

# Summary Part 1

19.11.2018

Equilibrium statistical systems

# Isolated system at equilibrium

*U is fixed*  
 $S(U), T, P(V, T)$

THE EQUILIBRIUM STATE IS A MACROSTATE

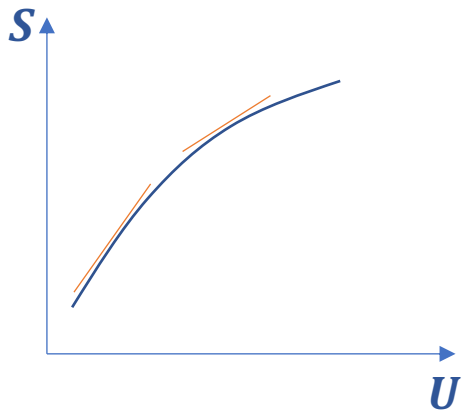
1. WHAT IS THE MULTIPLICITY OF A MACROSTATE?

2. WHAT IS THE ROLE OF ENTROPY?

3. WHAT IS THE CONDITION FOR EQUILIBRIUM?

# Isolated system at equilibrium

*U is fixed*  
 $S(U), T, P(V, T)$



Multiplicity of a macrostate  $\Omega(U, V, N)$  counts all **equally-likely** accessible microstates

However, if the particles are **indistinguishable** the total number of accessible microstates is reduced by the number of permutations  $N!$

$$\Omega(U, V, N) \rightarrow \frac{\Omega(U, V, N)}{N!}$$

Probability that the system is in a *specific microstate*

$$P(s) = \frac{1}{\Omega(U, V, N)}$$

Boltzmann's formula: Entropy of an equilibrium state at fixed U

$$S(U, V, N) = k \ln \Omega(U, V, N) \leftrightarrow S(U, V, N) = -k \sum_s P(s) \ln P(s)$$

Entropy is maximized for an equilibrium state  $dS = 0$

# THERMODYNAMIC PROPERTIES

*U is fixed*  
 $S(U), T, P(V, T)$

Thermodynamic identity for S

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

Temperature of an equilibrium state measures the tendency of the system to give or accept energy

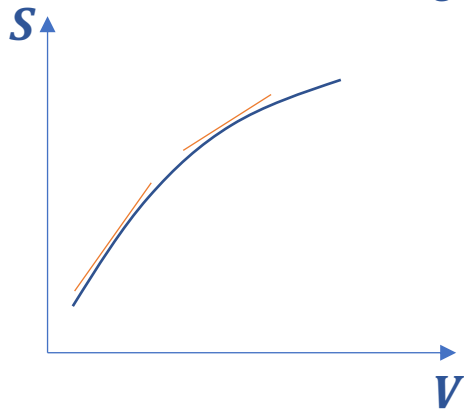
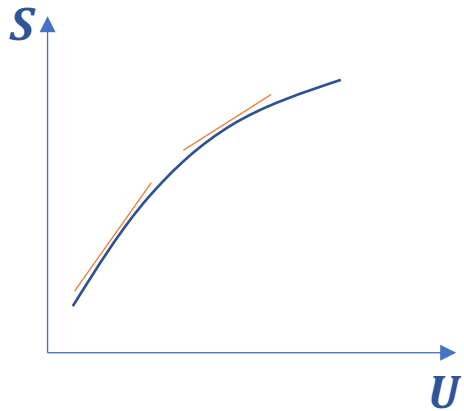
$$T = \left( \frac{\partial S}{\partial U} \right)^{-1}_{V,N}$$

Pressure is the measures the tendency of a system to expand or contract

$$P = T \left( \frac{\partial S}{\partial V} \right)_{U,N} \equiv - \left( \frac{\partial U}{\partial V} \right)_{S,N} \rightarrow P = P(V, T, N) \text{ equation of state}$$

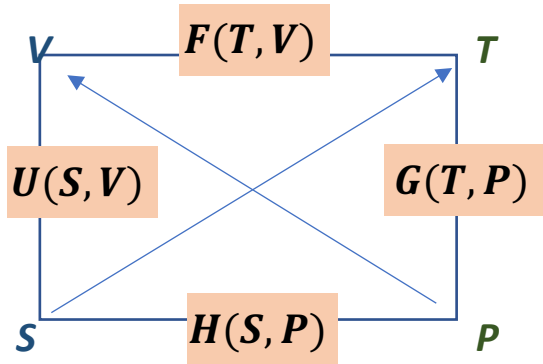
Chemical potential is the measures the tendency of a system to give or take particles

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



## THERMODYNAMIC PROPERTIES

*U is fixed*  
 $S(U), T, P(V, T)$



Helmholtz free energy

$$F = U - TS$$

Enthalpy

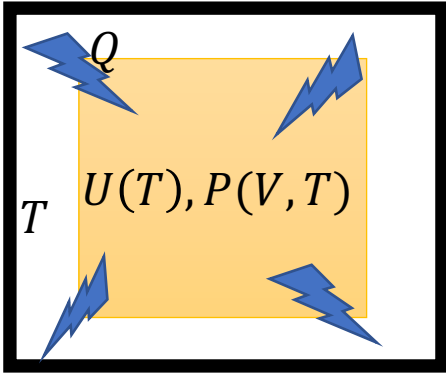
$$H = U + PV$$

Gibbs free energy

$$G = U - TS + PV = N\mu$$

*Chemical potential is the energy increase by adding a particle in to the system when the pressure and temperature are constant.*

$$\mu = \left( \frac{\partial G}{\partial N} \right)_{T,P}$$



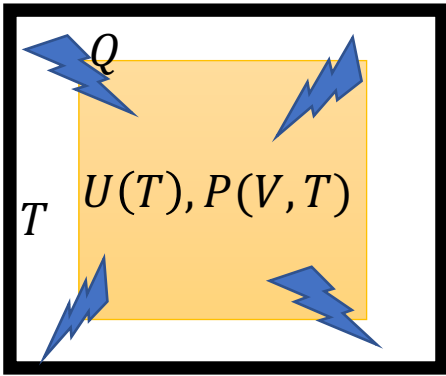
## A system in contact with a thermal bath

1. WHAT IS THE PARTITION FUNCTION?

2. WHAT ARE THE FLUCTUATING QUANTITIES?

3. WHAT IS THE EQUILIBRIUM CONDITION?

4. WHAT IS THE ROLE OF ENTROPY?



## A system in contact with a thermal bath

System+Thermal bath = isolated system

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

*Probability ratio between two microstates (the system can exchange energy with the thermal bath  $\Delta U_R = -\Delta E$ )*

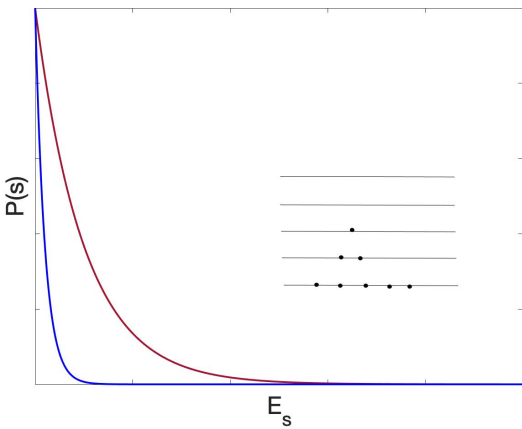
$$\frac{P(s_1)}{P(s_2)} = \frac{\Omega_R(s_1)}{\Omega_R(s_2)} = e^{\frac{[S_R(s_1)-S_R(s_2)]}{k}} = e^{\frac{[U_R(s_1)-U_R(s_2)]}{kT}} = e^{-\frac{[E(s_1)-E(s_2)]}{kT}}$$

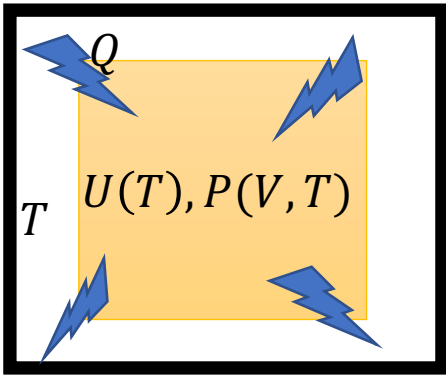
Probability of the system in a specific microstate a fixed temperature T

$$P(s) = \frac{1}{Z(T)} e^{-\frac{E_s}{kT}}$$

Boltzmann partition function

$Z(T) = \sum_s e^{-\frac{E_s}{kT}}$  counts all the accessible microstates weighted by the Boltzmann factor





## A system in contact with a thermal bath

$Z(T) = \sum_s e^{-\frac{E_s}{kT}}$  counts all the accessible microstates weighted by the Boltzmann factor

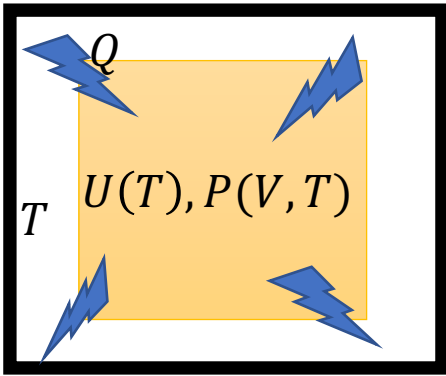
***N-distinguishable, identical and independent*** classical particles

$$Z_N(T, V) = \sum_{\{s_1, s_2 \dots s_N\}} e^{-\frac{E_N(s_1, \dots s_N)}{kT}} = Z_1^N(T, V)$$

***N-indistinguishable, identical and independent*** classical particles

$$\mathbf{Z}_N(T, V) = \sum_{\{s_1, s_2 \dots s_N\}} e^{-\frac{E_N(s_1, \dots s_N)}{kT}} = \frac{1}{N!} \mathbf{Z}_1^N(T, V)$$





# THERMODYNAMIC PROPERTIES AND AVERAGES

$$Z(\beta) = \sum_s e^{-\beta E_s}, \beta = \frac{1}{kT}$$

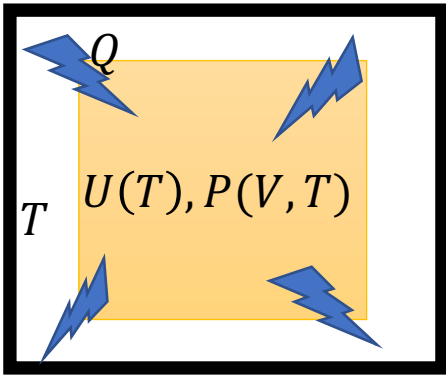
Due to energy exchange with the thermal bath, the energy fluctuations from one microstate to another. Thus, the total energy of an equilibrium macrostate is an average

$$U(T, V, N) = \langle E_s \rangle = \sum_s E_s e^{-\beta E_s} = -\frac{1}{Z} \left( \frac{\partial Z}{\partial \beta} \right)_{V, N} = - \left( \frac{\partial \ln Z}{\partial \beta} \right)_{V, N}$$

$$\langle E_s^2 \rangle = \sum_s E_s^2 e^{-\beta E_s} = \frac{1}{Z} \left( \frac{\partial^2 Z}{\partial \beta^2} \right)_{V, N}$$

*How entropy relates to the probability of a microstate*

$$S = -k \sum_s P(s) \ln P(s)$$



# HELMHOLTZ FREE ENERGY

$$Z(T, V, N) = \sum_s e^{-\beta E_s}, \beta = \frac{1}{kT}$$

*The partition function determines the thermodynamic potential which **minimized** at a given  $T$ ,  $V$  and  $N$ .*

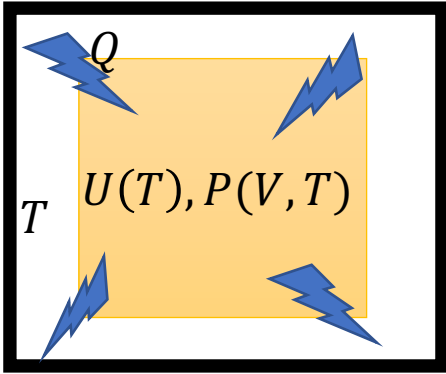
Helmholtz free energy

$$F(T, V, N) = -kT \ln Z(T, V, N) \leftrightarrow Z = e^{-\beta F}$$

Thermodynamic identity

$$dF = -S dT - PdV + \mu dN$$

## THERMODYNAMIC PROPERTIES



Thermodynamic identity

$$dF = -S dT - PdV + \mu dN$$

Entropy

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

Pressure

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \rightarrow P = P(V, T, N) \text{ equation of state}$$

Chemical potential

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

# Ideal gas in a thermal bath (High T-classical limit )

- Independent and indistinguishable quantum particles
- Quantum state of 1 particle is given by the quantized energy levels and the corresponding wavefunction (the energy is associated with a wavefunction rather than the particle itself!)

$$\epsilon_n = \frac{\vec{p} \cdot \vec{p}}{2m} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2), \quad \mathbf{n}_x, \mathbf{n}_y, \mathbf{n}_z = 0, 1, 2, \dots$$

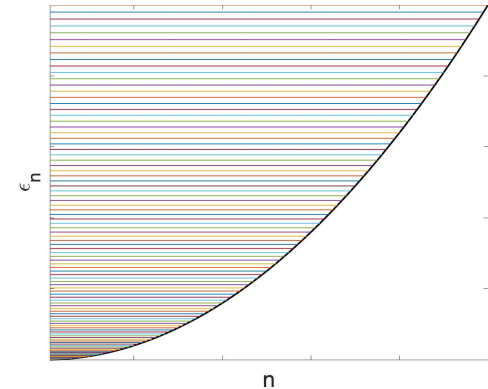
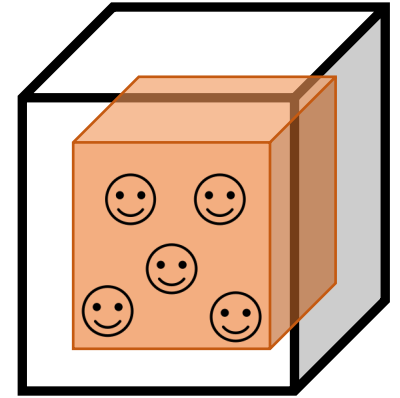
- One-particle partition function (3D)

$$Z_1(T, V) = \sum_{n_x} \sum_{n_y} \sum_{n_z} e^{-\beta \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2)},$$

$$Z_1(T, V) = \left( \sum_n e^{-\beta \frac{h^2}{8mL^2} n^2} \right)^3 \approx_{\substack{n \gg 1 \\ \text{high } T}} \frac{1}{2} \int_{-\infty}^{\infty} dn e^{-\beta \frac{h^2}{8mL^2} n^2} = \frac{V}{\Lambda^3(T)}, \quad \Lambda(T) = \sqrt{\frac{h}{2\pi mkT}} \text{ (quantum length)}$$

- N-particle partition function (3D)

$$Z_N(T, V) = \frac{1}{N!} \left( \frac{V}{\Lambda^3(T)} \right)^N$$



# Maxwell-Boltzmann distribution

- Probability that the particle in a state with velocity vector

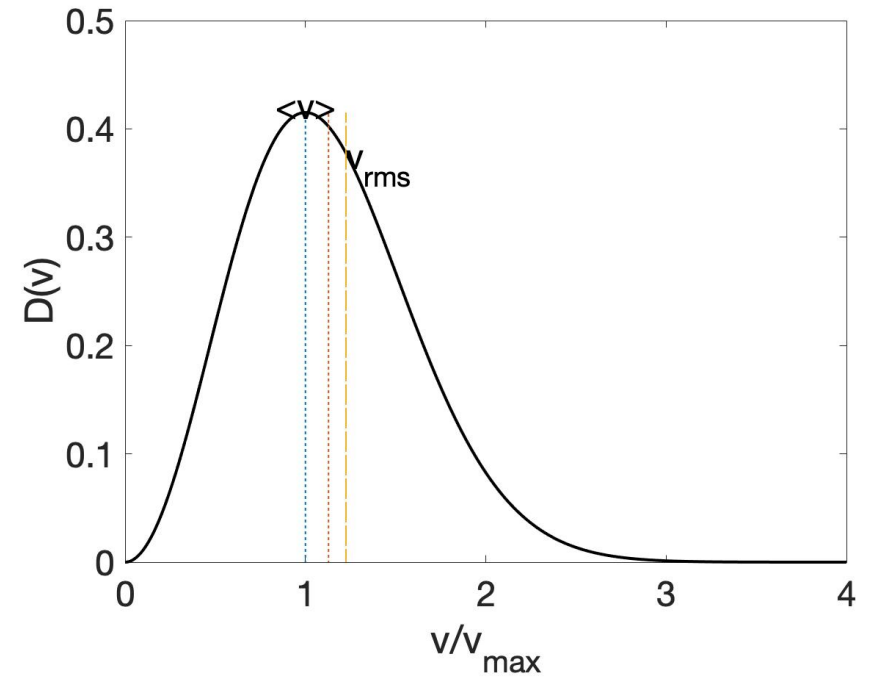
$$P_{3D}(\vec{V}) \sim e^{-\beta m \frac{\vec{V} \cdot \vec{V}}{2}}$$

- Probability that a particles has a *speed* between  $v$  and  $v + dv$  ( $v = |\vec{V}|$ )

$$D^{(3D)}(v)dv \sim P_{3D}(\vec{V})dV_x dV_y dV_z = e^{-\beta m \frac{v^2}{2}} 4\pi v^2 dv$$

$$\int_0^\infty dv D^{(3D)}(v) = 1$$

$$D^{(3D)}(v) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} 4\pi v^2 e^{-\frac{m}{2kT} v^2}$$



# N-free particles in a thermal bath

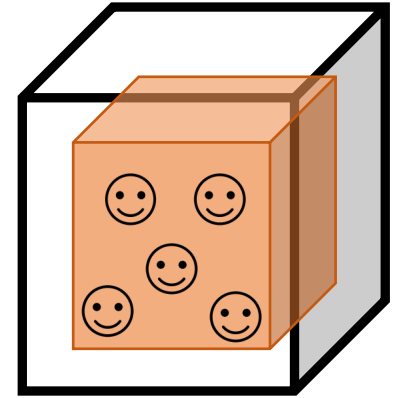
- N-particle partition function

$$Z_N(T, V) = \frac{Z_1^N}{N!} = \frac{1}{N!} \left( \frac{V}{\Lambda^3(T)} \right)^N$$

- Helmholtz free energy

$$F_N(T, V) = -kT \ln Z_N(T, V) = -NkT \left[ \ln \left( \frac{Z_1}{N} \right) - 1 \right]$$

$$F_N(T, V) = -NkT \left[ \ln \left( \frac{V}{N\Lambda^3(T)} \right) - 1 \right]$$



# N-free particles in a thermal bath

- N-particle partition function

$$Z_N(T, V) = \frac{Z_1^N}{N!} = \frac{1}{N!} \left( \frac{V}{\Lambda^3(T)} \right)^N, \quad \Lambda(T) = \sqrt{\frac{h^2}{2\pi m k T}}$$

- Energy

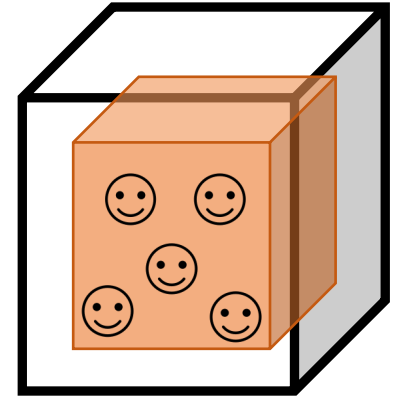
$$U = -\frac{\partial}{\partial \beta} \ln Z_N(T, V) = 3N \frac{d}{d\beta} \ln \Lambda(\beta) = \frac{3N}{2} kT$$

- Entropy

$$S = \frac{U - F}{T} = \frac{3Nk}{2} + Nk + Nk \left[ \ln \left( \frac{V}{N\Lambda^3(T)} \right) \right] = Nk \left[ \ln \left( \frac{V}{N\Lambda^3(T)} \right) + \frac{5}{2} \right]$$

- Equation of state

$$P = - \left( \frac{\partial F}{\partial V} \right)_{T, N} = \frac{kT}{V}$$



# N-free particles in a thermal bath

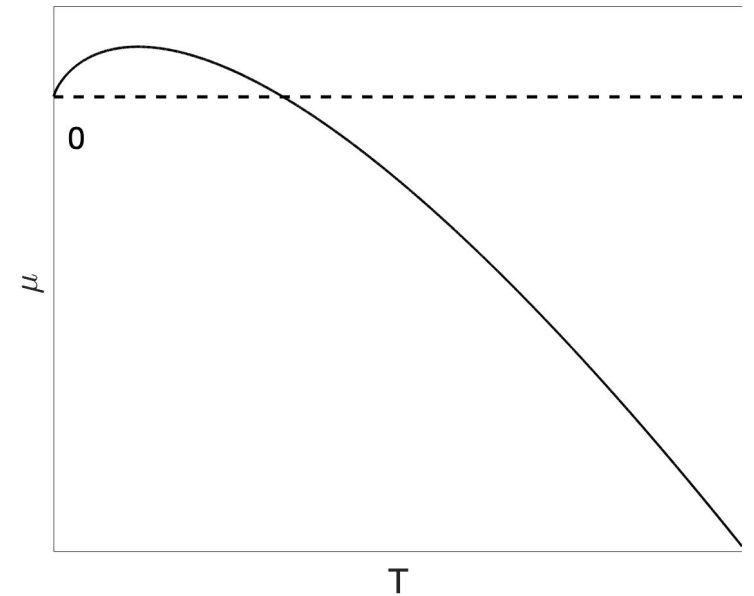
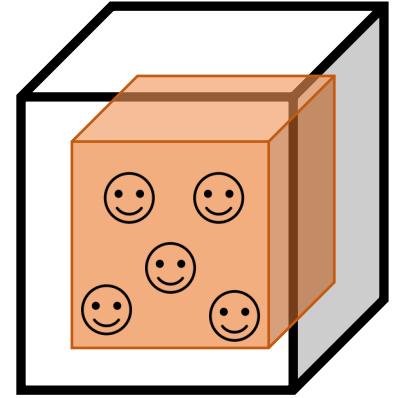
- Helmholtz free energy

$$F_N(T, V) = -NkT \left[ \ln \left( \frac{V}{N\Lambda^3(T)} \right) - 1 \right]$$

- Chemical potential

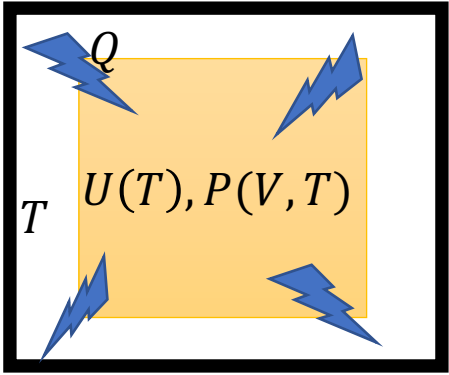
$$\mu(T, V) = \left( \frac{\partial F}{\partial N} \right)_{T, V} = -kT \ln \left( \frac{V}{N\Lambda^3(T)} \right)$$

$$Z_1 = \frac{V}{\Lambda^3(T)} = N e^{-\beta\mu}$$





## Ideal gas in contact with a thermal bath

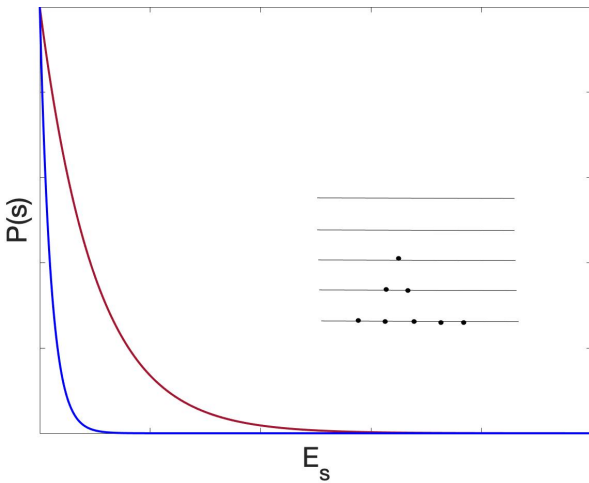


Probability of one particle to be in a in a specific energy state a fixed temperature  $T$

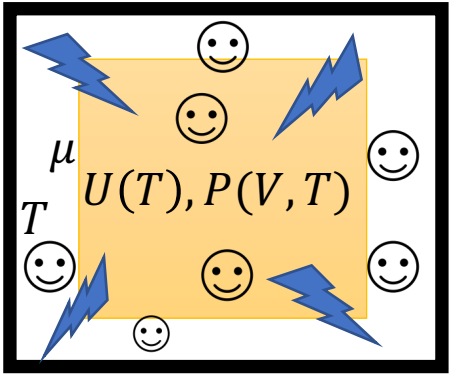
$$P(s) = \frac{1}{Z_1(T)} e^{-\beta E_s}$$

Boltzmann distribution for the average number of particles (occupation number) in a given energy state

$$\langle N_s \rangle = NP(s) = e^{-\beta(E_s - \mu)}$$



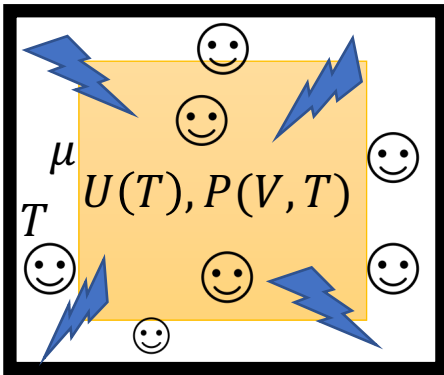
## A system in contact with a thermal and particle reservoir



**WHAT IS THE GIBBS FACTOR?**

**WHAT QUANTITIES FLUCTUATES?**

**WHAT IS THE EQUILIBRIUM CONDITION?**



## 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  $\Delta N_R = -\Delta N$ )*

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

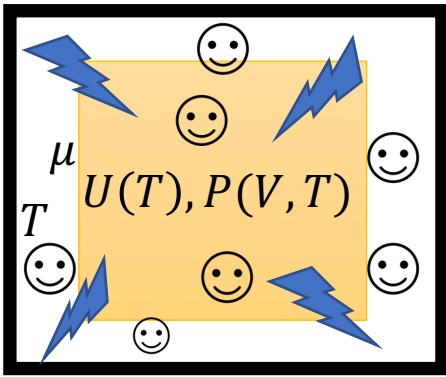
Probability of the system in a specific microstate a fixed  $T$  and  $\mu$

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

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

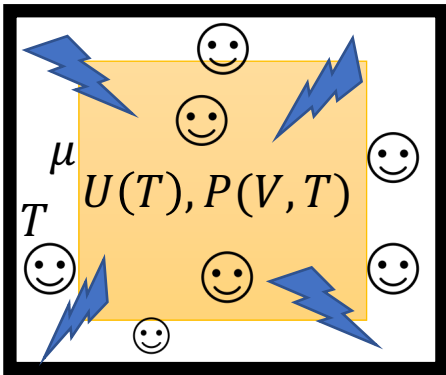
For  $N$  identical particles, we can have  $N_j$  number of particles (occupation number) in the energy state  $\epsilon_j$

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  $\mu$

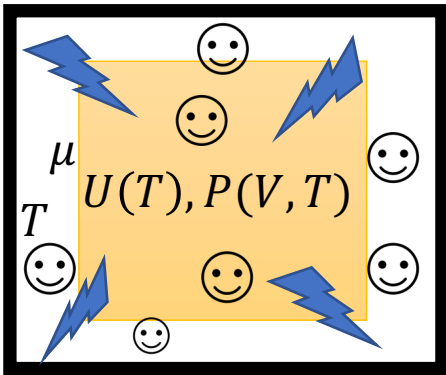
$$P(s) = \frac{1}{\Xi(T, \mu)} e^{-\beta(E_s - \mu N_s)} = \frac{e^{-\beta N_1(\epsilon_1 - \mu)} \cdot e^{-\beta N_2(\epsilon_2 - \mu)} \cdot e^{-\beta N_3(\epsilon_3 - \mu)} \dots}{\left(\sum_{N_1} e^{-\beta N_1(\epsilon_1 - \mu)}\right) \cdot \left(\sum_{N_2} e^{-\beta N_2(\epsilon_2 - \mu)}\right)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

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

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

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

$$P(N) = \frac{e^{-\beta N(\epsilon - \mu)}}{\left(\sum_N e^{-\beta N(\epsilon - \mu)}\right)}$$



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

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

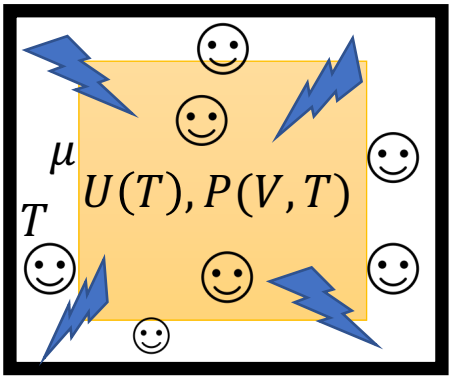
Probability for the occupation number  $N$  of the given energy state a fixed  $T$  and  $\mu$

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

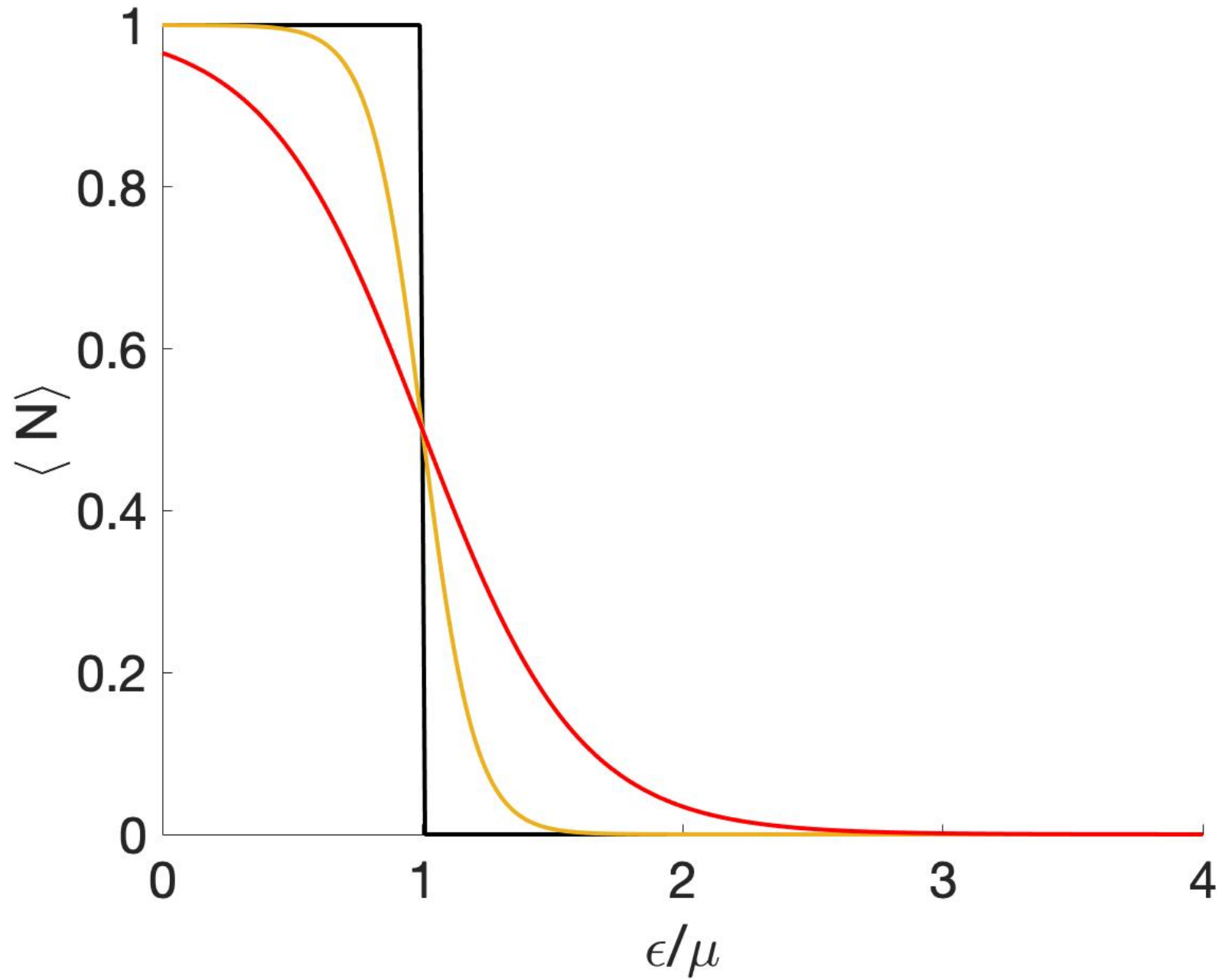
Average occupation number  $\langle N \rangle$  of the given energy state  $\epsilon$  a fixed  $T$  and  $\mu$

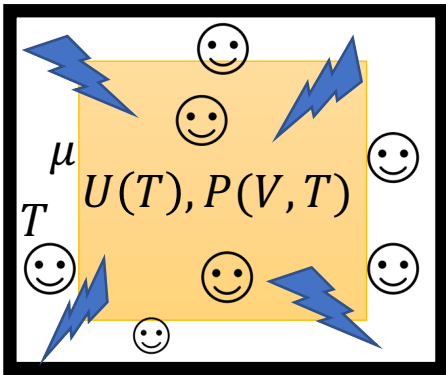
**FERMI-DIRAC distribution**

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



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  $\mu$

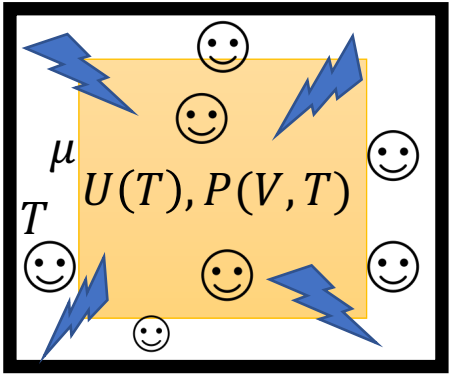
$$P(N) = (1 - e^{-\beta(\epsilon - \mu)}) e^{-\beta N(\epsilon - \mu)}$$

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

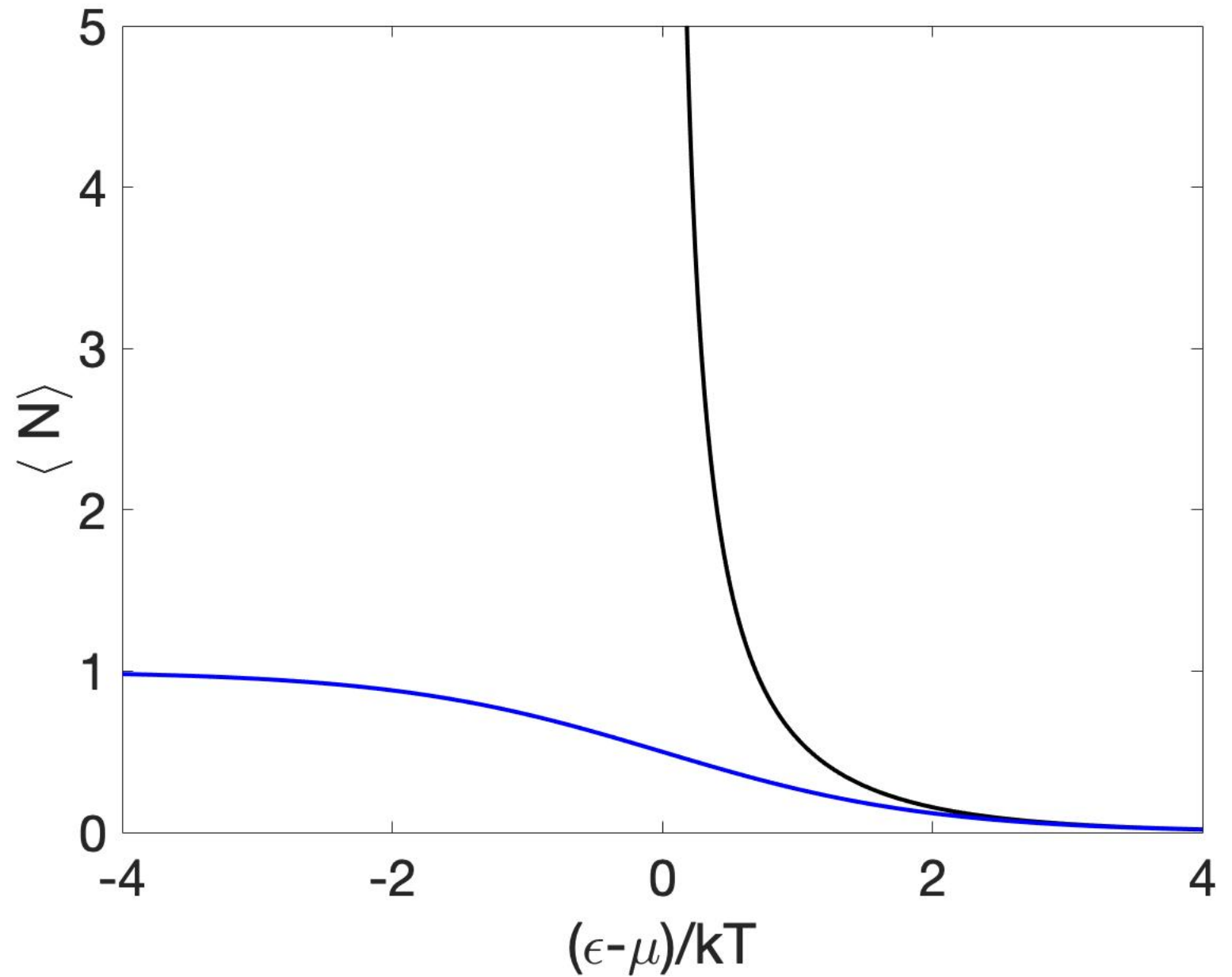
### BOSE-EINSTEIN distribution

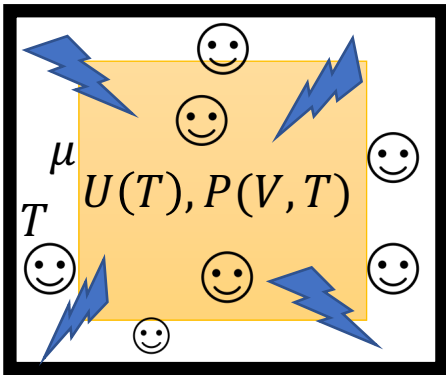
$$\langle N \rangle(\epsilon) = \sum_{N=0}^{\infty} N P(N) = (1 - e^{-\beta(\epsilon - \mu)}) \sum_{N=0}^{\infty} N e^{-\beta N(\epsilon - \mu)} \rightarrow \langle N \rangle(\epsilon) = \frac{1}{e^{\beta(\epsilon - \mu)} - 1}$$





**Bose Einstein distribution**





## Classical limit

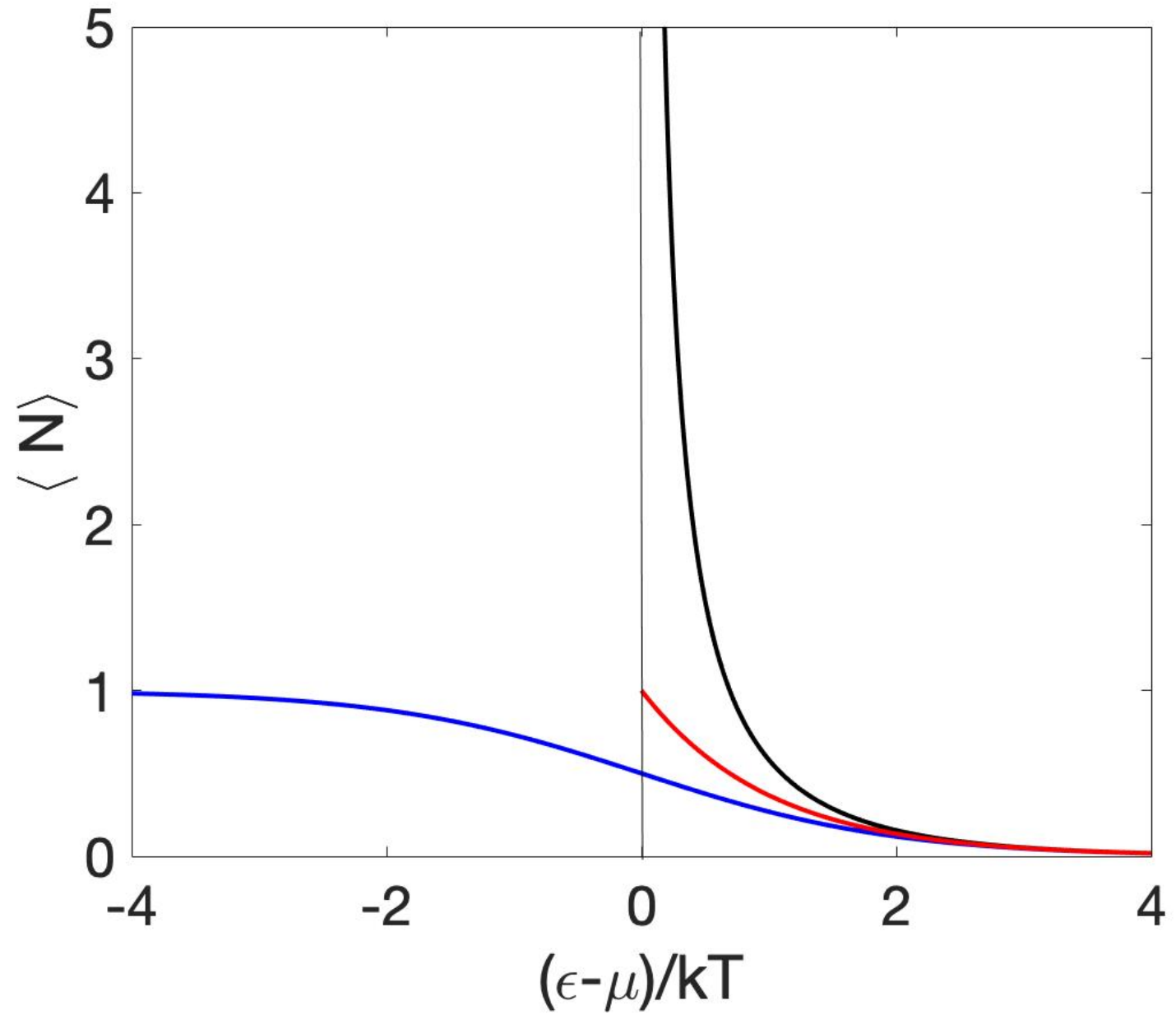
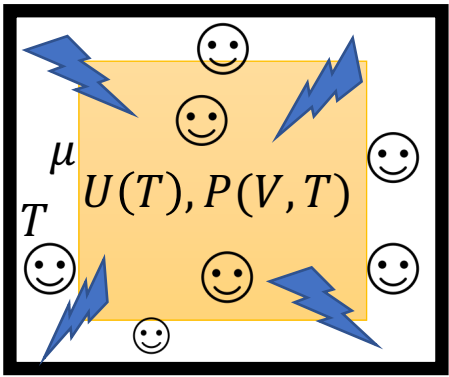
QUANTUM distribution for the average occupation number of an energy state

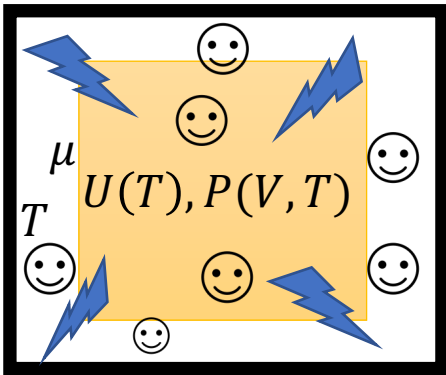
$$\langle N \rangle(\epsilon) = \frac{1}{e^{\beta(\epsilon - \mu)} \pm 1}$$

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

**BOLZMANN distribution**

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





## THERMODYNAMIC PROPERTIES AND DENSITY OF STATES

### Average energy

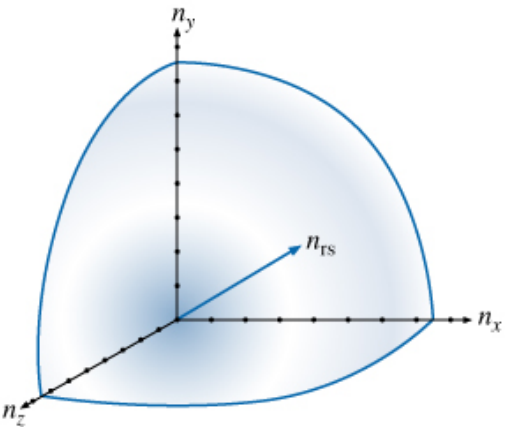
$$U = \sum_{n_x} \sum_{n_y} \sum_{n_z} \langle N \rangle(\epsilon) \cdot \epsilon(n_x, n_y, n_z) = \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z \epsilon \cdot \langle N \rangle = \int_0^\infty d\epsilon \, g(\epsilon) \epsilon \cdot \langle N \rangle$$

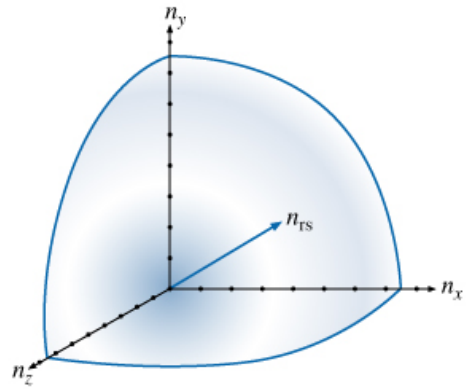
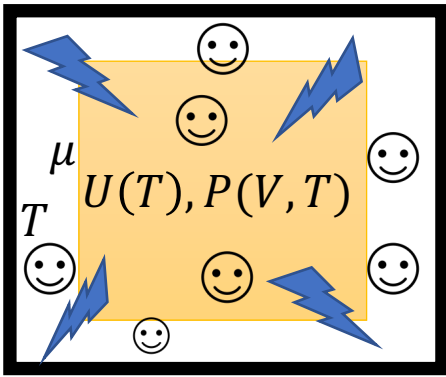
- Density of states  $g(\epsilon)$  comes because we need to count all the quantum states at a given energy  $\epsilon$ . Remember that the quantum state is given by the state of the wavefunction
- Number of states with energy between  $\epsilon$  and  $\epsilon + d\epsilon \equiv$  Number of states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

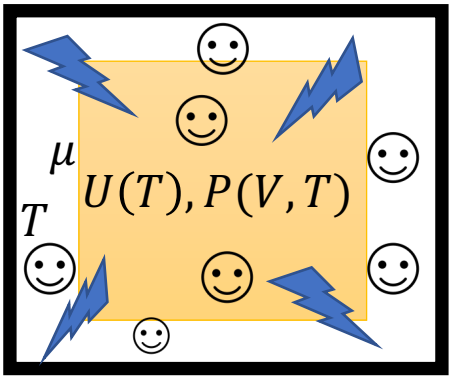
$$(3D) g(\epsilon)d\epsilon = 2 \times \frac{\pi}{2}n^2dn, \quad (2D)g(\epsilon)d\epsilon = 2 \times \frac{\pi}{2}ndn, (2D), \quad (1D)g(\epsilon)d\epsilon = 2 \times dn$$

**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

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



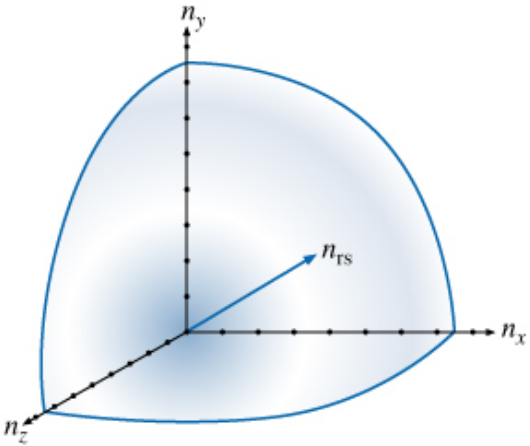
## Thermodynamic properties and **density of states**

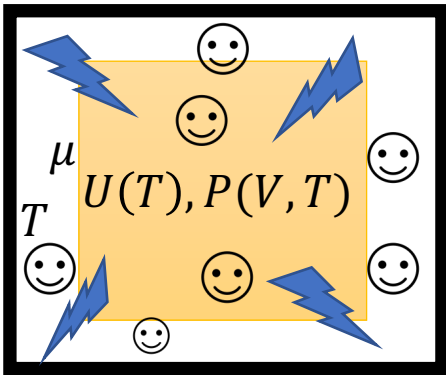
**Average energy**

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

**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

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

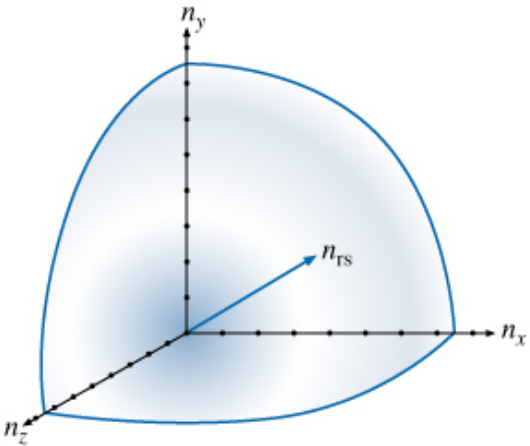
$$\epsilon_F(N) = \frac{h^2}{8mL^2} n_{max}^2 = \frac{h^2}{8mL^2} \left( \frac{N}{2} \right)^2$$

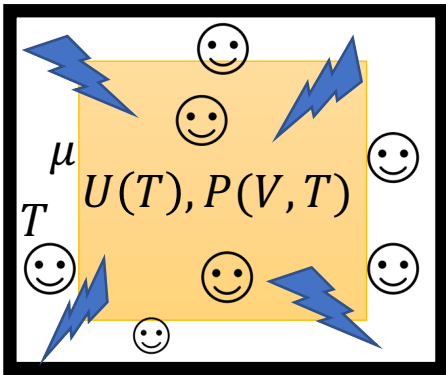
**Average energy**

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

**Average number of particles**

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





## Photons

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

### Average energy

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

### Average number of particles

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

