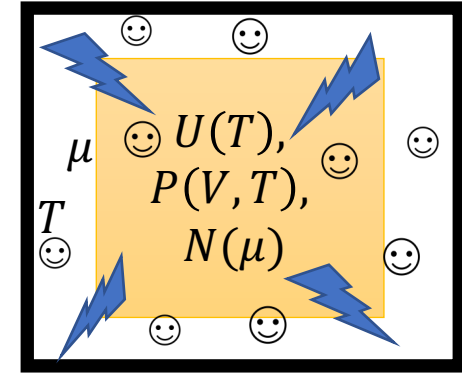
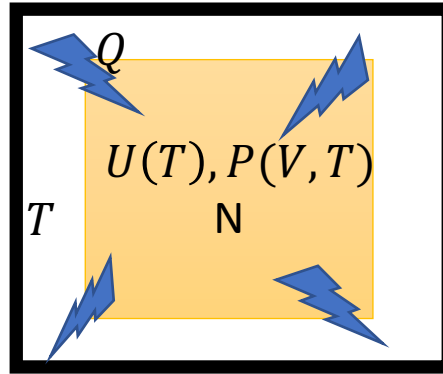
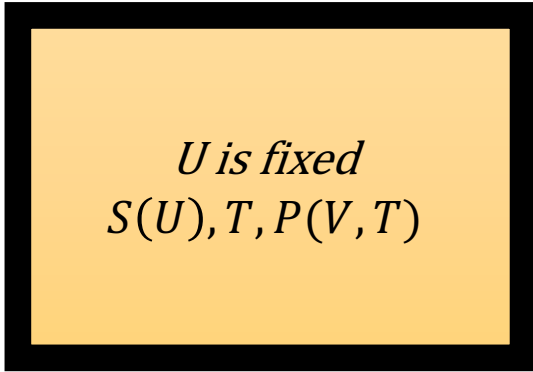


# Summary Part 2

21.11.2018

Thermodynamic laws

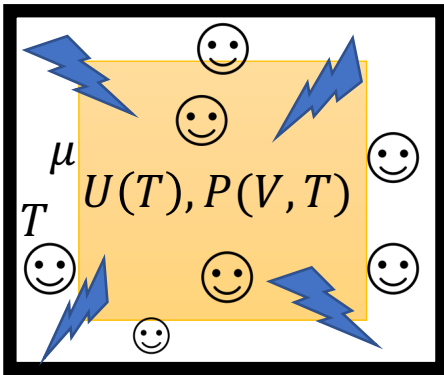
Thermodynamic processes



# Summary Part 1

Equilibrium statistical systems

CONTINUE....



## A system in contact with a thermal and particle reservoir

The system can exchange energy and particles with a reservoir and it is in equilibrium at a fixed  $T$  and chemical potential  $\mu$

Probability of the system being in a given microstate is proportional to the probability that the reservoir is in *any state that accomodate that particular microstate (hence the total number of microstates of the thermal bath corresponding to a given system's microstate)*

*Probability ratio between two microstates (the system can exchange energy  $\Delta U_R = -\Delta E$ , and particles  $\Delta N_R = -\Delta N$ )*

$$\frac{P(s_1)}{P(s_2)} = \frac{\Omega_R(s_1)}{\Omega_R(s_2)} = e^{\frac{[S_R(s_1) - S_R(s_2)]}{k}} = e^{\beta \Delta U_R} e^{-\beta \mu \Delta N_R} = e^{-\beta \Delta E} e^{\beta \mu \Delta N}$$

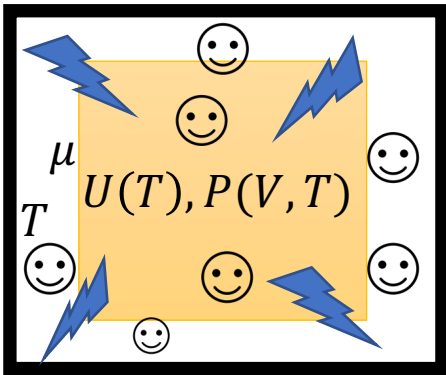
Probability of the system in a specific microstate a fixed  $T$  and  $\mu$

$$P(s) = \frac{1}{\Xi(T, \mu)} e^{-\beta(E_s - \mu N_s)}$$

Grand Partition function

$\Xi(T, \mu) = \sum_{\mathbf{s}} e^{-\beta(E_s - \mu N_s)}$  counts all the accessible microstates weighted by the Gibbs factor

What is the microstate  $\mathbf{s}$ ?



## Non-interacting particle system in contact with a thermal and particle reservoir

Each identical particle can occupy discrete energy states  $\epsilon_j$ ,  $j = 1, 2, \dots$  is the state number

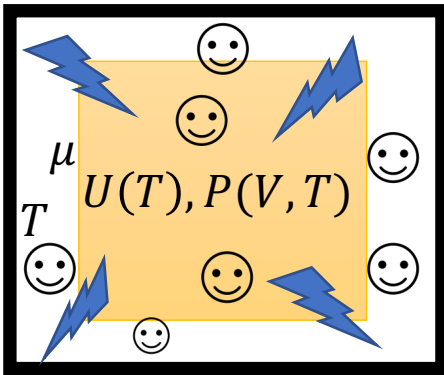
For  $N$  identical particles, we can have  $N_j$  number of particles (occupation number) in the energy state  $\epsilon_j$

The energy of a specific microstate with  $N_s = \sum_j N_j$  particles is  $E_s = \sum_j N_j \epsilon_j$

$\sum_s \equiv$  sum over all particles number  $N_s$  and over all the partitions of particles  $N_s$  in the quantum states with total energy  $E_s$

$$\Xi(T, \mu) = \sum_{N_s} \sum_{\substack{\{N_j\} \\ \sum_j N_j = N_s}} e^{-\beta(E_s - \mu N_s)} = \sum_{\{N_j\}} e^{-\beta \sum_j N_j (\epsilon_j - \mu)}$$

$$\Xi(T, \mu) = \left( \sum_{N_1} e^{-\beta N_1 (\epsilon_1 - \mu)} \right) \cdot \left( \sum_{N_2} e^{-\beta N_2 (\epsilon_2 - \mu)} \right) \cdots \left( \sum_{N_3} e^{-\beta N_3 (\epsilon_3 - \mu)} \right) \cdots$$



## Occupation number of a state

Probability of the system in a specific microstate a fixed  $T$  and  $\mu$

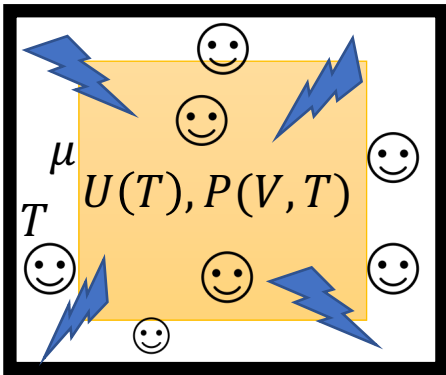
$$P(s) = \frac{1}{\Xi(T, \mu)} e^{-\beta(E_s - \mu N_s)} = \frac{e^{-\beta N_1(\epsilon_1 - \mu)} \cdot e^{-\beta N_2(\epsilon_2 - \mu)} \cdot e^{-\beta N_3(\epsilon_3 - \mu)} \dots}{\left(\sum_{N_1} e^{-\beta N_1(\epsilon_1 - \mu)}\right) \cdot \left(\sum_{N_2} e^{-\beta N_2(\epsilon_2 - \mu)}\right) \dots \left(\sum_{N_3} e^{-\beta N_3(\epsilon_3 - \mu)}\right) \dots}$$

$$P(s) = \frac{e^{-\beta N_1(\epsilon_1 - \mu)}}{\left(\sum_{N_1} e^{-\beta N_1(\epsilon_1 - \mu)}\right)} \cdot \frac{e^{-\beta N_2(\epsilon_2 - \mu)}}{\left(\sum_{N_2} e^{-\beta N_2(\epsilon_2 - \mu)}\right)} \cdot \frac{e^{-\beta N_3(\epsilon_3 - \mu)}}{\left(\sum_{N_3} e^{-\beta N_3(\epsilon_3 - \mu)}\right)} \dots$$

$$P(s) = P(N_1) \cdot P(N_2) \cdot P(N_3) \dots$$

Probability for the occupation number  $N$  of the given state at fixed  $T$  and  $\mu$

$$P(N) = \frac{e^{-\beta N(\epsilon - \mu)}}{\left(\sum_N e^{-\beta N(\epsilon - \mu)}\right)}, \quad Z = \sum_N e^{-\beta N(\epsilon - \mu)} \text{ (partition function of a single mode)}$$



## Non-interacting FERMIONS in contact with a thermal and particle reservoir

The occupation number for each quantum state is  $N = 0, 1$

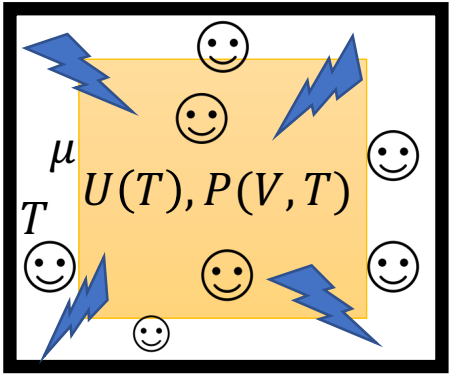
Probability for the occupation number  $N$  of the given energy state a fixed  $T$  and  $\mu$

$$P(N) = \frac{e^{-\beta N(\epsilon - \mu)}}{1 + e^{-\beta(\epsilon - \mu)}}$$

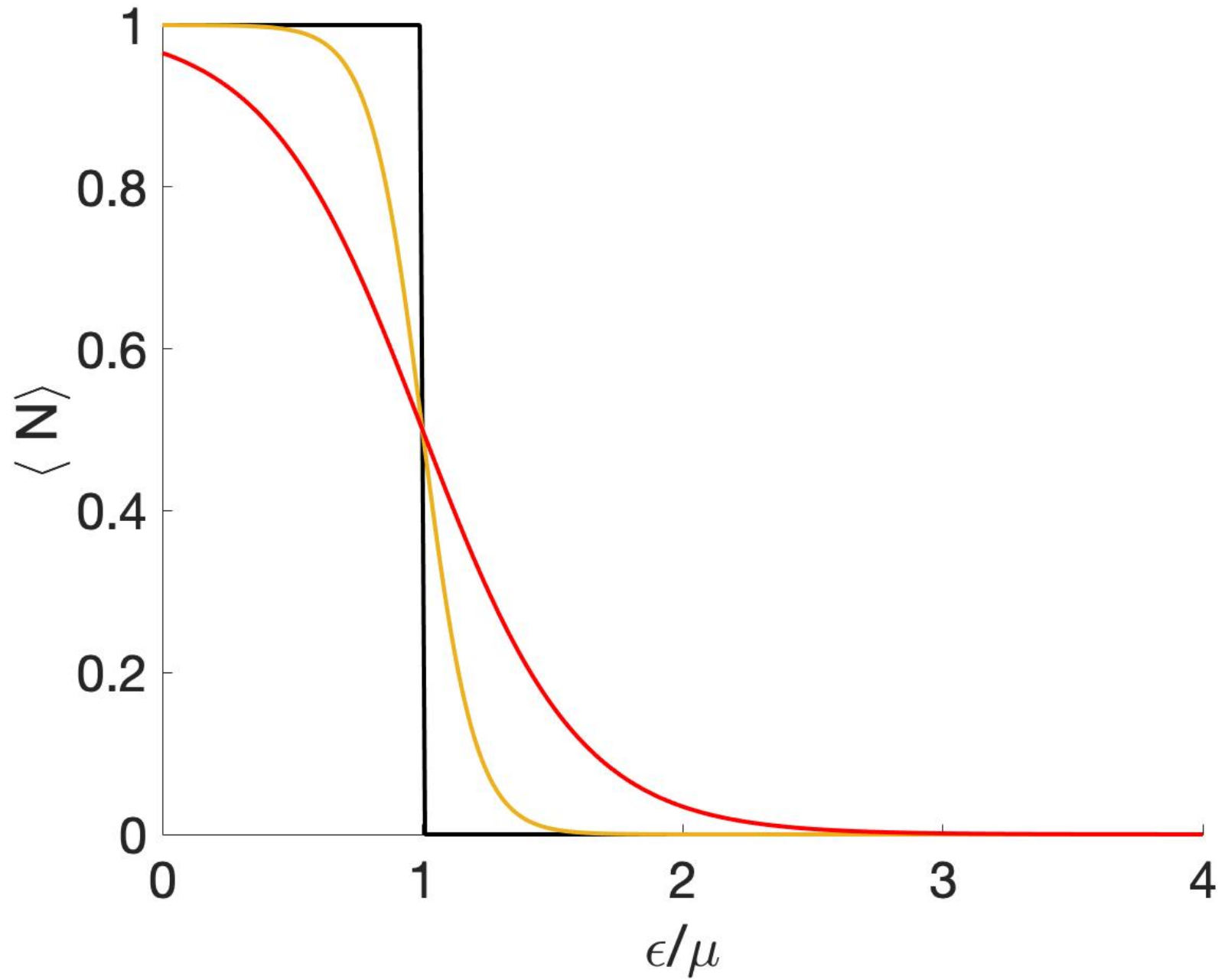
Average occupation number  $\langle N \rangle$  of the given energy state  $\epsilon$  a fixed  $T$  and  $\mu$

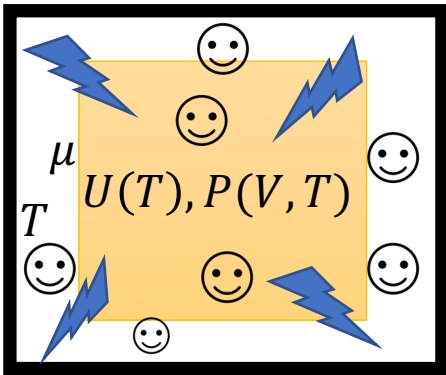
**FERMI-DIRAC distribution**

$$\langle N \rangle(\epsilon) = \sum_{N=0}^1 N P(N) = \frac{e^{-\beta(\epsilon - \mu)}}{1 + e^{-\beta(\epsilon - \mu)}} \rightarrow \langle N \rangle(\epsilon) = \frac{1}{e^{\beta(\epsilon - \mu)} + 1}$$



Fermi Dirac distribution





## Non-interacting BOSONS in contact with a thermal and particle reservoir

The occupation number for each state is  $N = 0, 1, 2 \dots$

$$\sum_{N=0}^{\infty} e^{-\beta N(\epsilon - \mu)} = \frac{1}{1 - e^{-\beta(\epsilon - \mu)}}, \quad \text{for } \mu < \epsilon \text{ (for every } \epsilon \text{!)}$$

Probability for the occupation number  $N$  of the given energy state a fixed  $T$  and  $\mu$

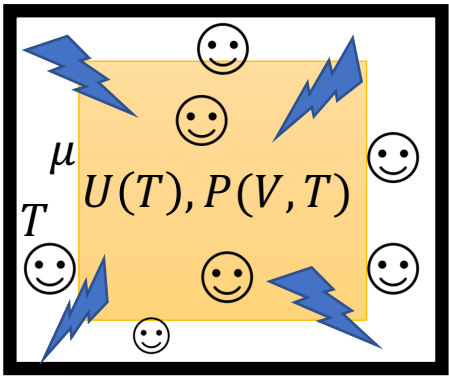
$$P(N) = (1 - e^{-\beta(\epsilon - \mu)}) e^{-\beta N(\epsilon - \mu)}$$

Average occupation number  $\langle N \rangle$  of the given energy state  $\epsilon$  a fixed  $T$  and  $\mu$

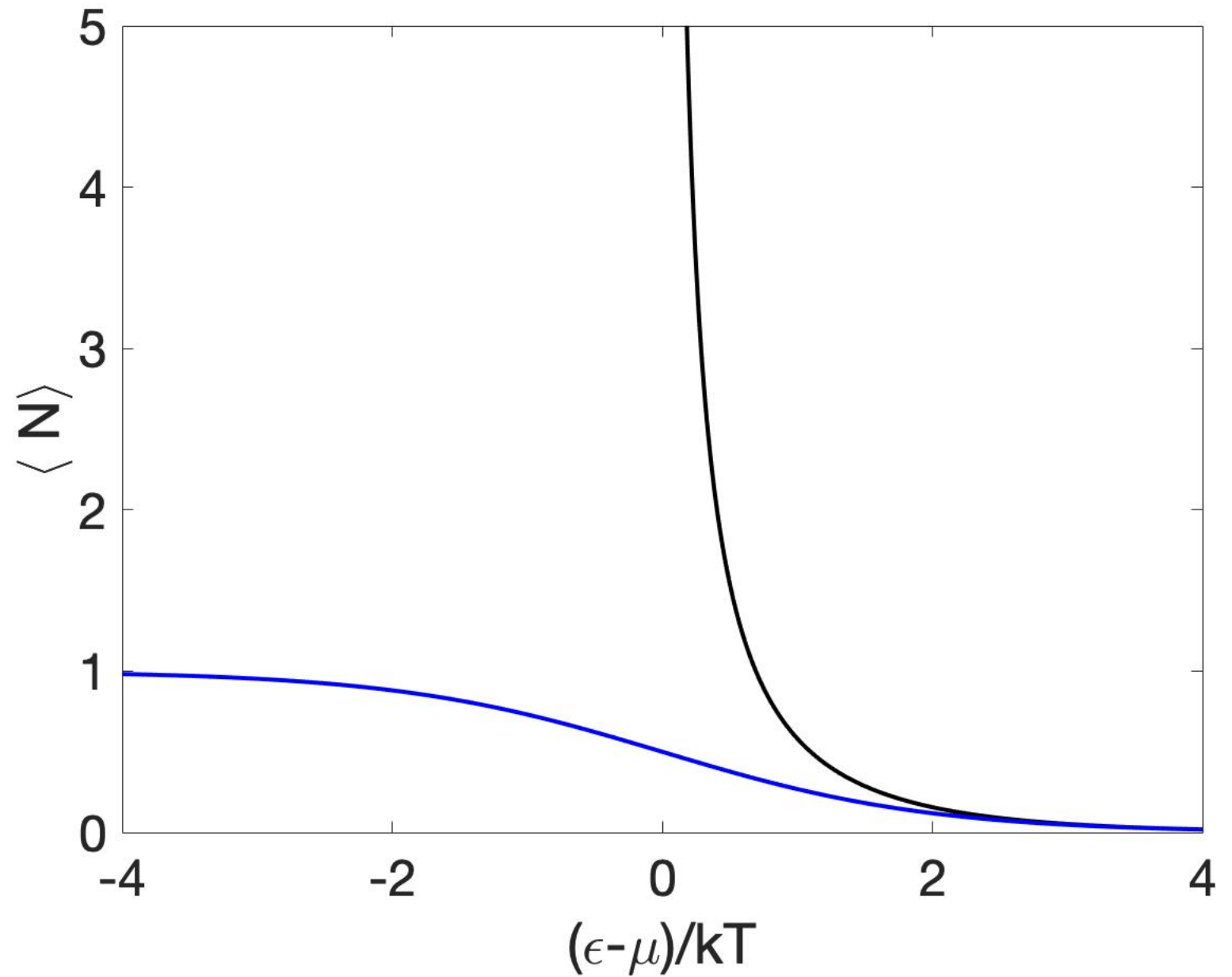
**BOSE-EINSTEIN distribution**

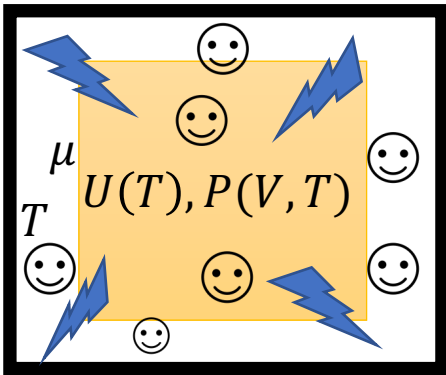
$$\langle N \rangle(\epsilon) = \sum_{N=0}^{\infty} N P(N) = (1 - e^{-\beta(\epsilon - \mu)}) \sum_{N=0}^{\infty} N e^{-\beta N(\epsilon - \mu)} \rightarrow \langle N \rangle(\epsilon) = \frac{1}{e^{\beta(\epsilon - \mu)} - 1}$$





**Bose Einstein distribution**





## Classical limit

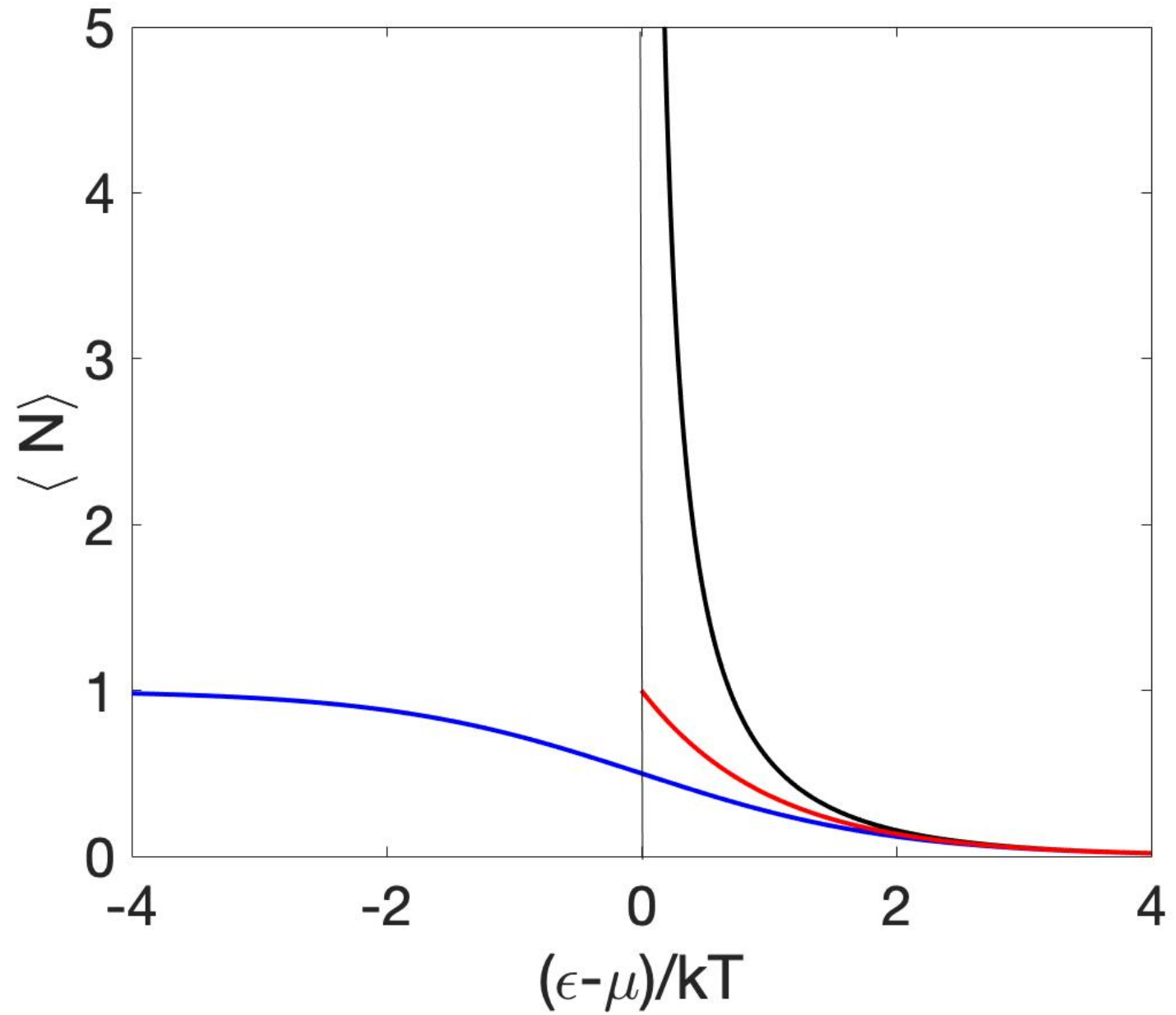
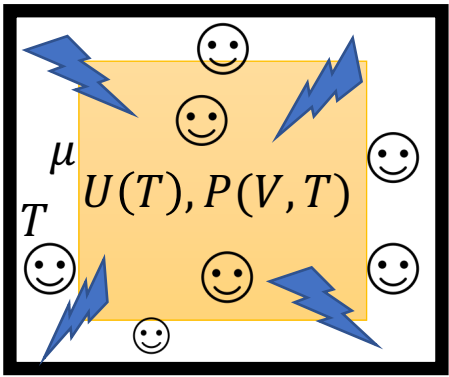
QUANTUM distribution for the average occupation number of an energy state

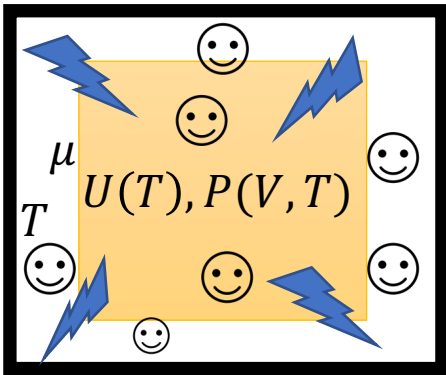
$$\langle N \rangle(\epsilon) = \frac{1}{e^{\beta(\epsilon - \mu)} \pm 1}$$

High T limit ( $\frac{\mu(T)}{kT} \ll 0$ )

**BOLZMANN distribution**

$$\langle N \rangle(\epsilon) = \frac{e^{\beta\mu}}{e^{\beta\epsilon} \pm e^{\beta\mu}} \rightarrow_{e^{\beta\mu} \rightarrow 0} \langle N \rangle(\epsilon) = e^{-\beta(\epsilon - \mu)}$$





## THERMODYNAMIC PROPERTIES AND DENSITY OF STATES

### Average energy

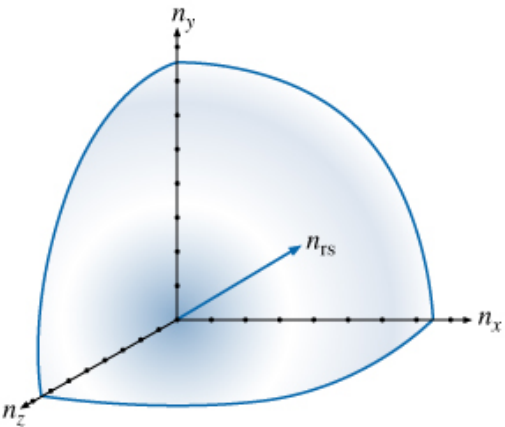
$$U = \sum_{n_x} \sum_{n_y} \sum_{n_z} \langle N \rangle(\epsilon) \cdot \epsilon(n_x, n_y, n_z) = \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z \epsilon \cdot \langle N \rangle = \int_0^\infty d\epsilon \, g(\epsilon) \epsilon \cdot \langle N \rangle$$

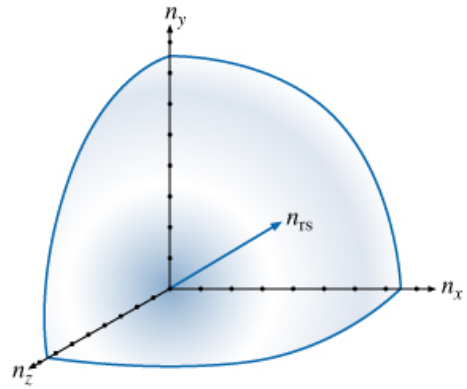
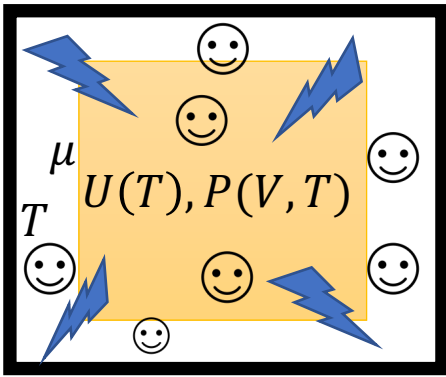
- Density of states  $g(\epsilon)$  comes because we need to count all the quantum states at a given energy  $\epsilon$ . Remember that the quantum state is given by the state of the wavefunction
- Number of states with energy between  $\epsilon$  and  $\epsilon + d\epsilon \equiv$  Number of states with state number between  $n$  and  $n + dn$  (*positive quadrant*)

$$(3D) \, g(\epsilon)d\epsilon = \frac{1}{8} 4\pi n^2 dn, \quad (2D) \, g(\epsilon)d\epsilon = \frac{1}{4} 2\pi n dn, \quad (1D) \, g(\epsilon)d\epsilon = dn$$

Energy  $\epsilon(n)$  is determined by the *quantum mechanics*:

- *Particle in a box*  $\epsilon(n) = \frac{h^2}{8mL^2} n^2$
- *Quantum harmonic oscillator*  $\epsilon(n) = n\hbar\omega$
- *Relativistic particles*  $\epsilon(n) = hf = \frac{hc}{2L} n$





## Density of states

Number of states with energy between  $\epsilon$  and  $\epsilon + d\epsilon \equiv$  Number of states with state number between  $n$  and  $n + dn$

$$(3D) g(\epsilon)d\epsilon = \frac{\pi}{2}n^2dn, \quad (2D)g(\epsilon)d\epsilon = \frac{\pi}{2}ndn, (2D), \quad (1D) g(\epsilon)d\epsilon = dn$$

**FERMIONS**: remember to multiply by factor 2 because there are two electrons per energy level (spin up and spin down)

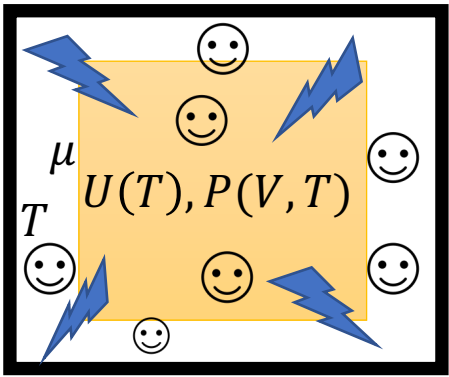
$$(3D) g(\epsilon)d\epsilon = 2 \times \frac{\pi}{2}n^2dn, \quad (2D)g(\epsilon)d\epsilon = 2 \times \frac{\pi}{2}ndn, (2D), \quad (1D)g(\epsilon)d\epsilon = 2 \times dn$$

**PHOTONS** : remember to multiply by factor 2 for the two transverse polarizations of the EM waves

$$(3D) g(\epsilon)d\epsilon = 2 \times \frac{\pi}{2}n^2dn,$$

**PHONONS**: remember to multiply by factor 3 for the three polarizations of the sound waves

$$(3D) g(\epsilon)d\epsilon = 3 \times \frac{\pi}{2}n^2dn$$



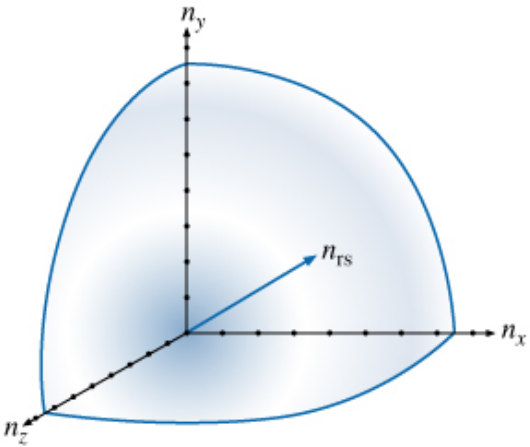
## Thermodynamic properties and **density of states**

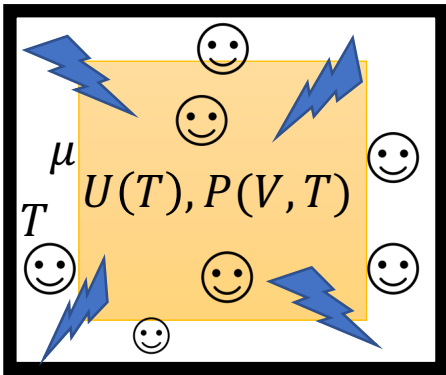
**Average energy**

$$U(T, V, \mu) = \int_0^\infty d\epsilon \, g(\epsilon) \langle N \rangle \epsilon = \int_0^\infty d\epsilon \, g(\epsilon) \frac{\epsilon}{e^{\beta(\epsilon-\mu)} \pm 1}$$

**Average number of particles**

$$N(T, V, \mu) = \int_0^\infty d\epsilon \, g(\epsilon) \langle N \rangle = \int_0^\infty d\epsilon \, g(\epsilon) \frac{1}{e^{\beta(\epsilon-\mu)} \pm 1}$$





## DEGENERATE FERMIONS

$$\epsilon(n) = \frac{h^2}{8mL^2} n^2 \rightarrow g^{(3D)}(\epsilon) d\epsilon = \pi n^2 dn \rightarrow g^{(3D)}(\epsilon) = \frac{\pi}{2} \left( \frac{8m}{h^2} \right)^3 \sqrt{\epsilon}$$

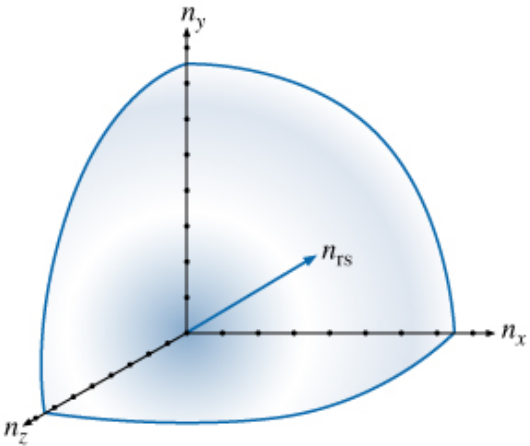
$$\epsilon_F(N) = \frac{h^2}{8mL^2} n_{max}^2 = \frac{h^2}{8mL^2} \left( \frac{N}{2} \right)^2$$

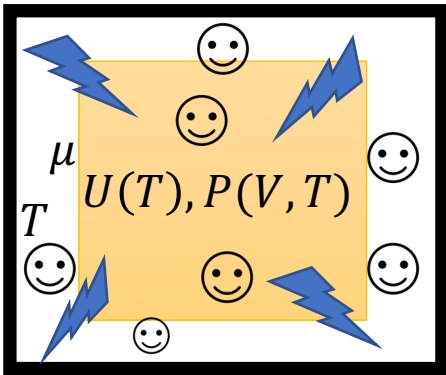
**Average energy**

$$U(T, V, \epsilon_F) = \int_0^{\epsilon_F} d\epsilon \, g(\epsilon) \epsilon$$

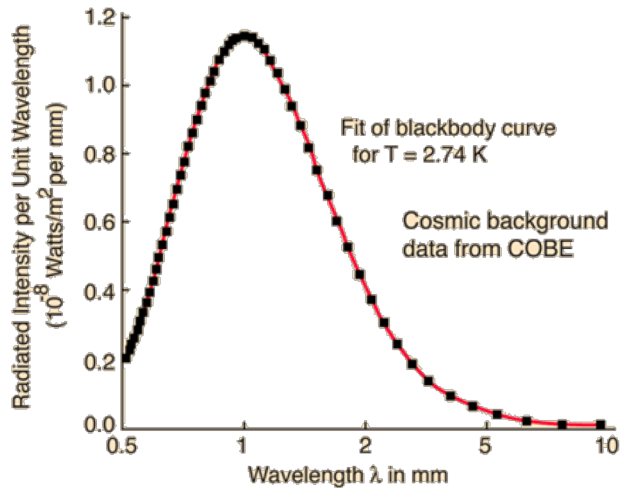
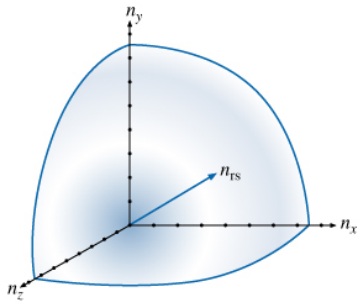
**Average number of particles**

$$N(T, V, \epsilon_F) = \int_0^{\epsilon_F} d\epsilon \, g(\epsilon)$$





## Photons



$$\epsilon = hf = hc/\lambda$$

$$\epsilon_n = \frac{hc}{2L} n \rightarrow g(\epsilon)d\epsilon = \pi n^2 dn \rightarrow g(\epsilon) = \frac{8\pi V}{(hc)^3} \epsilon^2$$

Average energy

$$U(T, V) = \int_0^\infty d\epsilon \, g(\epsilon) \frac{\epsilon}{e^{\beta\epsilon} - 1} = \frac{8\pi V}{(hc)^3} \int_0^\infty d\epsilon \frac{\epsilon^3}{e^{\beta\epsilon} - 1} = \frac{8\pi^5 (kT)^4}{15 (hc)^3}$$

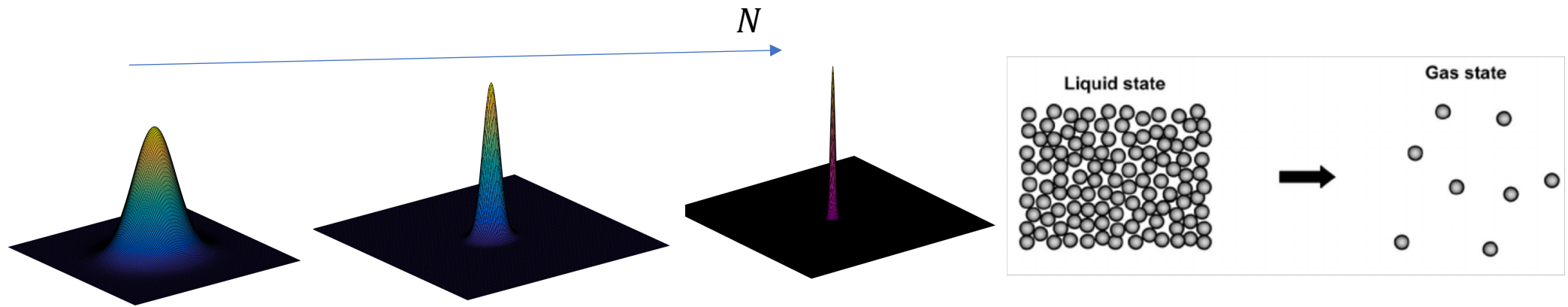
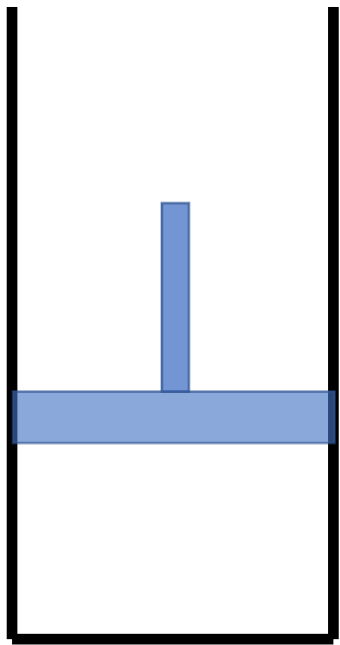
Planck distribution

$$u(f) = \frac{8\pi h}{c^3} \frac{f^3}{e^{\beta hf} - 1}$$

Average number of particles

$$N(T, V) = \int_0^\infty d\epsilon \, g(\epsilon) \frac{1}{e^{\beta\epsilon} - 1} = \frac{8\pi V}{(hc)^3} \int_0^\infty d\epsilon \frac{\epsilon^2}{e^{\beta\epsilon} - 1}$$



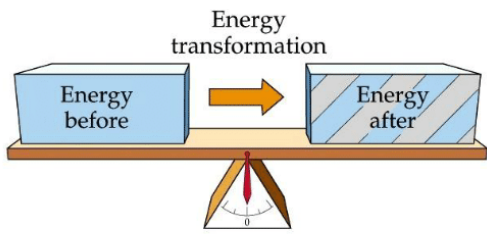


# Summary Part 2

21.11.2018

Thermodynamic laws

Thermodynamic processes



## First law of thermodynamics: CONSERVATION OF ENERGY

Change in the **internal energy** of a system is due to heat or work exchanges with its surrounding

$$dU = \delta Q + \delta W$$

Reversible

$$dU = TdS - PdV$$

$$\Delta U = Q + W$$

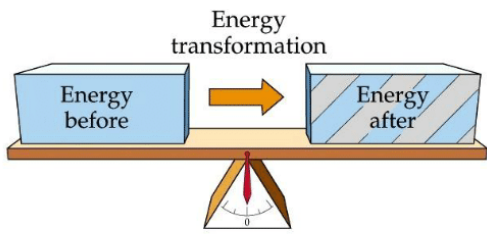
**The change in the «stored» energy equal the sum of «energies in transit»**

**The infinitesimal change in internal energy**

$$dU = \delta Q + \delta W$$

**Infinitesimal reversible process**

$$dU = TdS - PdV$$



## First law of thermodynamics: CONSERVATION OF ENERGY

$$dU = \delta Q + \delta W$$

Reversible

$$dU = TdS - PdV$$

### Clausius equality

$$dS = \frac{\delta Q_{rev}}{T}$$

### Heat capacities

$$C_V = \left( \frac{\delta Q}{dT} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V \rightarrow dU = C_V dT$$

$$C_P = \left( \frac{\delta Q}{dT} \right)_P = C_V + Nk$$

## Second law of thermodynamics

*Irreversible heat flow*

*Entropy increase*

Irreversible heat transfer is smaller than the reversible heat exchange at a given T

$$\frac{\delta Q_{irrev}}{T} < \frac{Q_{rev}}{T}$$

Clausius inequality

$$dS \geq \frac{\delta Q}{T}$$

Isolated system

Entropy tends to increase as the system spontaneously finds its equilibrium state

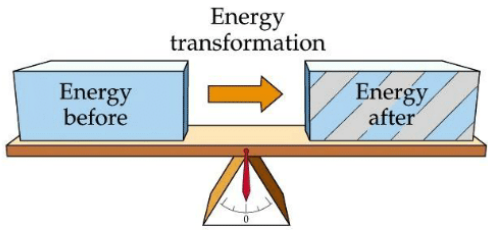
$$dS \geq 0$$

Clausius inequality:

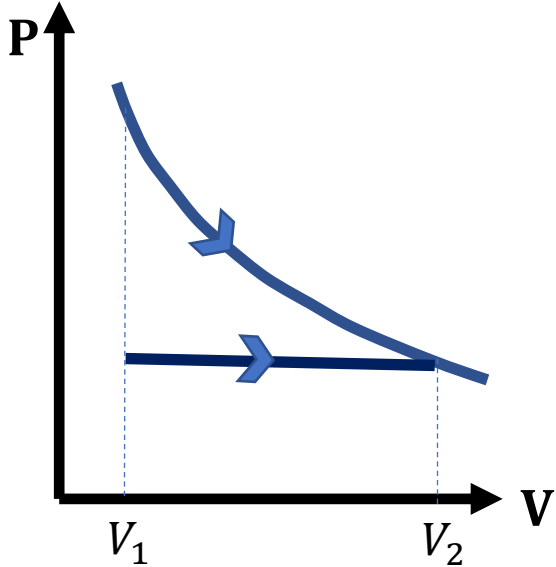
$$dS \geq \frac{\delta Q}{T}$$

Entropy of the Universe:

$$dS \geq 0$$



## Example of (reversible) transformations of an ideal gas:



1. Isothermal process:  $T_1 = T_2 \rightarrow U_1 = U_2$  ( $\Delta U = W_{rev} + Q_{rev} = 0$ )

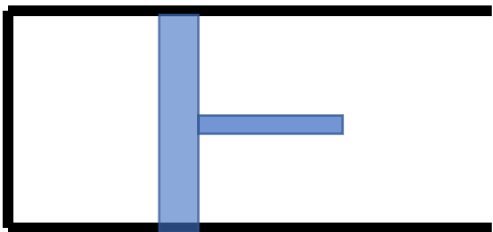
$$W_{rev} = - \int_{V_1}^{V_2} P dV = -NkT \ln \left( \frac{V_2}{V_1} \right)$$

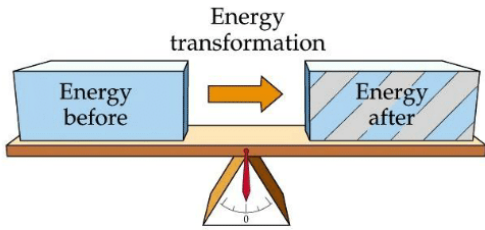
$$\Delta S = \frac{Q_{rev}}{T} = Nk \ln \left( \frac{V_2}{V_1} \right)$$

2. Isobaric process:  $P_1 = P_2 = P$  ( $C_V dT = TdS - PdV$ )

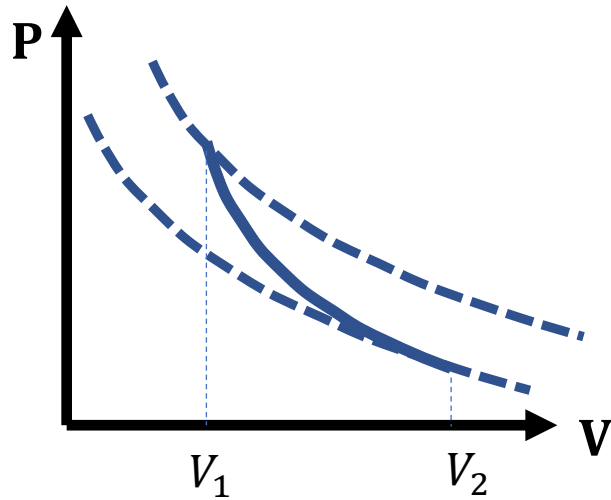
$$W_{rev} = - \int_{V_1}^{V_2} P dV = -P (V_2 - V_1)$$

$$\Delta S = \int_{isobaric} \frac{\delta Q_{rev}}{T} = C_P \int_{T_1}^{T_2} \frac{dT}{T} = C_P \ln \left( \frac{T_2}{T_1} \right)$$





Example of reversible transformations of an ideal gas:



3. Adiabatic process:  $\delta Q_{rev} = 0 \rightarrow dU = -PdV$

$$C_V dT = -PdV \rightarrow C_V \frac{dT}{T} = -Nk \frac{dV}{V} \rightarrow \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{C_p}{C_V}-1}$$

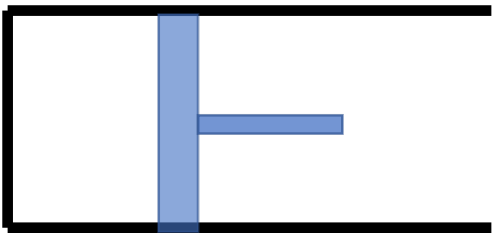
$$W_{rev} = - \int_{V_1}^{V_2} P dV = C_V(T_2 - T_1)$$

$$\Delta S = 0$$

4. Isochoric process:  $V_1 = V_2$  ( $C_V dT = TdS$ )

$$W_{rev} = - \int_{V_1}^{V_2} P dV = 0$$

$$\Delta S = \int_{isochoric} \frac{\delta Q_{rev}}{T} = C_V \int_{T_1}^{T_2} \frac{dT}{T} = C_V \ln \left(\frac{T_2}{T_1}\right)$$



Second law of thermodynamics:  
*In search for the most probable state*

Boltzmann's formula

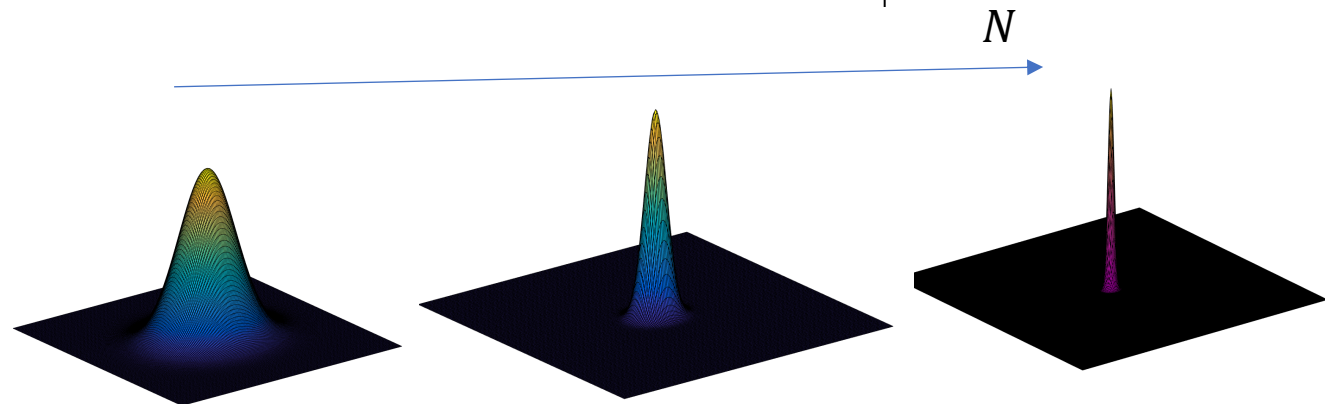
$$\Delta S = k \ln \frac{\Omega_{\text{final}}}{\Omega_{\text{initial}}}$$

*An isolated system will spontaneously evolve towards the most likely equilibrium state, i.e. The macrostate with maximum multiplicity  $\Omega$*

Things that are more  
probability, tend to occur  
more often

$$\Omega_{\text{final}} \geq \Omega_{\text{initial}}$$

Entropy cannot decrease  
 $\Delta S \geq 0$



# Two weakly interacting ideal gases

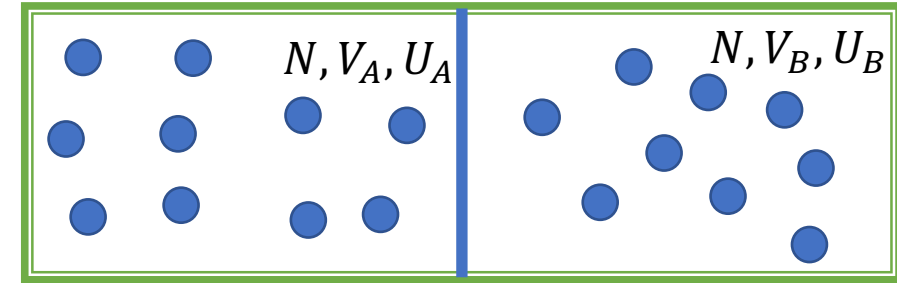
- Total multiplicity:  $\Omega_{total} = f(N)^2 (V_A V_B)^N (U_A U_B)^{\frac{3N}{2}}$
- $\Omega_{total}^{max} = f(N)^2 \left(\frac{V}{2}\right)^{2N} \left(\frac{U}{2}\right)^{3N}$
- States near the most likely state by varying U

$$U_A = \frac{U}{2} + x, U_B = \frac{U}{2} - x \text{ with } x \ll U/2, \text{ while } V_A = V_B = \frac{V}{2}$$

$$\ln \Omega_{total} \sim \frac{3N}{2} \ln \left[ \left(\frac{U}{2}\right)^2 - x^2 \right] \sim 3N \ln \left(\frac{U}{2}\right) - \frac{3N}{2} \left(\frac{2x}{U}\right)^2$$

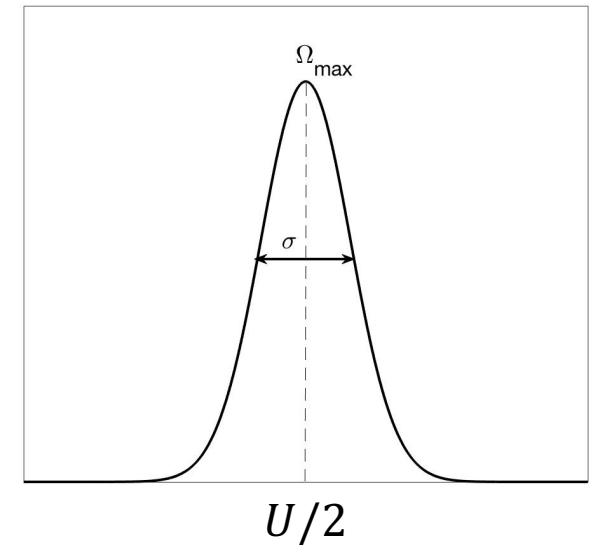
$$\Omega_{total}(U_A) = \Omega_{total}^{max} \cdot \exp \left( -\frac{3N}{2} \left(\frac{2}{U}\right)^2 \left(U_A - \frac{U}{2}\right)^2 \right)$$

The width scales as  $\sigma_U = 2 \cdot \frac{U}{2} \sqrt{\frac{2}{3N}} = \frac{U}{\sqrt{\frac{3N}{2}}} \rightarrow 0 \text{ as } N \rightarrow \infty$



$$U = U_A + U_B$$

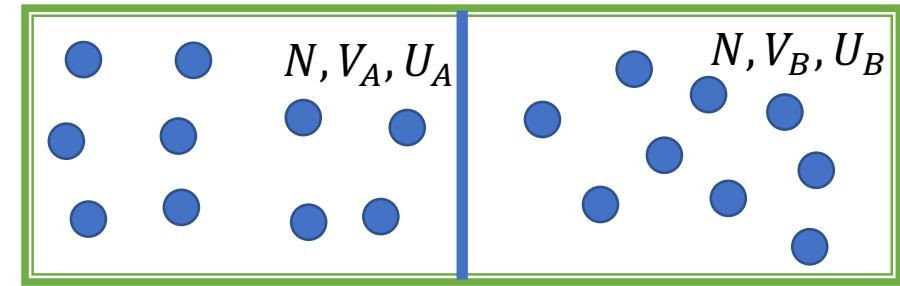
$$V = V_A + V_B$$





# Two weakly interacting ideal gases

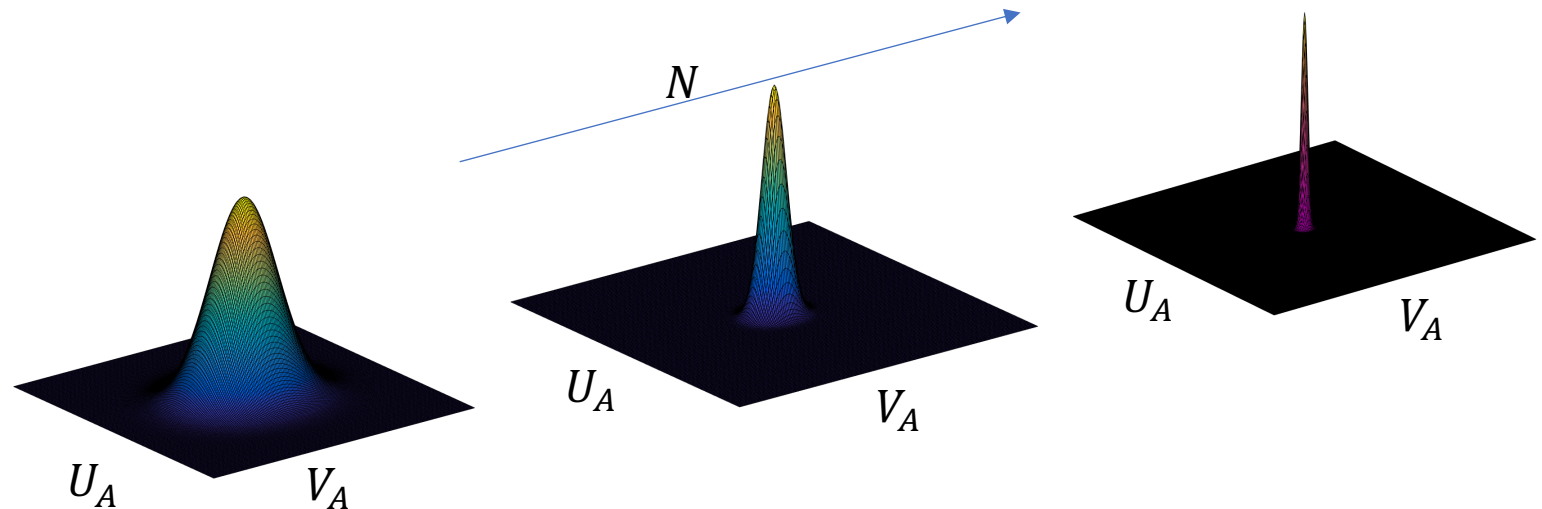
- Macrostates near *the-most-likely* macrostate (aka THE EQUILIBRIUM STATE)

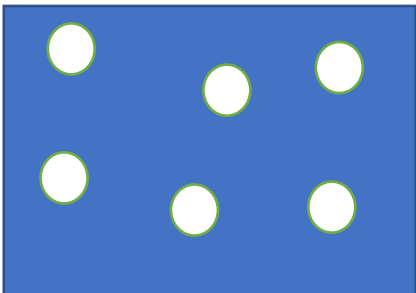
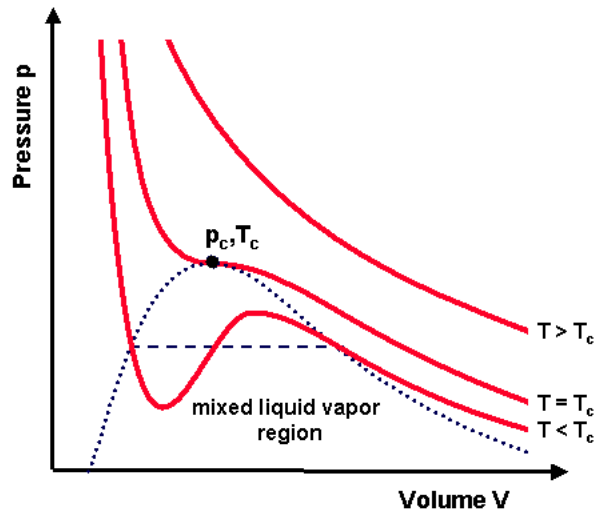
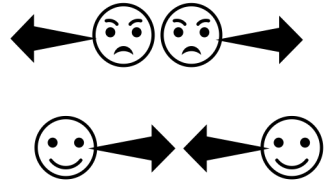
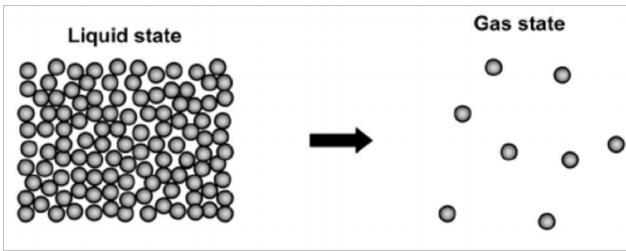


$$\Omega_{total}(V_A, U_A) = \Omega_{total}^{max} \cdot \exp\left(-N \left(\frac{2}{V}\right)^2 \left(V_A - \frac{V}{2}\right)^2\right) \cdot \exp\left(-\frac{3N}{2} \left(\frac{2}{U}\right)^2 \left(U_A - \frac{U}{2}\right)^2\right)$$

$$U = U_A + U_B$$
$$V = V_A + V_B$$

The number of microstates away from the equilibrium macrostate decay very rapidly,  
hence they are extremely unlikely





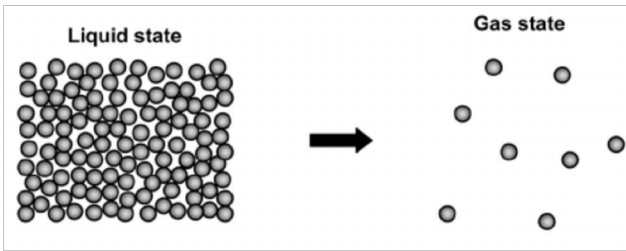
## Liquid-gas phase transition

Van der Waals equation of state for fluids

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = NkT \rightarrow P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}$$

- **Maxwell's equal-area construction:** The phase transition happens at constant **PRESSURE!** We find the pressure on the P-V diagram by the equal areas construction of a given isotherm
- **Phase transition from liquid to vapor at a constant Gibbs free energy**  
 $G(P, T, N)$

$$dG_l = dG_g$$



## Liquid-gas phase transition

Phase transition from liquid to vapor at a constant Gibbs free energy  $G(P, T, N)$

$$dG_l = dG_g$$

Clausius Clapeyron relation

$$-S_l dT + V_l dP = -S_g dT + V_g dP$$

$$\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l} = \frac{\Delta S}{\Delta V} = \frac{L}{T \Delta V}, \quad L \text{ is the latent heat of the phase transition}$$

- Entropy jumps going from a liquid to a gas
- Volume expansion going from a liquid to a gas

Clausius Clapeyron relation tells us how much the phase transition pressure changes with changing temperature



How does the boiling temperature of water depend on the altitude (pressure)?

