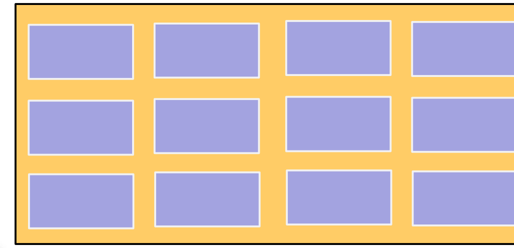
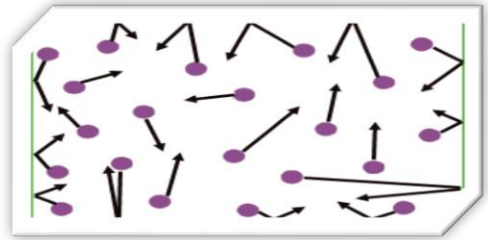
Statistical Thermodynamics

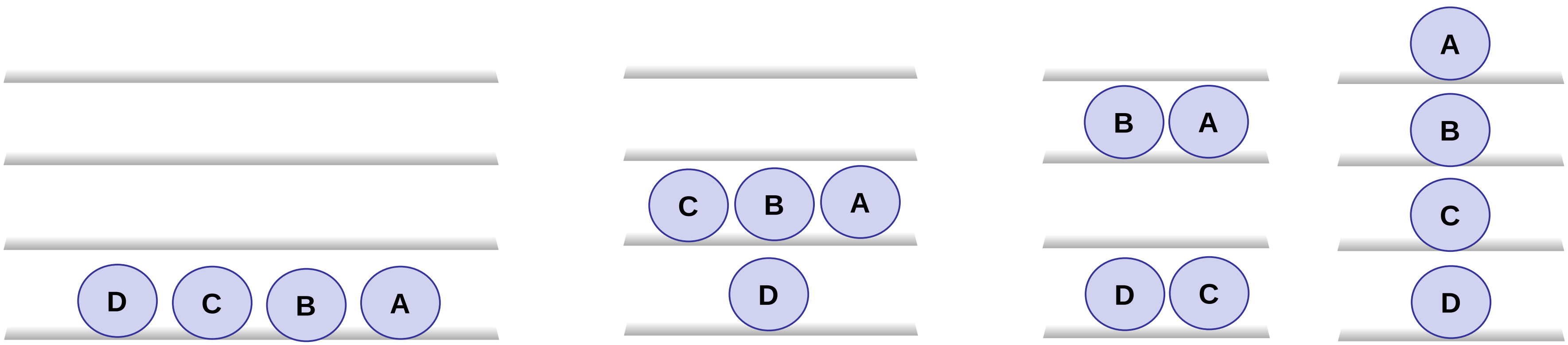
Can we start with "microscopic" knowledge and learn something about bulk properties of matter such as temperature?



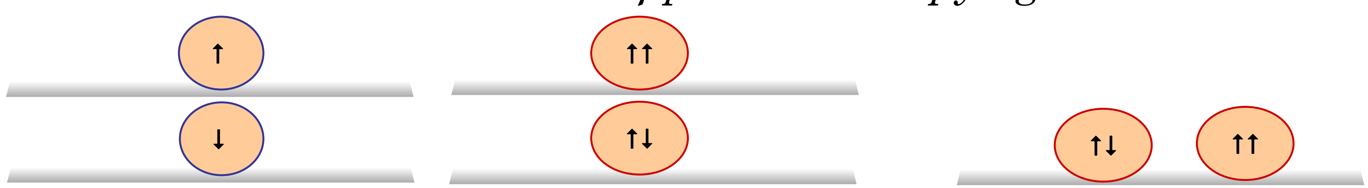
- *Particles have identical physical properties…but can be distinguished by following their (well defined) classical paths?*



- *In equilibrium, the energy distribution of the particles will converge to the most probable allowed.*



☞ *In principle, there is no limit on the number of particles occupying each state.*

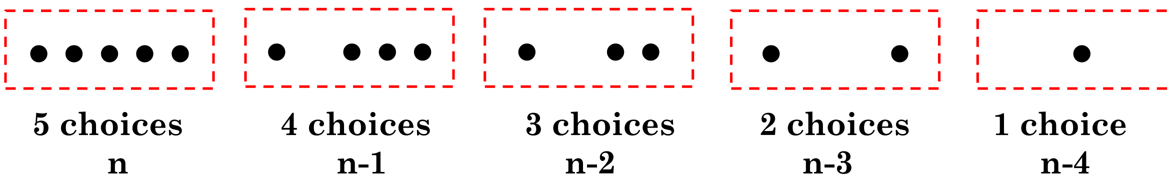


Will the peculiar rules governing the behavior of an individual particle or small group of particles (such as the Pauli principle) influence the properties of the matter they compose?

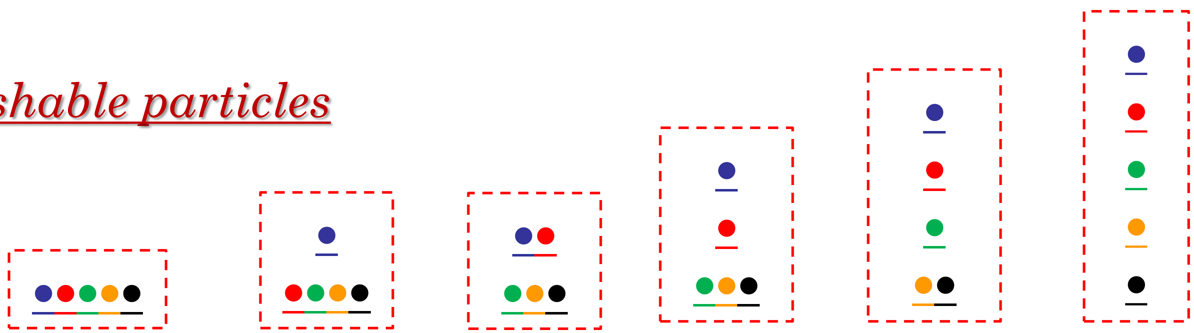
Counting the number of "permutations"

If you are making choices from n objects, then on your first pick you have n choices. On your second pick, you have (n-1) choices, (n-2) for your third choice and so forth. As illustrated for 5 objects, the number of ways to pick from 5 objects is 5!

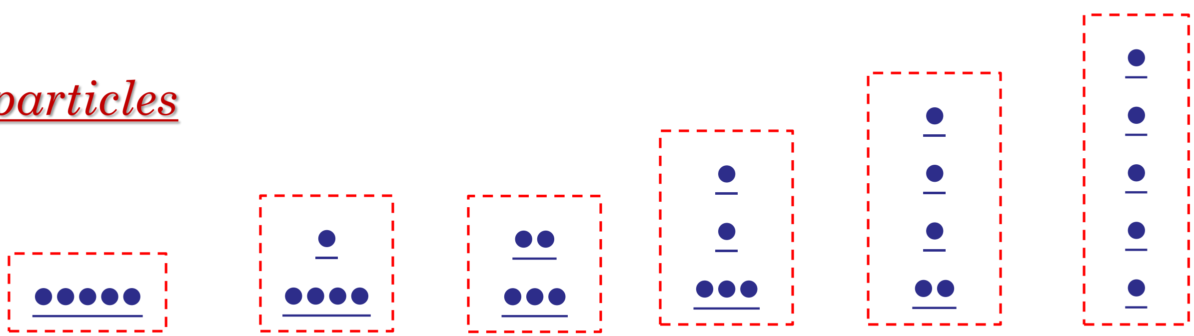
Number of permutations of 5 objects is 5!



Distinguishable particles

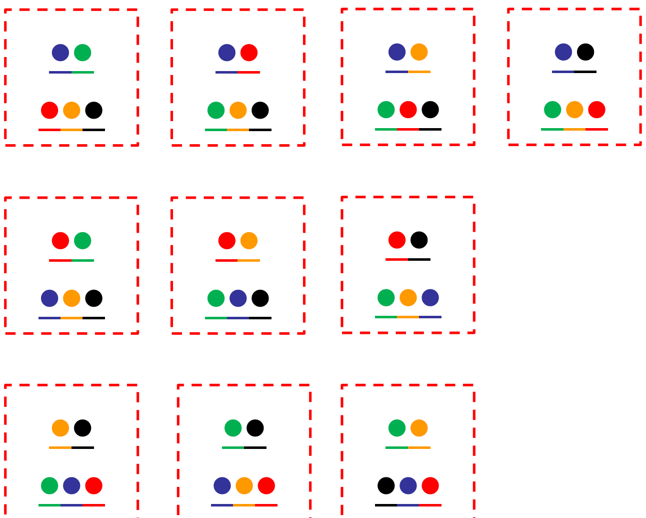


Identical particles



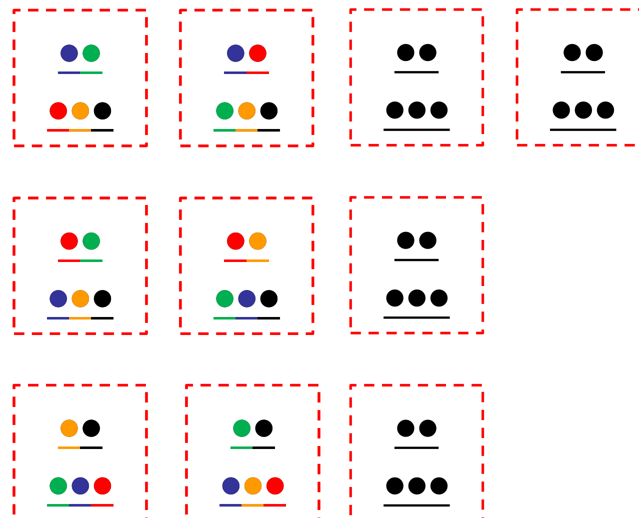
Distinguishable particles

Number of particles = 5
Energy states = 2
Total arrangements
i.e. $\frac{5!}{3!2!} = 10$



Indistinguishable / Identical particles

Interchange of particle doesn't produces a new state



Counting the distinguishable states

$$\frac{6!}{5!\,1!} = 6 \qquad \frac{6!}{3!\,2!\,1!} = 60 \qquad \frac{6!}{2!\,2!\,1!\,1!} = 180 \qquad \frac{6!}{2!\,1!\,1!\,1!\,1!} = 360 \qquad \frac{6!}{1!\,1!\,1!\,1!\,1!\,1!} = 720$$

$$\textit{Number of microstates} = \frac{N!}{n_1!n_2!n_3!......n_i!}$$

N= *Total number of particles and*
n_i = *number of particles in level i*

$$W = \frac{N!}{\prod_{i=1}^{i} n_i!}$$

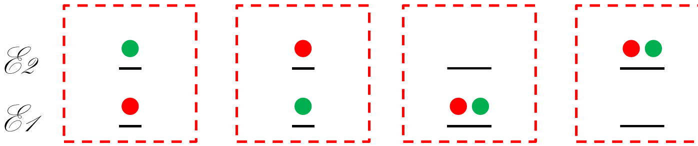
- *If each of these "microstates" is equally likely (and we assumed that we will converge on the most probable), which means that nature doesn't favor the situation where one particle has all of the energy.*
- We assume that each "microstate" (unique permutation) is equally probable.

Classical Statistics:

- *Particles are distinguishable*

Maxwell-Boltzmann Statistics:

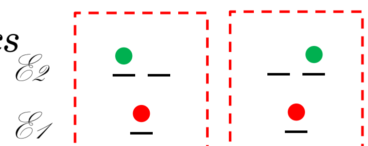
- *Any number of particle in any state*



$$W = \frac{N!}{\prod_{i=1}^{i} n_i!}$$

- *We get 4 states of the above system as whole. Half of the states have particles in the same states and half of them in separate states.*
- *Particles with distinguishable states are known as 'Maxwellons/Boltzons'.*
- *If i^{th} state has degeneracy g_i, then there will be an additional $g_i^{n_i}$ ways of distributing these N particles.*
- *Boltzmann statistics*

$$\boxed{W = \prod_{i=1}^{i} \frac{g_i^{n_i}}{n_i!}}$$



- *M-B statistics*

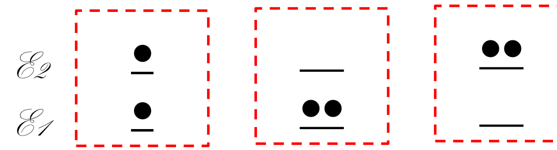
$$\boxed{W = N!\prod_{i=1}^{i} \frac{g_i^{n_i}}{n_i!}}$$

Quantum Statistics

- *Particles are indistinguishable*

1. Bose-Einstein Statistics

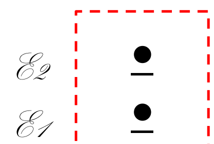
- *Any number of particle can be in one state*



- *We get 3 states of the above system as whole. 2/3 the states have particles in the same states and 1/3 of them in separate states.*
- *Particles with integer spin 0, 1, 2 etc. shows such statistics and known as 'Bosons'*
- *Do not obey the Pauli principle*

2. Fermi-Dirac Statistics

- *No more than one particle can be in one state.*



- *We get 'one' state of the system as whole with particles in separate states and known as 'Fermions'*
- *'Fermions' : Particles with half-spins obey the Pauli principle*

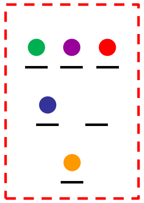
Bosons → wave-functions - Symmetric
Fermions → wave-function - Antisymmetric

Maxwell-Boltzmann Statistics:

$\mathcal{E}_3$

$\mathcal{E}_2$

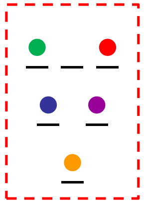
$\mathcal{E}_1$



$$W_{MB} = 5!\left(\frac{3^3.2^1.1^1}{3!\quad 1!\quad 1!}\right)$$

$$W_{MB} = 120\left(\frac{27\times 2\times 1}{3\times 2\times 1\times 1\times 1}\right)$$

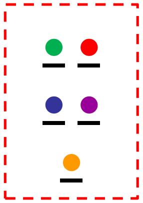
$$W_{MB} = 1080$$



$$W_{MB} = 5!\left(\frac{3^2.2^2.1^1}{2!\quad 2!\quad 1!}\right)$$

$$W_{MB} = 120\left(\frac{9\times 4\times 1}{2\times 1\times 2\times 1\times 1}\right)$$

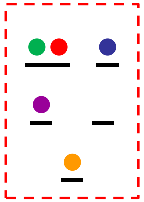
$$W_{MB} = 1080$$



$$W_{MB} = 5!\left(\frac{2^2.2^2.1^1}{2!\quad 2!\quad 1!}\right)$$

$$W_{MB} = 120\left(\frac{4\times 4\times 1}{2\times 1\times 2\times 1\times 1}\right)$$

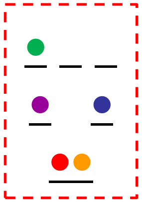
$$W_{MB} = 480$$



$$W_{MB} = 5!\left(\frac{2^3.2^1.1^1}{3!\quad 1!\quad 1!}\right)$$

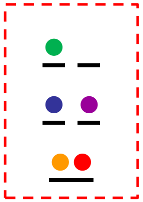
$$W_{MB} = 120\left(\frac{8\times 2\times 1}{3\times 2\times 1\times 1\times 1}\right)$$

$$W_{MB} = 320$$



$$W_{MB} = 5!\left(\frac{3^1.2^2.1^2}{1!\quad 2!\quad 2!}\right)$$

$$W_{MB} = 360$$



$$W_{MB} = 5!\left(\frac{2^1.2^2.1^2}{1!\quad 2!\quad 2!}\right)$$

$$W_{MB} = 240$$

Probability distribution W and the entropy are expressed by the relation:

$$\boxed{S = k \ln W}$$

The probability distribution must be 'maximum' for an equilibrium state,

$$\boxed{S = k \ln W_{max}}$$

For a closed system:

ε_i	n_i	$n_i\varepsilon_i$
$\vdots$		$\vdots$
ε_2	n_2	$n_2\varepsilon_2$
ε_1	n_1	$n_1\varepsilon_1$

Total number of particles are constant, i.e.

$$\boxed{\sum_i n_i = N} \dashrightarrow \boxed{\sum_i dn_i = dN = 0}$$

Total Energy E of the system is constant, i.e.

$$\boxed{\sum_i n_i\varepsilon_i = E} \dashrightarrow \boxed{\sum_i \varepsilon_i dn_i = dE = 0}$$

Probability distribution

$$W = N!\prod_{i=1}^{i}\frac{g_i^{n_i}}{n_i!}$$

Taking logarithm on both the side, we get

$$\ln W = \ln\left(N!\prod_{i=1}^{i}\frac{g_i^{n_i}}{n_i!}\right)$$

$$\ln W = \ln N! + \sum_i n_i \ln g_i - \sum_i \ln n_i!$$

…by applying Stirling approximation

$$\ln W = N\ln N - N + \sum_i n_i \ln g_i - \sum_i (n_i \ln n_i - n_i)$$

$$\ln W = N\ln N + \sum_i n_i \ln g_i - \sum_i n_i \ln n_i$$

…differentiating equation results in (N and g_i are constant):

$$d\ln W = \sum_i n_i\,(d\ln g_i) + \sum_i \ln g_i\,(dn_i) - \sum_i n_i\,(d\ln n_i) - \sum_i \ln n_i\,(dn_i)$$

$$d\ln W = \sum_i \ln g_i\,(dn_i) - \sum_i n_i\,(d\ln n_i) - \sum_i \ln n_i\,(dn_i)$$

$$\sum_i n_i\,(d\ln n_i) = \sum_i n_i \frac{dn_i}{n_i} = 0$$

$$d\ln W = \sum_i \ln g_i\,(dn_i) - \sum_i \ln n_i\,(dn_i)$$

$$d\ln W = \sum_i \ln\frac{g_i}{n_i}(dn_i)$$

At equilibrium…

$$\sum_i \ln\frac{g_i}{n_i}(dn_i) = 0$$

In order to determine most probable state i.e. maximum probability, using **Lagrangian** *undetermined multipliers…..*

$$\sum_i dn_i = dN = 0$$ … *multiply with α* $$\alpha \sum_i dn_i = 0 \quad ....(1)$$

$$\sum_i \varepsilon_i dn_i = dE = 0$$ … *multiply with β* $$\beta \sum_i \varepsilon_i dn_i = 0 \quad ....(2)$$

Subtract equation (1) and (2) from the equation………. $$\sum_i ln \frac{g_i}{n_i}(dn_i) = 0$$

We get…

$$\sum_i ln \frac{g_i}{n_i}(dn_i) - \alpha \sum_i dn_i - \beta \sum_i \varepsilon_i dn_i = 0$$

$$\sum_i \left[ln\left(\frac{g_i}{n_i}\right) - \alpha - \beta\varepsilon_i \right](dn_i) = 0$$

We choose α and β such that…

$$\left[ln\left(\frac{g_i}{n_i}\right) - \alpha - \beta\varepsilon_i \right] = 0$$

$$ln\, g_i - \alpha - \beta\varepsilon_i = ln\, n_i \longrightarrow n_i = g_i e^{-\alpha-\beta\varepsilon_i}$$

$$\frac{n_i}{g_i} = \frac{1}{e^{\alpha+\beta\varepsilon_i}}$$

Eq. is known as M-B distribution function of particles among cells in phase space at equilibrium.

Bose-Einstein Statistics

- *Consider an array of n_i particles and $(g_i - 1)$ partitions needed to divide them into g_i groups. The number of ways of permuting n_i particles among g_i levels equals the number of ways of permuting objects and partitions. i.e. $(n_i + g_i - 1)!$.*

- *Now the particles are indistinguishable, the number of ways of permuting them is_*

$$W_{BE} = \prod_{i=1}^{N} \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}$$

Taking logarithm on both the side, we get

$$\boxed{ln\,W = ln\left(\prod_{i=1}^{N} \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}\right)}$$

$$\boxed{ln\,W = ln\left(\prod_{i=1}^{N} \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}\right)}$$

$$\boxed{ln\,W = \sum_i ln(n_i + g_i - 1)! - \sum_i ln\,n_i! - \sum_i ln(g_i - 1)!}$$

...by applying Stirling approximation

$$\boxed{ln\,W = \sum_i \left[(n_i + g_i)\,ln\,(n_i + g_i) - (n_i + g_i) - (n_i\,ln\,n_i - n_i) - (g_i\,ln\,g_i - g_i)\right]}$$

$$(n_i + g_i - 1) = (n_i + g_i) \text{ and } (g_i - 1) = (g_i)$$

...differentiating w.r.t. n_i ... equation results in (N and g_i are constant):

$$\boxed{d\,ln\,W = \sum_i \left[(n_i + g_i)\frac{1}{(n_i + g_i)}(dn_i) + (dn_i)\,ln\,(n_i + g_i) - n_i\,(d\,ln\,n_i) - (dn_i)\,ln\,n_i\right]}$$

$$\boxed{d\,ln\,W = \sum_i (dn_i)\,ln\,\frac{n_i + g_i}{n_i}}$$

At equilibrium...for most probable distribution

$$\boxed{\sum_i (dn_i)\,ln\,\frac{n_i + g_i}{n_i} = 0}$$

In order to determine most probable state i.e. maximum probability, using **Lagrangian** *undetermined multipliers.....*

$$\sum_i dn_i = dN = 0$$ *... multiply with α* $$\alpha \sum_i dn_i = 0 \quad ....(1)$$

$$\sum_i \varepsilon_i dn_i = dE = 0$$ *... multiply with β* $$\beta \sum_i \varepsilon_i dn_i = 0 \quad ....(2)$$

Subtract equation (1) and (2) from the equation..........

$$\sum_i (dn_i) \ln \frac{n_i + g_i}{n_i} = 0$$

We get...

$$\sum_i \ln\left(\frac{n_i + g_i}{n_i}\right)(dn_i) - \alpha \sum_i dn_i - \beta \sum_i \varepsilon_i dn_i = 0$$

$$\sum_i \left[\ln\left(\frac{n_i + g_i}{n_i}\right) - \alpha - \beta\varepsilon_i\right](dn_i) = 0$$

$$\left[\ln\left(\frac{n_i + g_i}{n_i}\right) - \alpha - \beta\varepsilon_i\right] = 0$$

$$\alpha + \beta\varepsilon_i = \ln\left(1 + \frac{g_i}{n_i}\right)$$

$$e^{(\alpha + \beta\varepsilon_i)} = \left(1 + \frac{g_i}{n_i}\right) \longrightarrow e^{(\alpha + \beta\varepsilon_i)} - 1 = \frac{g_i}{n_i}$$

$$\frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta\varepsilon_i} - 1}$$

Eq. is known as B-E distribution function of particles among cells in phase space at equilibrium.

Fermi-Dirac Statistics

- *Consider an array of n_i particles to distribute them into g_i states. The number of ways of permuting n_i particles among g_i states is equals the number of ways of permuting objects i.e. $g_i!/(g_i - n_i)!$.*

- *Now the particles are indistinguishable, the number of ways of permuting them is_*

$$W_{FD} = \prod_{i=1}^{N} \frac{g_i!}{n_i!(g_i - n_i)!}$$

Taking logarithm on both the side, …by applying Stirling approximation & …differentiating w.r.t. n_i … equation results in (N and g_i are constant):

$$d\ln W = \sum_i (dn_i) \ln\left(\frac{g_i - n_i}{n_i}\right)$$

At equilibrium…for most probable distribution

$$\sum_i (dn_i) \ln\left(\frac{g_i - n_i}{n_i}\right) = 0$$

In order to determine most probable state i.e. maximum probability, using **Lagrangian** *undetermined multipliers…..*

$$\sum_i \ln\left(\frac{g_i - n_i}{n_i}\right)(dn_i) - \alpha \sum_i dn_i - \beta \sum_i \varepsilon_i dn_i = 0$$

$$\left[\ln\left(\frac{g_i - n_i}{n_i}\right) - \alpha - \beta\varepsilon_i\right] = 0$$

$$\alpha + \beta\varepsilon_i = \ln\left(\frac{g_i}{n_i} - 1\right) \longrightarrow e^{(\alpha + \beta\varepsilon_i)} = \left(\frac{g_i}{n_i} - 1\right)$$

$$\frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta\varepsilon_i} + 1}$$

Eq. is known as F-D distribution function of particles among cells in phase space at equilibrium.

The distribution of energy

We assume that each "microstate" (unique permutation) is equally probable and exists.

To find the average number of particles in each state

$$\bar{n}_j = n_{j_1} p_1 + n_{j_2} p_2 + \ldots$$

Average number of particles in the jth energy level

count the number of particles in each state for this distribution

multiply by the number of permutations that can produce this distribution divided by the total number of permutation for all distributions

Maxwell-Boltzmann Statistics

$$\frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta\varepsilon_i}} \rightarrow n_i = \frac{g_i}{e^{\alpha} e^{\beta\varepsilon_i}} = \frac{1}{Ae^{\beta\varepsilon_i}} = \frac{1}{Ae^{\varepsilon_i / kT}}$$

Bose-Einstein Statistics

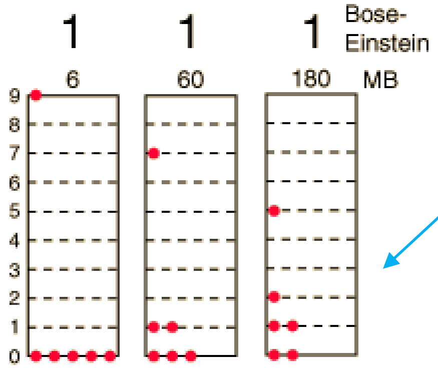
$$\frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta\varepsilon_i} - 1} \rightarrow n_i = \frac{1}{Ae^{\varepsilon_i / kT} - 1}$$

Fermi-Dirac Statistics

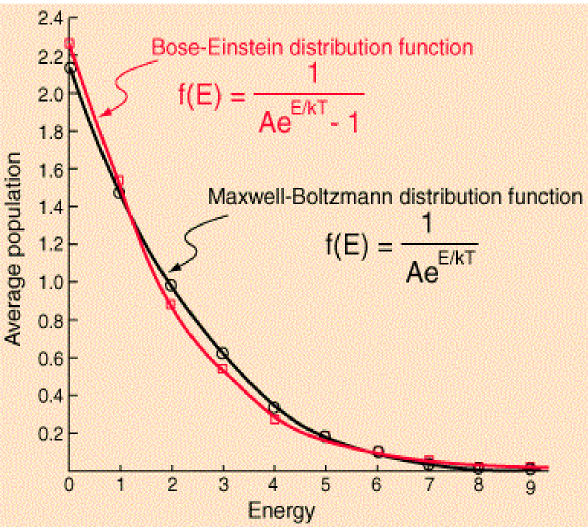
$$\frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta\varepsilon_i} + 1} \rightarrow \frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta\varepsilon_i} + 1}$$

Maxwell-Boltzmann statistics Vs. Bose-Einstein statistics

There are 26 possible distributions of 9 units of energy among 6 particles, and if those particles are indistinguishable and described by Bose-Einstein statistics, all of the distributions have equal probability. To get a distribution function of the number of particles as a function of energy, the average population of each energy state must be taken. The average for each of the 9 states is shown below compared to the result obtained by Maxwell-Boltzmann statistics.



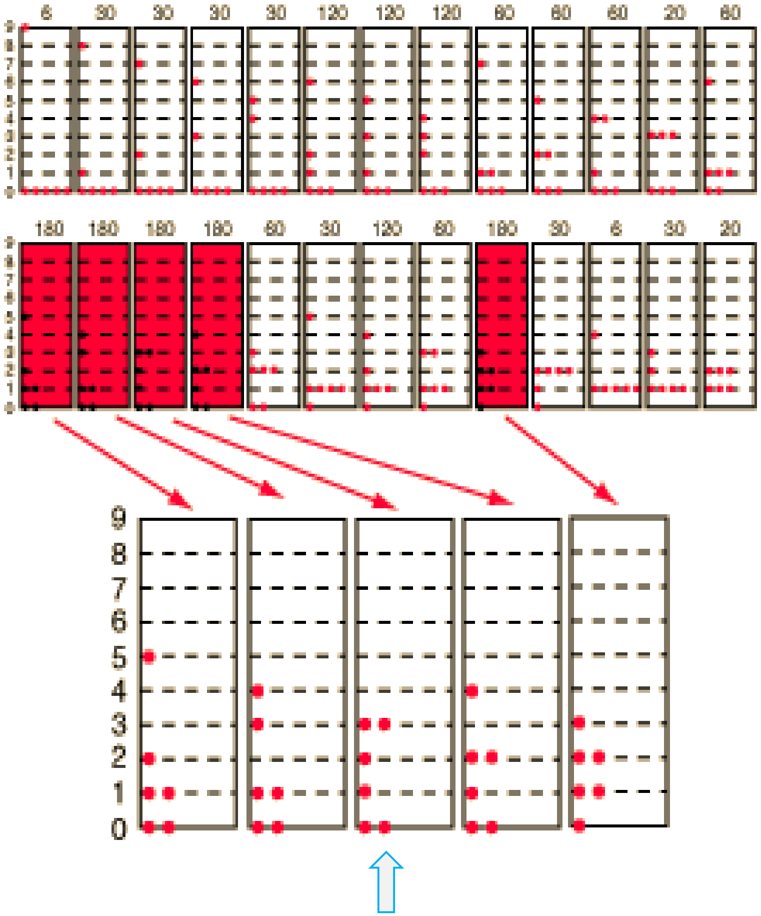
Low energy states are more probable with Bose-Einstein statistics than with the Maxwell-Boltzmann statistics. While that excess is not dramatic in this example for a small number of particles, it becomes very dramatic with large numbers and low temperatures. At very low temperatures, bosons can "condense" into the lowest energy state. The phenomenon called Bose-Einstein condensation.



Energy level	Average number M-B	Average number B-E
0	2.143	2.269
1	1.484	1.538
2	0.989	0.885
3	0.629	0.538
4	0.378	0.269
5	0.210	0.192
6	0.105	0.115
7	0.045	0.077
8	0.015	0.038
9	0.003	0.038

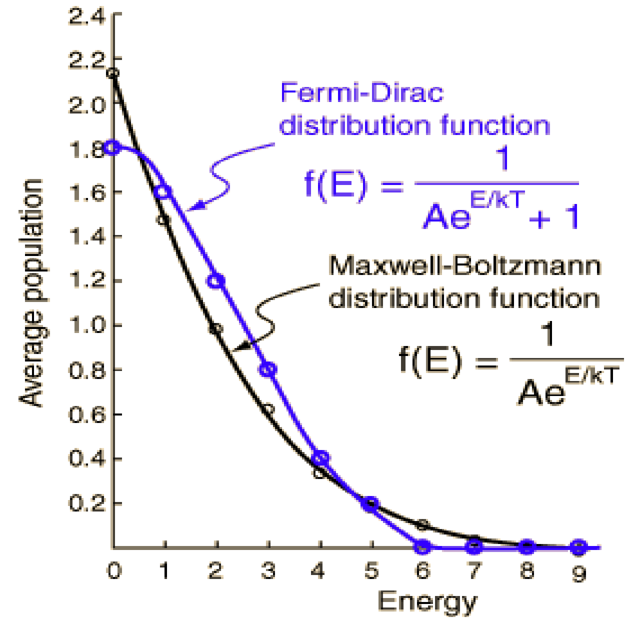
Ref: http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/disbex.html#c2
Georgia State University

Maxwell-Boltzmann statistics Vs. Fermi-Dirac Statistics



Unlike the boson case, only five energy distributions are allowed! All others have more than the permitted two particles in each state in violation of the exclusion principle.

- Low energy states are less probable with Fermi-Dirac statistics than with the Maxwell-Boltzmann statistics
- Difference is not seen very dramatic in this example for a small number of particles (06), it becomes very dramatic with large numbers and low temperatures. At absolute zero all of the possible energy states up to a level called the Fermi energy are occupied, and all the levels above the Fermi energy are vacant.



Ref: http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/disbex.html#c2
Georgia State University

Further reading and references:

https://readingfeynman.org/tag/bose-einstein-distribution/

Physics of Materials by ***Dr. Prathap Haridoss****,Department of Metallurgical & Materials Engineering, IIT Madras. For more details on NPTEL visit http://nptel.iitm.ac.in*

https://www.youtube.com/watch?v=1aHFG7VLr-g

Ref: https://www.youtube.com/user/SeriousScience

Nobel Prize winning physicist Prof. **Wolfgang Ketterle** from MIT on the candidates for Bose-Einstein condensation

https://www.youtube.com/watch?v=FuB2GrEmFIE&t=23s

https://www.youtube.com/watch?v=D0aPQKqA7rE