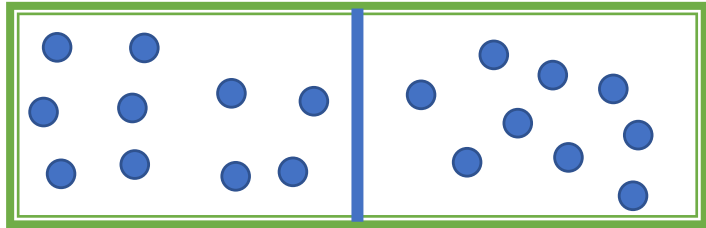
- Entropy:
$$S(U, V, N) = kN \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3h^2 N} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \right]$$
$$S(U, V, N) = kN \left[\ln f(N) + \ln V + \frac{3}{2} \ln U \right]$$

- Equation of state:

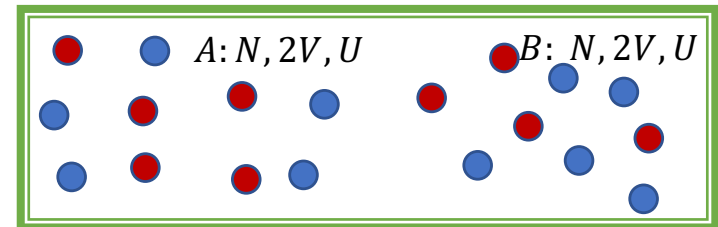
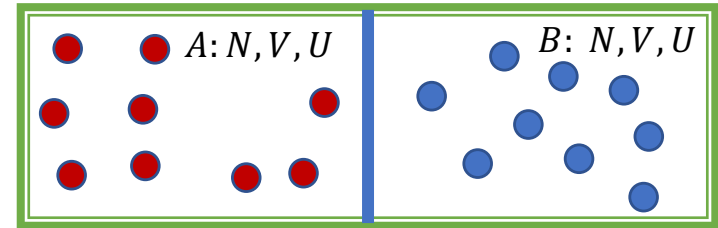
$$P = T \left(\frac{\partial S}{\partial V} \right)_{U, N} = NkT \frac{d}{dV} \ln V = \frac{NkT}{V} \rightarrow \mathbf{PV = NkT}$$

This is now derived from counting the number of microstates of the gas particles!

Entropy of mixing



$\Delta S=?$



$\Delta S=?$

Entropy of mixing: ΔS

If the gas is **the same** on both sides of the wall

$$S_{initial} = S_A + S_B = 2S(U, V, N)$$

$$\Delta S_{tot} = S(2U, 2V, 2N) - 2S(U, V, U)$$

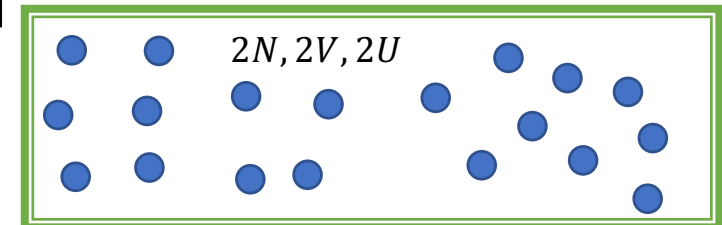
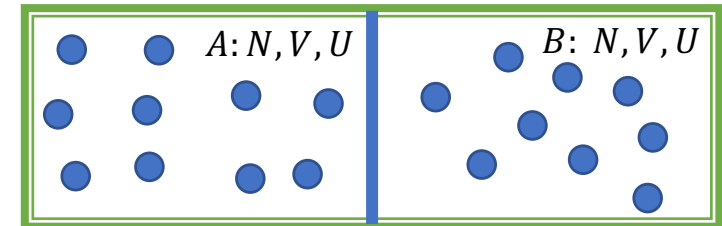
Using Sackur-Tetrode formula

$$S(U, V, N) = kN \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3h^2 N} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \right] = kN \left[\ln \frac{V}{N} + \frac{3}{2} \ln \frac{U}{N} + const \right]$$

$$\Delta S_t = k2N \left[\ln \frac{2V}{2N} + \frac{3}{2} \ln \frac{2U}{2N} + const \right] - 2kN \left[\ln \frac{V}{N} + \frac{3}{2} \ln \frac{U}{N} + const \right]$$

$$\Delta S_t = 0$$

Nothing changes, when we remove the wall!



Entropy of mixing: ΔS

- If the gas is **different (distinguishable)** on both sides of the wall

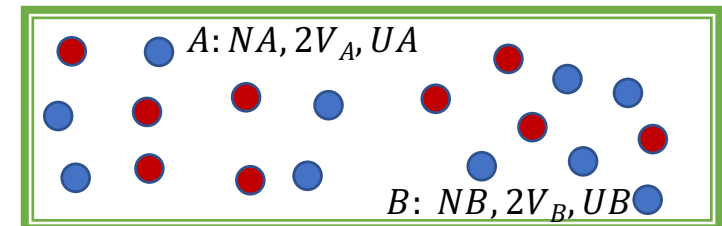
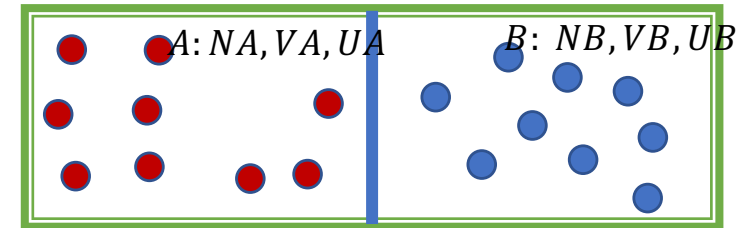
$$\Delta S_t = \Delta S_A + \Delta S_B$$

Using Sackur-Tetrode formula

$$S(U, V, N) = kN \left[\ln \frac{V}{N} + \frac{3}{2} \ln \frac{U}{N} + f(N) \right]$$

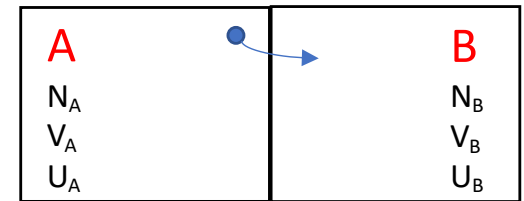
$$\Delta S_t = kN \ln \frac{V_{A,final}}{V_{A,initial}} + kN \ln \frac{V_{B,final}}{V_{B,initial}}$$

$$\Delta S_t = 2kN \ln 2$$



- Entropy increases when we mix *different* gases
- Effectively, the available volume increases upon mixing hence the number of configurations increases

Ideal mixtures



$$\begin{aligned} N &= N_A + N_B \\ V &= V_A + V_B \\ U &= U_A + U_B \end{aligned}$$

Thermal and mechanical equilibrium: $T_A = T_B, P_A = P_B$

Composition: $x_i = \frac{N_i}{N}, i = A, B, \quad x_A + x_B = 1, \quad \rho = \frac{N_A}{V_A} = \frac{N_B}{V_B} = \frac{N}{V}$

Ideal gas and ideal mixture = **U and P are independent of composition:** $U = U_A + U_B = \text{const.}$

Remove wall between A & B: Equilibrium criterium: $\left(\frac{\partial S_A}{\partial N_A}\right)_{U_A, V_A} = \left(\frac{\partial S_B}{\partial N_B}\right)_{U_B, V_B}, U_A, V_A \rightarrow U, V$

Entropy change on mixing $\Delta S_i = kN_i \ln \frac{V}{V_i} = kN \left(\frac{N_i}{N} \ln \frac{N}{N_i}\right) = -kN x_i \ln x_i$

Entropy of mixture $S_i(x_i) = S_{i,0}(x_i = 1) + \Delta S_i(x_i)$

Chemical potential of mixture:

$$\begin{aligned} \mu_A &\equiv -T \left(\frac{\partial S_A}{\partial N_A}\right)_{U, V, N_B} & \frac{\partial x_A}{\partial N_A} &= \frac{\partial N_A / N}{\partial N_A} = \frac{1}{N} \\ &= -\frac{T}{N} \left(\frac{\partial S_A}{\partial x_A}\right)_{U, V, N_B} \\ &= -\frac{T}{N} \left(\frac{\partial S_{A,0}}{\partial x_A}\right)_{U, V, N_B} - \frac{T}{N} \left(\frac{\partial \Delta S_A}{\partial x_A}\right)_{U, V, N_B} \\ &= \mu_{A,0} + \frac{T}{N} \left(\frac{\partial kN x_A \ln x_A}{\partial x_A}\right)_{U, V, N_B} = \mu_{A,0} + kT \left(\frac{\partial x_A \ln x_A}{\partial x_A}\right)_{U, V, N_B} \\ &= \mu_{A,0} + kT(\ln x_A + 1) \\ &= \mu_{A,0}^* + kT \ln x_A \end{aligned}$$

Equilibrium criterium: $\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B} \Rightarrow \mu_A = \mu_B$ ideal mixtures $\Rightarrow \ln x_A = \ln x_B \Rightarrow x_A = x_B$

▶ State variables and functions: $N, V, P, T, \mu, U, S, (H, F, G)$

▶ 1. law: $\Delta U = Q + W$

▶ 2. law: $\Delta S \geq 0$ for isolated system

▶ 3. law: $S \rightarrow \text{constant}$ when $T \rightarrow 0$

▶ Equilibria

▶ Thermal: $\frac{\partial S_1}{\partial U_1} = \frac{\partial S_2}{\partial U_2} \Leftrightarrow$

$$T_1 = T_2$$

▶ Mechanical: $\frac{\partial S_1}{\partial V_1} = \frac{\partial S_2}{\partial V_2} \Leftrightarrow$

$$P_1 = P_2$$

▶ Chemical: $\frac{\partial S_1}{\partial N_1} = \frac{\partial S_2}{\partial N_2} \Leftrightarrow$

$$\mu_1 = \mu_2$$

▶ Defined

▶ Temperature:

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U} \right)_{N,V}$$

▶ Pressure:

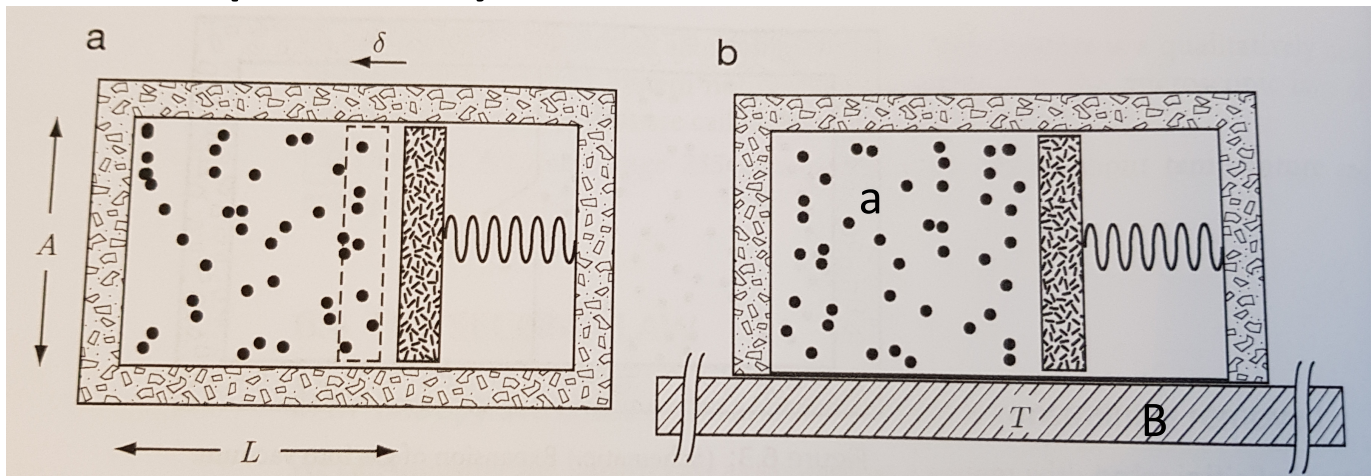
$$P \equiv T \left(\frac{\partial S}{\partial V} \right)_{N,U}$$

▶ Chemical potential:

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

▶ Heat Capacity: $C_V \equiv \left(\frac{\partial U}{\partial T} \right)_{N,V}$

Open systems



First law $\Delta U = Q + W = T\Delta S - P\Delta V$

Adiabatic compression: $Q = 0$

$\Delta V < 0, \quad \Delta N = 0, \quad \Delta U = ?$

Heat: $Q = T\Delta S = 0$

$S(U, V, N) = k \left[N \ln V + \frac{3N}{2} \ln U + f(N) \right]$

Entropy: $\Delta S = k \left[N \ln \frac{V_2}{V_1} + \frac{3N}{2} \ln \frac{U_2}{U_1} \right] = 0$

$\frac{3}{2} \ln \frac{U_2}{U_1} = -\ln \frac{V_2}{V_1}$

$\frac{U_2}{U_1} = \frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{2/3} > 1 \Rightarrow$ **heating**

With thermal reservoir:

(NVT) constant instead of (NVU) constant

$T_2 = T_1 \quad \Rightarrow \quad Q = T\Delta S < 0$

how can $\Delta S < 0$?

2nd law: $\Delta S_{tot} = \Delta S + \Delta S_R \geq 0$
 $\Delta S_R = ?$

TDI $dU = TdS - PdV + \mu dN$

$\Rightarrow \quad dS_R = \frac{1}{T} dU_R = \frac{1}{T} dU$

$dS_{tot} = \frac{1}{T} (TdS - dU) \geq 0$

$F = U - TS, \quad dF = dU - TdS - SdT$

\Rightarrow 2nd law using only system variables: **$dF \leq 0$**