

PHY2001 Statistical Mechanics

- **Importance**

- Statistical mechanics is used to describe large numbers of particles, where it is impossible to define individual parameters (e.g. position and momentum) of every particle. Instead the parameters are described by probability distributions.
- In many situations a classical description of the particles is OK but for high densities and low temperatures the quantum nature of the particles must be accounted for, i.e. whether the particles are fermions (which must obey the Pauli exclusion principle) or bosons.

- **Examples of applications**

- **Classical**

- Velocity distributions of gas or liquid molecules which determine the rate of chemical reactions
- Electron energies in plasmas (e.g. stars) which determine strength of atomic emission lines
- Properties of solids at room temperature such as heat capacity, magnetic susceptibility etc.

- **Quantum**

- Electrons (fermions) in a white dwarf star, or conductors and semiconductors
- Pairs of electrons (which act like bosons) in superconductors
- Liquid helium at low temperatures, vibrations in solids at low temperatures
- Photons (bosons) emitted from a blackbody (e.g. spectral emission from stars, hot objects)

Recommended Book

Statistical Physics, Tony Guénault

2nd editions are available in the library

Section 1: Introduction to statistical mechanics

- **Topics**
 - Definitions in Statistical Mechanics
 - Identifying microstates for simple systems
 - Finding distributions and calculating their statistical weights for simple systems
 - The Central Postulate of statistical mechanics and mean distributions
 - Statistical definition of entropy
 - Distinguishable and indistinguishable particles
- **Objectives**
 - To learn the terminology of statistical mechanics
 - To be able to articulate the central postulate and its consequences for finding average distributions
 - To know how to relate entropy to numbers of microstates
 - To understand the concept of distinguishability of particles

1.1 - Definitions

- Systems Under Consideration

Weakly Interacting particles

- “The energy associated with interaction between particles is negligible compared to the total energy of the system”
- For example in a low pressure gas the potential energy between gas molecules is much less than the kinetic energy of the molecules as there is a large average distance between the particles. However, there is sufficient interaction between particles for thermal equilibrium to be reached quickly.

Isolated from Surroundings

- “There is no transfer of energy or particles to the surroundings”
- Hence the number of particles N , volume V , total energy U etc. of the system are conserved.

- Macrostate

- “A macrostate is specified by the global properties of the system”
- For example N, V, U , Pressure P , Temperature T

1.1 – Definitions

- **Single Particle State**

- “A single particle state is the set of parameters that describe an individual particle”
- For example
 - The classical position, momentum of a particle
 - The wavefunction of the particle
(within which position, momentum, energy are defined probabilistically)

- **Microstate**

- “A microstate is a set of single particle states (one for every particle in the system) that in total correspond to a given macrostate”
- For example consider a litre of an atomic gas at STP (corresponding to about 3×10^{22} particles)
 - In classical mechanics this corresponds to knowing the momentum and position of every particle.
 - In quantum mechanics this corresponds to knowing the wavefunction for every particle.
- If ε_j is the energy of particle j , the total energy of the macrostate is the sum over particles

$$U = \sum_{j=1}^N \varepsilon_j$$

- There are many possible microstates which could produce a single macrostate

1.2 –Distributions

- **Distribution**

- “A distribution provides statistical information on the particles in the system”
- It is not practical to describe the properties of a system by its microstates, while a macrostate lacks more detailed information on the make up of the system. Distributions provide an intermediate amount of information on the system.
- For example a distribution can predict the fraction of particles in a gas which will have a certain range of velocities – a velocity distribution.

- **Distribution in Single Particle States**

- Consider a single particle state i with an energy ε_i . In the system there are n_i particles in state i .
- The system has a distribution of $(n_1, n_2, n_3, n_4 \dots)$ particles in each state.
- $\{n_i\} = (n_1, n_2, n_3, n_4 \dots)$ is shorthand notation denoting a particular distribution
- The number of microstates associated with a distribution is called the **statistical weight**, often denoted t .

- **Distribution in Energy Levels**

- From quantum mechanics it is possible for more than one state to have the same energy (degeneracy). An electron energy level has two possible states (spin up, spin down) and hence has a degeneracy of $G = 2$.
- It is also convenient to represent a number g_i of single particle states which are closely spaced in energy as a single energy level ε_i with a degeneracy of g_i
- **For this course we often deal with distribution in levels where $\{n_i\} = (n_1, n_2, n_3, n_4 \dots)$ is a particular distribution within levels having an energy ε_i and degeneracy g_i**

Simple Example: An isolated system has $N = 3$ **distinguishable** particles A, B, C with single particle states equally spaced at intervals of ϵ and a total energy $U = 3\epsilon$ (i.e. the macrostate is defined by $N = 3$, $U = 3\epsilon$)

Microstates

$\{n_i\}$
 n_4
 n_3
 n_2
 n_1

Distributions

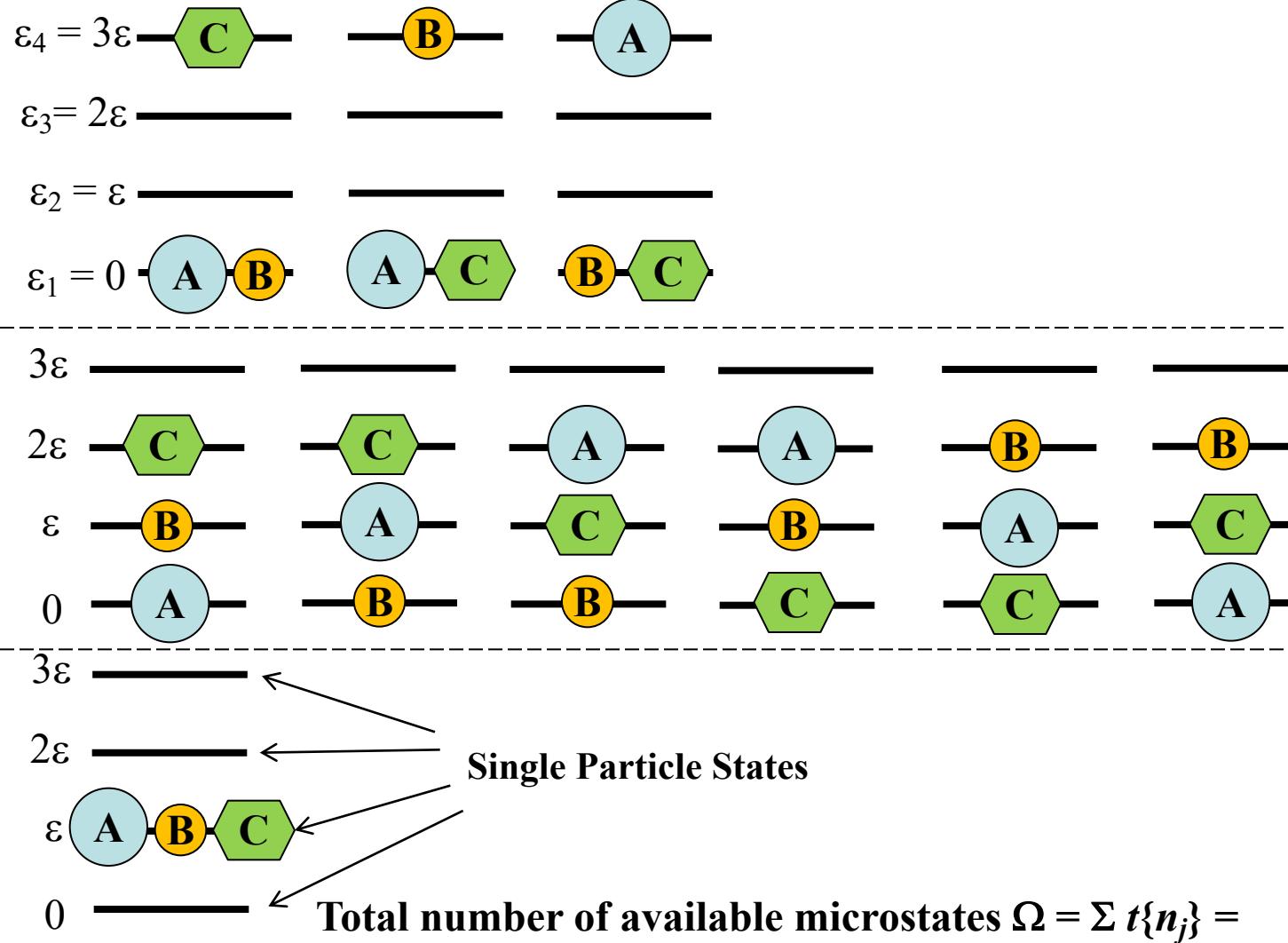
**Statistical Weight
of each
distribution**
 $t\{n_i\}$

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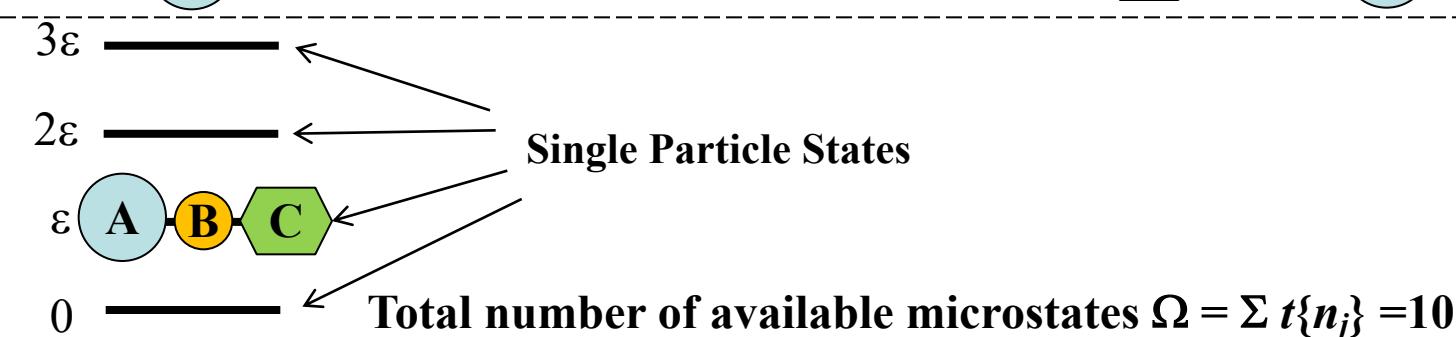
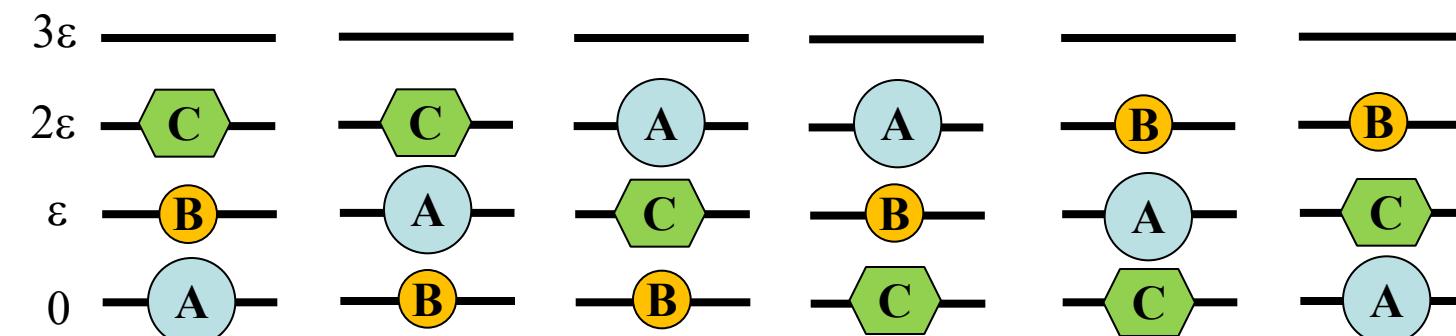
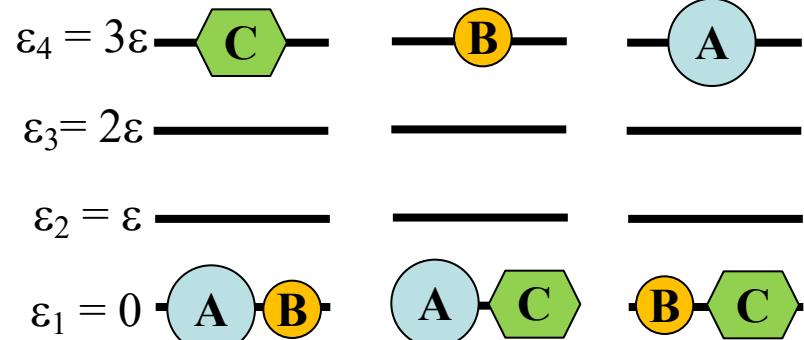
$\{n_i\}$
 n_4
 n_3
 n_2
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**Statistical Weight
of each
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 $t\{n_i\}$



Simple Example: An isolated system has $N = 3$ **distinguishable** particles A, B, C with single particle states equally spaced at intervals of ε and a total energy $U = 3\varepsilon$ (i.e. the macrostate is defined by $N = 3$, $U = 3\varepsilon$)

Microstates



$\{n_i\}$
 n_4
 n_3
 n_2
 n_1

1
0
0
2

0
1
1
1

0
0
3
0

Distributions

Statistical Weight
of each
distribution
 $t\{n_i\}$

Calculating the statistical weight: the Multinomial Theorem

- If you have a total of N distinguishable particles of which there are n_1 in state ε_1 , n_2 in state ε_2 , n_i in state ε_i , etc., how many different ways are there for distributing these particles? I.e. what is the statistical weight t of this distribution?
- The answer is given by the multinomial theorem, which in mathematics is used to determine the coefficients of the multinomial expansion $(x + y)^N$.

$$t\{n_i\} = \frac{N!}{\prod_i n_i!}$$

- E.g. in the example (previous page) for the distribution $\{2, 0, 0, 1\}$ the statistical weight is

$$t\{2, 0, 0, 1\} = \frac{3!}{2!0!0!1!} = 3$$

1.3 – Central Postulate

- **Central Postulate of Statistical Mechanics**
 - “**All accessible microstates in an isolated system are equally probable**”
 - If there are Ω possible microstates for a given macrostate, then the probability of being in each of these microstates is $1/\Omega$
 - This is a natural consequence of all the possible microstates being “explored” quickly.
 - To illustrate this consider a gas which is initially in a microstate corresponding to all the particles moving from left to right with the same momentum. Due to collisions the trajectories are quickly randomised so that all possible microstates are quickly accessed and thus equilibrium is reached.
 - Sometimes known as averaging or ergodic hypothesis
 - The total number of accessible microstates, Ω , is of profound significance in the interpretation of statistical mechanics and thermodynamics, as we shall see very soon!

1.4 The Average Distribution

- In Statistical Mechanics we often need to determine the average distribution for a given macrostate. Using the central postulate, we can work this out once we know all the microstates. E.g., for the simple example above:

Total Particles N

3

Total Energy U

3

Single Particle States (SPS)

Distributions

0

1

2

3

Statistical Weight t

1

2

0

0

1

3

2

1

1

1

0

6

3

0

3

0

0

1

$\Omega = 10$

Totals

Sum of particles occupying each SPS for all microstates

$$2 \times 3 + 1 \times 6 + 0 \times 1 = 12$$

9

6

3

$$N\Omega = 30$$

Average distribution

$$12/\Omega = 1.2$$

0.9

0.6

0.3

$$N=3$$

Average Energy

0

0.9

1.2

0.9

$$U=3$$

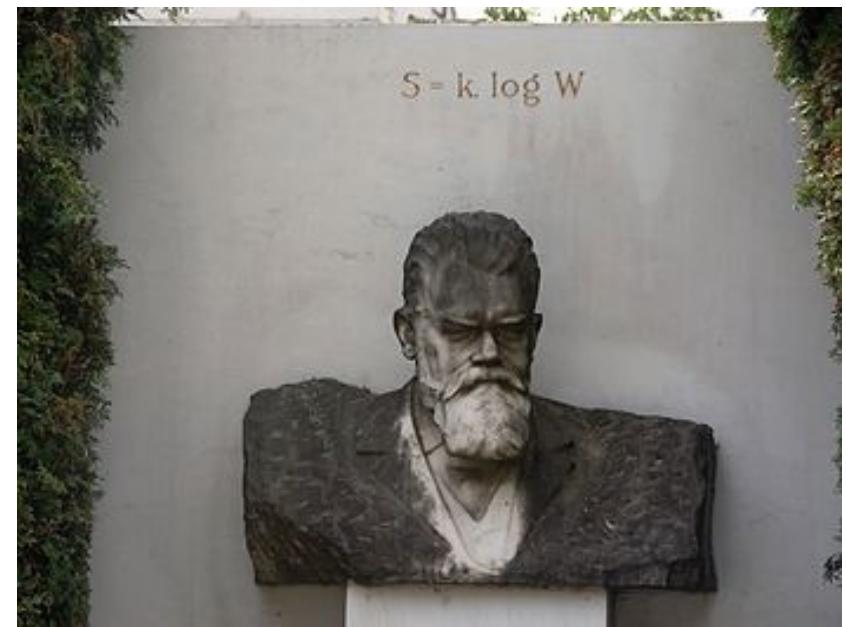
1.5 - Statistical Entropy

$$S = k_B \ln \Omega$$

1.5 - Statistical Entropy



Ludwig Boltzmann
(1844 – 1906)



1.5 - Statistical Entropy

- From L1 Physics you were introduced to the concept of entropy S which was a measure of the disorder of the system.
- In thermodynamics, a change in entropy is related to temperature and flow of heat. How is this concept related to microscopic quantities?
- More disorder corresponds to a larger total number of available microstates of the system Ω . This dependence is logarithmic and entropy is defined microscopically as

$$S = k_B \ln \Omega$$

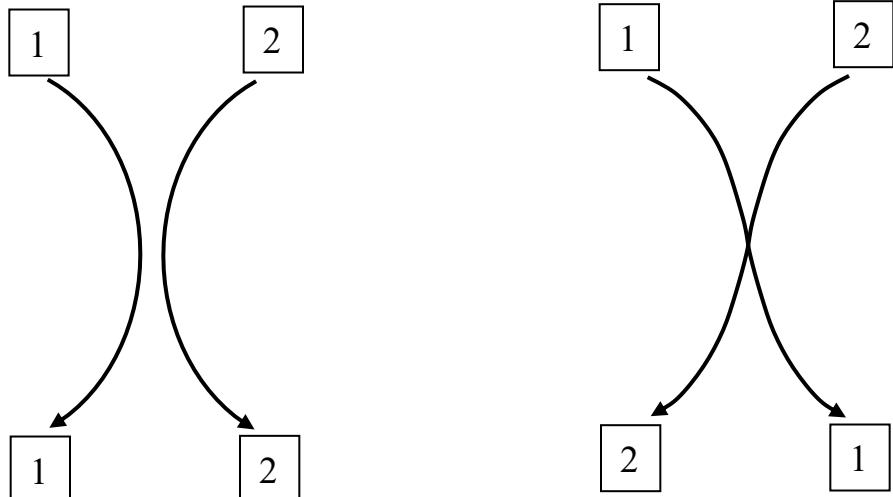
(k_B is Boltzmann's constant)

- So for the simple example where $N = 3$ and $U = 3\varepsilon$, then $S = k_B \ln 10$.
- If we force particle A to be in the ground state, the number of available microstates is reduced to 4 and $S = k_B \ln 4$, i.e. the system is more ordered

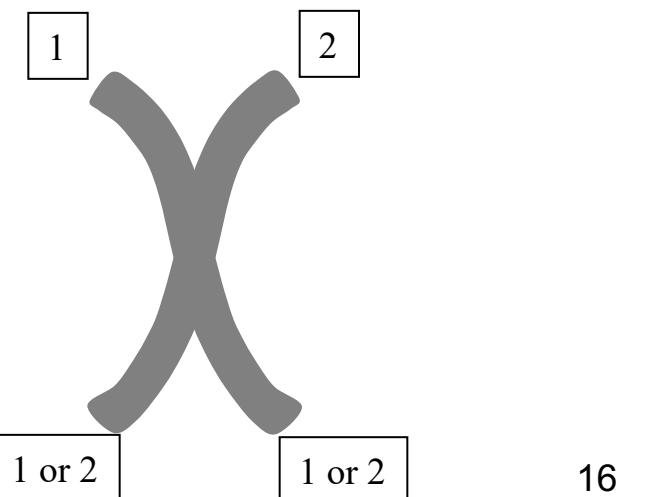
1.6 – Distinguishable / Indistinguishable Particles

- **Identical Particles** - have the same intrinsic properties, e.g. mass, charge, magnetic moment
- **Distinguishable Particles** - can in principle be separately identified by observation of
 - Differences in their intrinsic properties (particles are non-identical), e.g. an electron and a positron
 - Differences in their extrinsic properties, i.e. differences in the particles' trajectories
- **Classical mechanics** - *identical particles are distinguishable* by accurate trajectory measurement
- **Quantum mechanics** - *identical particles are indistinguishable* due to the uncertainty principle.
 - Two fundamental types for indistinguishable particles: fermions and bosons; more on this later

Classical paths can be distinguished for identical particles



Quantum paths can't be distinguished for identical particles due to Uncertainty Principle



Section 2: Boltzmann Distribution

- **Topics**

- Central Postulate of Statistical Mechanics revisited
- Calculating distributions for many particle systems
- Formulating the Classical Boltzmann Distribution as applied to systems of many distinguishable particles distributed for systems with few levels
- Examples of Boltzmann Distributions in Atomic States
- Examples of Boltzmann Distributions applied to paramagnetic solid

- **Objectives**

- To be able to articulate the central postulate and its consequences for finding average distributions
- To be able to derive the Classical Boltzmann distribution
- To show the application of the Boltzmann distribution to some simple few level systems

2.1 – Central postulate revisited

- **Recall: Central Postulate of Statistical Mechanics**
 - “All accessible microstates in an isolated system are equally probable”
 - If there are Ω possible microstates for a given macrostate, then the probability of being in each of these microstates is $1/\Omega$
- **The Central Postulate applied to large systems**
 - For a large number of particles the number of distributions is huge, but fortunately the statistical weight for most distributions is negligible. This means that there are only a small number of distributions that are significant and therefore the most probable distribution (the one with the highest statistical weight) is equivalent to the average distribution
 - **Average distribution ≡ Most probable distribution (i.e. one with highest statistical weight)**

2.2 - Deriving the Thermal Equilibrium Distribution

1. Find the possible single particle states of the system and their degeneracy (by classical or quantum mechanics)
2. Find all possible distributions consistent with macrostate conditions (where n_i is the number of particles in the state i with energy ε_i):

$$N = \sum_i n_i \quad U = \sum_i n_i \varepsilon_i \quad \text{where sums run over } \underline{\text{all single particle states}} \text{ of the system.}$$

3. Determine the number of possible microstates (statistical weight) for each distribution .

For distinguishable particles it is

$$t\{n_i\} = \frac{N!}{\prod_i n_i!} \quad (\text{again, } i \text{ runs over } \underline{\text{all single particle states}} \text{ of the system})$$

4. Use Central Postulate

Most Probable Distribution \approx Average Distribution

5. Find most probable distribution by differentiating the statistical weight t

Finding the Most Probable Distribution: Distinguishable Particles

To find most probable (likely) distribution:

- Maximise $t\{n_i\}$. Maximising $\ln(t)$ will also maximise t

$$\ln(t\{n_i\}) = \ln N! - \sum_i \ln n_i!$$

- Use an approximation

Stirling's formula valid for large x : $\ln x! = x \ln x - x$

$$\ln(t\{n_i\}) = N \ln N - N - \sum_i (n_i \ln n_i - n_i)$$

- Differentiate $\ln(t)$ with respect to n_i and set to zero to maximise (N is constant, n_i the variables, i.e. the total particles is fixed but the number in each distribution can be changed)

$$d \ln(t) = - \sum_i \ln n_i d n_i = 0$$

- If we also differentiate expressions for N and U (which are constant) we obtain

$$N = \sum_i n_i \quad U = \sum_i n_i \varepsilon_i$$

$$0 = \sum_i d n_i \quad 0 = \sum_i \varepsilon_i d n_i$$

2.3 – The Boltzmann Distribution

Copied from last slide:

$$-\sum_i \ln n_i dn_i = 0 \quad N = \sum_i n_i \quad U = \sum_i n_i \varepsilon_i$$
$$0 = \sum_i dn_i \quad 0 = \sum_i \varepsilon_i dn_i$$

- We can multiply the constraints by constants α and β and add them to the maximised expression

$$0 = \alpha \sum_i dn_i \quad 0 = \beta \sum_i \varepsilon_i dn_i$$

$$\sum_i (\alpha + \beta \varepsilon_i - \ln n_i) dn_i = 0$$

- For this expression to be true for all states then $\alpha + \beta \varepsilon_i - \ln n_i = 0$ giving

$$n_i = \exp(\alpha + \beta \varepsilon_i)$$

- This gives us the distribution, i.e. the average number of particles in a given state.
- This is the **Boltzmann distribution**, which holds true for systems of distinguishable particles (generally applicable to systems that are described well by Classical Mechanics)

2.4 – The nature of α

But what are α and β ?

- α – related to the number of particles N

$$n_i = \exp(\alpha + \beta \varepsilon_i)$$

$$N = \sum_i n_i = e^\alpha \sum_i \exp(\beta \varepsilon_i) = e^\alpha Z$$

$$e^\alpha = \frac{N}{Z}$$

$$Z = \sum_i \exp(\beta \varepsilon_i)$$

(recall, index i runs over all single particle states of the system)

- Therefore α is a measure of the amount of material (particles) in the system
- **Z is called the partition function** which performs the important job of normalising the distribution.
- $n_i = \frac{N}{Z} \exp(\beta \varepsilon_i)$
- Z can be found provided we know the energies of the states and the nature of β

2.5 – The nature of β

β – related to the internal energy U

- From the **first law of thermodynamics**, the change in internal energy is the heat going into the system dQ minus the work done by the system dW

$$dU = dQ - dW$$

- For a system absorbing an amount of heat dQ , the change in entropy dS is dQ/T , while the work done by an expanding a gas is PdV giving

$$dU = T dS - P dV$$

Since $U = \sum_i \varepsilon_i n_i$, $dU = \sum_i \varepsilon_i dn_i + \sum_i n_i d\varepsilon_i$

- We know that the energy levels of systems depend on the volume. For instance from QM the separation of the energy levels of a particle in a box decrease when the volume is increased, hence we use a plausibility argument to suggest that we can equate the final terms in each equation

$$-P dV = \sum_i n_i d\varepsilon_i$$

2.5 – The nature of β

- We have previously seen that at a microscopic level entropy S is determined by the number of available microstates Ω ($S = k_B \ln \Omega$), so a change in the entropy (disorder) of the system will be determined by changes in the number particles in a level i . Hence, we equate

$$T dS = \sum_i \varepsilon_i dn_i$$

- Given that statistical mechanics assumes that the distribution of the system is the most likely one and the probability of being in a different distribution is negligible, then number of available microstates Ω is just equal to the statistical weight of the distribution $t\{n_i\}$

$$\Omega \approx t\{n_i\} = \frac{N!}{\prod_i n_i!}$$

$k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$ (Boltzmann's Constant)

- Hence $TdS = kTd(\ln \Omega) = kTd \ln(t) = -kT \sum_i \ln n_i dn_i$

$$-kT \sum_i \ln n_i dn_i = \sum_i \varepsilon_i dn_i$$

since $\sum_i n_i = N$ $\sum_i dn_i = 0$

$$-kT \sum_i (\alpha + \beta \varepsilon_i) dn_i = \sum_i \varepsilon_i dn_i$$

$$\alpha \sum_i dn_i + \beta \sum_i \varepsilon_i dn_i = -\frac{1}{kT} \sum_i \varepsilon_i dn_i$$

$$\beta = -\frac{1}{k_B T}$$

2.6 – Occupation probability and Partition Function

- We now have single particle state populations given by $n_i = \exp(\alpha + \beta\epsilon_i) = \frac{N}{Z} \exp\left(-\frac{\epsilon_i}{k_B T}\right)$ where Z is the partition function
- When we work with energy levels (rather than single particle states) we need to take into account the degeneracy of each level g_i which gives (sums now over energy levels):

$$n_i = \frac{g_i N}{Z} \exp\left(-\frac{\epsilon_i}{k_B T}\right)$$

$$Z = \sum_i g_i \exp\left(-\frac{\epsilon_i}{k_B T}\right)$$

- Often a more useful parameter is the probability p_i of being in level i

$$p_i = \frac{n_i}{N} = \frac{g_i}{Z} \exp\left(-\frac{\epsilon_i}{k_B T}\right)$$

- The internal energy of the system is

$$U = \sum_i n_i \epsilon_i = \frac{N}{Z} \sum_i \epsilon_i g_i \exp\left(-\frac{\epsilon_i}{k_B T}\right)$$

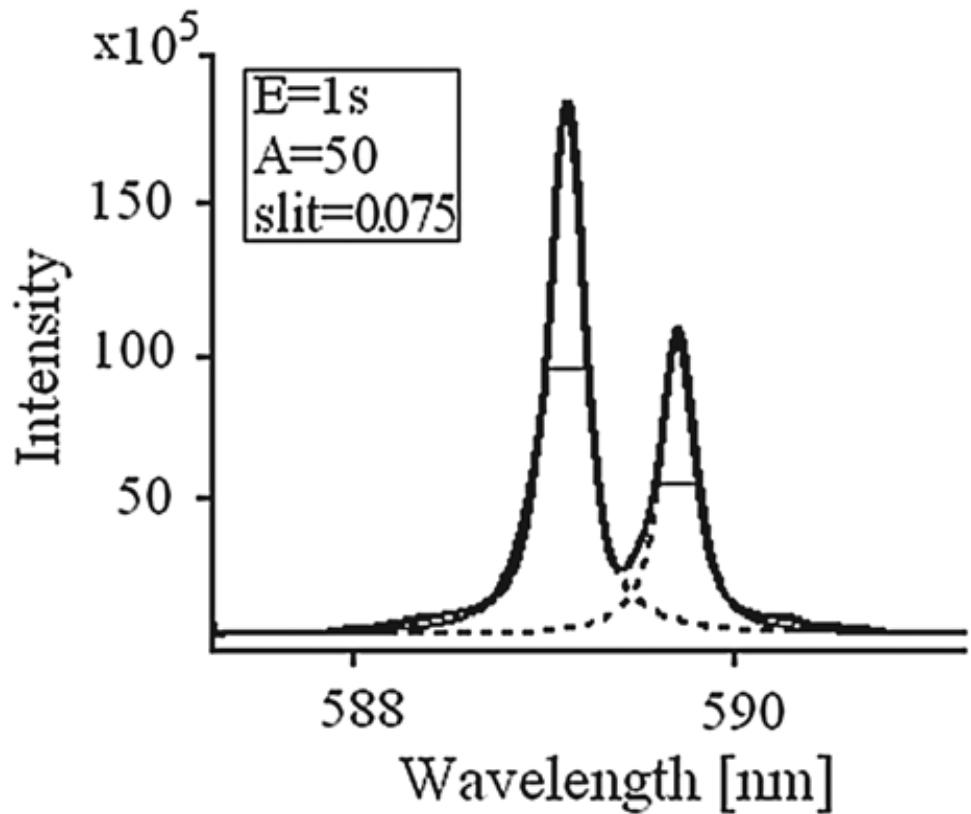
2.7 Boltzmann Distribution Examples: Energy Levels in Sodium Atom



Spectra of street lights:

Image from Palomar Observatory blog (2009, 05)

2.7 Boltzmann Distribution Examples: Energy Levels in Sodium Atom



*High resolution spectrum of the
Na D lines:
from Kasalica et al. 2013,
Journal of Analytical Stomie
Spectroscopy, 28, 92*

2.7 Boltzmann Distribution Examples: Energy Levels in Sodium Atom

- Consider sodium atoms in a sodium lamp at a temperature of 2200 K ($k_B T = 0.19$ eV)
- The 4 lowest energy levels of the sodium atom are
- Assuming only these levels are populated
 - Calculate the partition function Z
 - Determine the fraction of atoms in each of the levels

Level	Energy (eV)	Degeneracy g_i
$3s_{1/2}$	0	2
$3p_{1/2}$	2.012	2
$3p_{3/2}$	2.015	4
$4s_{1/2}$	3.192	2

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- The partition function is

$$Z = \sum_i g_i \exp(-\varepsilon_i / k_B T) =$$

- Giving populations

$$p_i = \frac{g_i}{Z} \exp(-\varepsilon_i / k_B T)$$

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Level	p_i
$3s_{1/2}$	
$3p_{1/2}$	
$3p_{3/2}$	
$4s_{1/2}$	

In a sodium lamp transitions from the $3p_{1/2}$ and $3p_{3/2}$ levels to the ground state generate the familiar orange light. These two transitions are very close in wavelength but as the $3p_{3/2}$ level is twice the probability of being populated, its transition is twice the intensity

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- The partition function is

$$Z = \sum_i g_i \exp(-\varepsilon_i / k_B T) = 2 + 2e^{-10.589} + 4e^{-10.605} + 2e^{-16.8} \approx 2$$

- Giving populations

$$p_i = \frac{g_i}{Z} \exp(-\varepsilon_i / k_B T)$$

Level	p_i
$3s_{1/2}$	≈ 1
$3p_{1/2}$	2.5×10^{-5}
$3p_{3/2}$	5.0×10^{-5}
$4s_{1/2}$	5.0×10^{-8}

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2.7 Boltzmann Distribution Examples: Curie-Langevin Paramagnetism

Measure the magnetisation in a paramagnetic solid as a function of the applied magnetic field and/or the temperature:

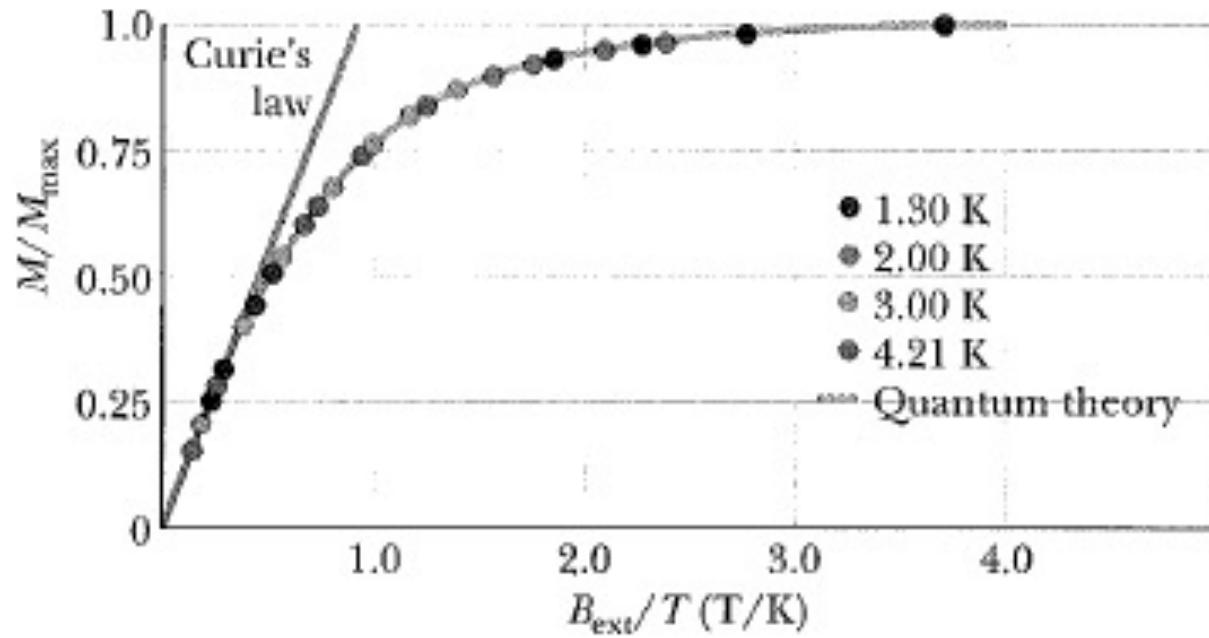
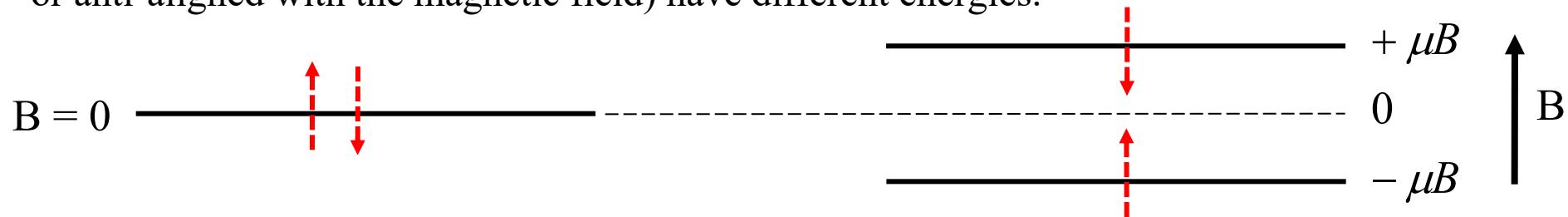


Image from www.transtutors.com

2.7 Boltzmann Distribution Examples: Curie-Langevin Paramagnetism

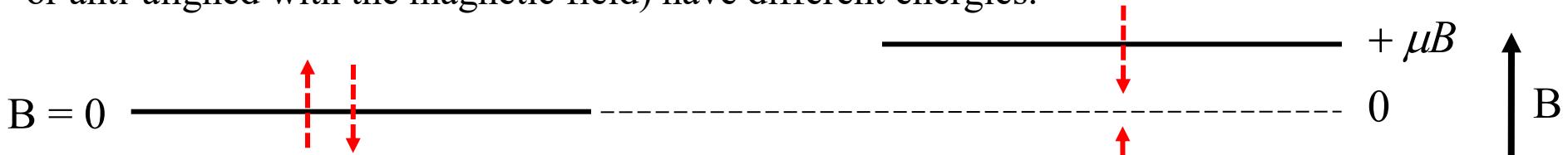
- Consider an ensemble of N particles with a spin $\frac{1}{2}$. There are 2 possible spin states, “up” and “down”
- The spin gives the particle a magnetic dipole moment μ and the two states are normally degenerate
- When an external magnetic field is applied, the energy of the dipole is given classically by
$$E = -\mu \cdot B$$
- Therefore the degeneracy is raised as the two states (corresponding to the magnetic moment aligned or anti-aligned with the magnetic field) have different energies.



2.7 Boltzmann Distribution Examples: Curie-Langevin Paramagnetism

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$$E = -\mu \cdot \mathbf{B}$$
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- The partition function is $Z = \sum_i g_i \exp\left(-\frac{\epsilon_i}{k_B T}\right) = \exp\left(+\frac{\mu B}{k_B T}\right) + \exp\left(-\frac{\mu B}{k_B T}\right)$
 - The fraction of particles in the ground and excited states is $p = \frac{g_i}{Z} \exp\left(-\frac{\epsilon_i}{k_B T}\right)$
- $$p_0 = \frac{1}{Z} \exp\left(+\frac{\mu B}{k_B T}\right) \quad p_1 = \frac{1}{Z} \exp\left(-\frac{\mu B}{k_B T}\right)$$

Boltzmann Distribution Example: Curie-Langevin Paramagnetism

- So the difference in the populations is

$$p_0 - p_1 =$$

- As there are more particles in their ground state (magnetic dipole along the field) there is a net magnetisation of the ensemble. Magnetisation M is defined as the dipole moment per unit volume

$$M =$$

- For **high temperatures and low fields** $k_B T \gg \mu B$
the exponents have small values, so using $e^x \approx 1 + x$, for small x

$$M = \text{Curie's Law}$$

- For **low temperatures and high fields** $k_B T \ll \mu B$ only the large positive exponents contribute giving

$$M =$$

so all the dipoles are aligned in the direction of the external field

Boltzmann Distribution Example: Curie-Langevin Paramagnetism

- So the difference in the populations is

$$p_0 - p_1 = \frac{\exp\left(+\frac{\mu B}{k_B T}\right) - \exp\left(-\frac{\mu B}{k_B T}\right)}{\exp\left(+\frac{\mu B}{k_B T}\right) + \exp\left(-\frac{\mu B}{k_B T}\right)} = \frac{\sinh\left(\frac{\mu B}{k_B T}\right)}{\cosh\left(\frac{\mu B}{k_B T}\right)} = \tanh\left(\frac{\mu B}{k_B T}\right)$$

- As there are more particles in their ground state (magnetic dipole along the field) there is a net magnetisation of the ensemble. Magnetisation M is defined as the dipole moment per unit volume

$$M = \frac{N}{V} \mu (p_0 - p_1) = \frac{N}{V} \mu \tanh\left(\frac{\mu B}{k_B T}\right)$$

- For **high temperatures and low fields** $k_B T \gg \mu B$
the exponents have small values, so using $e^x \approx 1 + x$, for small x

$$M = \frac{N}{V} \frac{\mu^2 B}{k_B T} \propto \frac{1}{T} \quad \text{Curie's Law}$$

- For **low temperatures and high fields** $k_B T \ll \mu B$ only the large positive exponents contribute giving

$$M = \frac{N}{V} \mu$$

so all the dipoles are aligned in the direction of the external field

Section 3: Many Level Systems and Distribution Functions

In Section 2, we have applied the principles of statistical mechanics to systems with large numbers of particles and shown how Boltzmann statistics help us to study an astonishing variety of physical systems in which the particles can be considered distinguishable. However, we restricted ourselves to systems in which the number of available energy levels was small.

To apply our methods more generally, we need to consider systems with far larger numbers of available states (recall our “Kahoot” from Lecture 1), and systems in which the quantum mechanical consequences of indistinguishability are included. The study of such systems is the crowning glory of modern statistical mechanics!

Section 3: Many Level Systems and Distribution Functions

- **Topics**

- Symmetries of two-particle wavefunctions and an introduction to fermions and bosons
- The Fermi exclusion principle
- Spin degeneracy
- Representing systems with large numbers of states
- Statistical weights and distribution functions for fermions, bosons and dilute gases

- **Objectives**

- To know the fundamental properties of fermions and bosons, and the origin of the exclusion principle
- To be familiar with spin and spin degeneracy
- To be able to treat many level systems using degeneracies
- To be able to derive expressions for the Fermi-Dirac, Bose-Einstein and dilute-gas (Boltzmann) distribution functions

3.1 – Indistinguishable Particles

- **Distinguishable particles (recap)**
 - So far we have focussed on distinguishable particles: in Classical Mechanics, if two particles are identical (same intrinsic properties, e.g. mass), it is still possible in principle to distinguish them by their external properties (e.g. position, momentum)
 - In a classical treatment of statistical mechanics, the particles are always distinguishable.
 - A distribution of a system of distinguishable particles is governed by **Boltzmann Statistics** (as discussed in Section 2).
- **Indistinguishable**
 - In Quantum Mechanics identical particles are *indistinguishable*, and one of two types: **Fermions** or **Bosons**
 - **Fermions** and **Bosons** differ from each other in several important ways:
 - the symmetry properties of their wavefunctions (see next slide)
 - their spin (and spin degeneracy)
 - Fermions obey the exclusion principle while Bosons do not

3.2 – Two Particle Wavefunctions

Let us consider two identical particles (1, 2) which do not interact with each other.

If there is no interaction between the particles, then the motion of one particle is independent of the other and the wavefunction describing both is separable into two single-particle wavefunctions.

Suppose that:

- Particle 1 is in a quantum state labelled α , which corresponds to a single-particle wavefunction $\psi_\alpha(x_1)$
- Particle 2 is in a quantum state labelled β , which corresponds to a single-particle wavefunction $\psi_\beta(x_2)$

Let's call the complete wavefunction describing the two particles $\psi_{\alpha,\beta}(x_1, x_2)$. The interpretation of this wavefunction is that the quantity

$$\left| \psi_{\alpha,\beta}(x_1, x_2) \right|^2 dx_1 dx_2$$

gives the probability of finding Particle 1 in a range dx_1 around position x_1 **and** Particle 2 in dx_2 around position x_2 . (This makes sense if you recall that for a single particle system $|\psi(x)|^2$ is the probability density for the particle's position.)

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Since the wavefunction is separable, it is reasonable to expect that the complete function could be the product $\psi_\alpha(x_1)\psi_\beta(x_2) \dots$

3.2 – Two Particle Wavefunctions

However, if the particles are indistinguishable, the probability density must be the same upon **interchange of the particles**, i.e.

$$|\psi_{\alpha,\beta}(x_1, x_2)|^2 = |\psi_{\alpha,\beta}(x_2, x_1)|^2$$

This is not satisfied for $\psi_{\alpha,\beta}(x_1, x_2) = \psi_\alpha(x_1)\psi_\beta(x_2)$ since swapping the particles would give

$$\psi_{\alpha,\beta}(x_2, x_1) = \psi_\alpha(x_2)\psi_\beta(x_1),$$

meaning that $\psi_{\alpha,\beta}(x_1, x_2)$ and $\psi_{\alpha,\beta}(x_2, x_1)$ are different, unless the particles are in the same state (i.e. unless $\psi_\alpha = \psi_\beta$). So $\psi_\alpha(x_1)\psi_\beta(x_2)$ cannot be the valid wavefunction consistent with the particles being indistinguishable.

However, for indistinguishable particles, the form suggested by the interchange of particles above, $\psi_\alpha(x_2)\psi_\beta(x_1)$ is just as valid a description of the state as our original guess $\psi_\alpha(x_1)\psi_\beta(x_2)$, and this presents a solution: **since the Schrodinger Wave Equation is linear, we can consider linear combinations of these two representations** (next slide...)

3.2 – Two Particle Wavefunction Symmetries

Specifically, the following two linear combinations DO satisfy our particle exchange requirement

$$\psi_{\alpha\beta}^+ = C[\psi_\alpha(x_1)\psi_\beta(x_2) + \psi_\alpha(x_2)\psi_\beta(x_1)] \quad \text{symmetric}$$

$$\psi_{\alpha\beta}^- = C[\psi_\alpha(x_1)\psi_\beta(x_2) - \psi_\alpha(x_2)\psi_\beta(x_1)] \quad \text{anti-symmetric}$$

[C is an appropriate normalisation constant, $= 1/\sqrt{2}$ if ψ_α and ψ_β are normalised.]

The first is symmetric under particle exchange: i.e. if we exchange the particles, $\psi_{\alpha\beta}^+ \rightarrow \psi_{\alpha\beta}^+$

The second is anti-symmetric under particle exchange: i.e. if we exchange them, $\psi_{\alpha\beta}^- \rightarrow -\psi_{\alpha\beta}^-$

Both of these possibilities are allowed since observable properties always involve $\psi_{\alpha\beta}^* \psi_{\alpha\beta}$.

These two classes of multi-particle wavefunctions correspond to the two types of particle:

- **Bosons** have wavefunctions that are **symmetric** under particle exchange
- **Fermions** have wavefunctions that are **anti-symmetric** under particle exchange

3.2 – The Pauli Exclusion Principle

Fermions have anti-symmetric wavefunctions:

$$\psi_{\alpha\beta}^- = C [\psi_\alpha(x_1) \psi_\beta(x_2) - \psi_\alpha(x_2) \psi_\beta(x_1)]$$

If both particles are in the same quantum state $\alpha = \beta$ then $\psi_{\alpha\beta}^- = 0$ i.e. two identical Fermions cannot occupy the same quantum state: this is the Pauli Exclusion Principle.

- You will be familiar with this expression of the **Pauli Exclusion Principle** for fermions
In a multielectron atom there can never be more than one electron in the same quantum state
- This follows directly from the arguments above. A stronger expression of the principle is
A system containing several electrons (or identical fermions) must be described by an anti-symmetric total wavefunction.

Note that there is no such exclusion principle for Bosons: the symmetric wavefunction permits multiple Bosons to exist in the same quantum state.

3.3 – Spins of Bosons and Fermions

- Particles have an intrinsic property known as **spin angular momentum** (which can be measured via their intrinsic magnetic dipole moment); in fact this determines whether particles have a symmetric or anti-symmetric wavefunction under particle exchange:

Particle	Spin Value	Wavefunction	Examples
Fermion	Half-integer	Anti-symmetric	Electron, proton, neutron, ${}^3\text{He}$
Boson	Integer	Symmetric	Photon, alpha particle, ${}^4\text{He}$

3.3 – Spin Degeneracy

- The electron has a **spin angular momentum quantum number** $s = \frac{1}{2}$. In analogy with the orbital angular momentum, l , the projection of this vector onto the z axis results in two possible states with quantum numbers $m_s = \pm\frac{1}{2}$ (spin up and spin down).
- Therefore for e.g. each state of the **hydrogen atom**, defined by quantum numbers n, l, m_l , there are two possible spin states (up and down). This spin degeneracy must be considered to explain the number of electrons occupying atomic orbitals:

- For each n level in hydrogen there are the following degeneracies

n different l -states ($l=0$ up to $l=n-1$) which each have

$(2l + 1)$ different m_l -states which each have

2 different m_s -states

- So the total number of states (degeneracy) for hydrogen in each l -state is

For $s(l=0)$ states, $g = 2$

For $p(l=1)$ states, $g = 6$

For $d(l=2)$ states, $g = 10$

For $f(l=3)$ states, $g = 14$

(Note: the use of $s, p, d, f \dots$ when naming particle states is called *spectroscopic notation*, and is very common.)

3.3 – Spin Degeneracy

- More generally, if a particle has **spin angular momentum quantum number s** . The projection of this vector onto the z axis results in possible states with quantum numbers

$$m_s = -s, -s+1, -s+2 \dots s$$

- Therefore the spin degeneracy factor for particles of spin s is $G = 2s + 1$

3.4 – Many-Level Systems

- For the examples considered in Section 2, we focussed on systems where only a few energy levels need to be considered (e.g. internal energies of an ensemble of atoms). More often there are too many energy levels to consider individually.
- Consider a system comprising of an ideal gas enclosed in a container. For simplicity the container is a 1D box (we will consider the 3D case later)....what kinetic energies can hydrogen molecules (H_2) have if they are trapped in a 1D box 1 cm in length?
 - We have seen (QM notes) that the energy levels are given by (we use ε for energy):

$$\varepsilon = \frac{\pi^2 \hbar^2}{2ma^2} n^2 \quad n = 1, 2, 3\dots$$

so that

$$\varepsilon_1 = \frac{(1.05 \times 10^{-34} \pi)^2}{2 \times 2 \times 1.66 \times 10^{-27} \times (0.01)^2} = 1.6 \times 10^{-37} \text{ J} = 1.0 \times 10^{-18} \text{ eV}$$

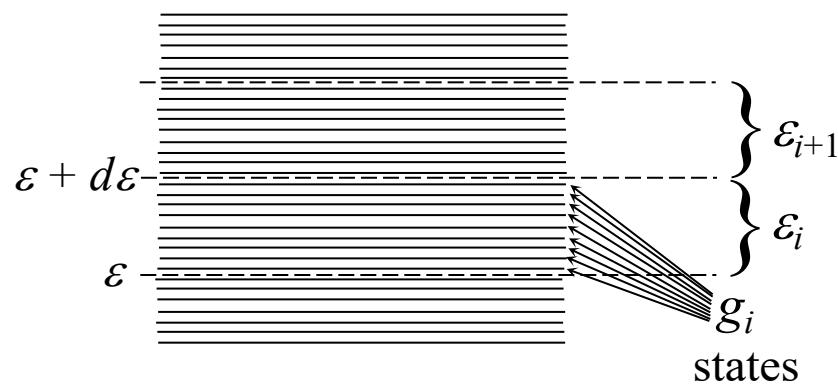
$$\varepsilon_2 = 6.6 \times 10^{-37} \text{ J} = 4.0 \times 10^{-18} \text{ eV}$$

$$\varepsilon_3 = 1.5 \times 10^{-36} \text{ J} = 9.3 \times 10^{-18} \text{ eV}$$

for comparison, $kT = 0.025 \text{ eV}$ at room temperature:
i.e. huge compared to separation of energy levels

3.4 – Many-Level Systems

- Therefore for a macroscopic gas, the states are incredibly closely spaced, so it is more sensible to treat a *group of levels* as a single entity.
- This group (“level” of energy ε_i) encompasses a number g_i of states (i.e. degeneracy) in the energy range ε to $\varepsilon + d\varepsilon$



3.5 – “Continuous” Energy Levels

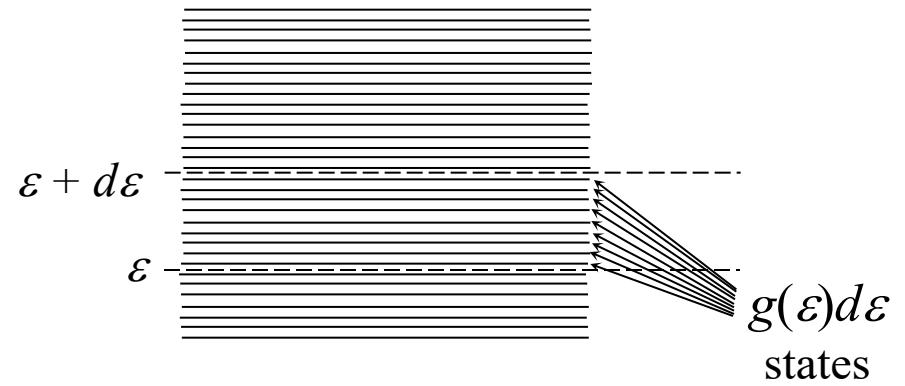
- A natural extension for systems with closely spaced energy levels is to represent the levels as a continuous function. E.g. if the system obeys Boltzmann statistics, the distribution is now transformed from

$$n_i = \frac{Ng_i}{Z} \exp\left(-\frac{\varepsilon_i}{k_B T}\right) \quad \text{to} \quad n(\varepsilon)d\varepsilon = \frac{Ng(\varepsilon)}{Z} \exp\left(-\frac{\varepsilon}{k_B T}\right)d\varepsilon$$

where $n(\varepsilon)d\varepsilon$ is the number of particles with energy between ε and $\varepsilon + d\varepsilon$ and $g(\varepsilon)d\varepsilon$ is the number of available states between ε and $\varepsilon + d\varepsilon$

- The partition function is now an integral

$$Z = \int_0^{\infty} g(\varepsilon) \exp\left(-\frac{\varepsilon}{k_B T}\right) d\varepsilon$$



$g(\varepsilon)$ is called the **density of states** (in energy)

3.6 – Statistical Weights for Indistinguishable Particles

- In Section 2 we considered the statistics of distinguishable particles and showed how the Boltzmann distribution factor can be derived from an appropriate expression for the statistical weight.
- We will now consider the distributions for particles in three further cases by allowing for indistinguishability and for very large numbers of states:

1. Fermi-Dirac statistics (applies to fermions)

2. Bose-Einstein statistics (applies to bosons)

3. Dilute gasses (this is an approximation that can apply to Fermions or Bosons provided that the number of particles is very small compared to the number of states: it shows how the classical limit is recovered from the two QM cases)

- In all cases, the steps of the argument are equivalent to those we considered in detail for the classical Boltzmann distribution in Section 2.

3.6 – Statistical Weights for Indistinguishable Particles

- Let us first consider n_i indistinguishable fermions occupying a level ε_i with a degeneracy of g_i .
- There are n_i states which are filled and $(g_i - n_i)$ unfilled states. The number of ways these can be distributed for a maximum of one particle per state (Pauli Exclusion Principle, i.e. $n_i \leq g_i$) is given by the binomial theorem.
- The statistical weight for **one level being occupied by n_i particles** is

$$t_i = \frac{g_i!}{n_i!(g_i - n_i)!}$$

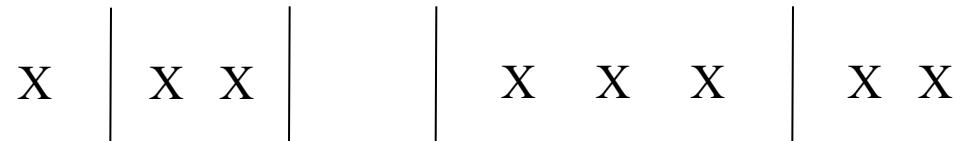
- Therefore for a particular distribution $\{n_i\}$ the total statistical weight is that of the individual levels multiplied together

FERMIONS: $t_{FD}\{n_i\} = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!}$ (Fermi-Dirac Statistics)

3.6 – Statistical Weights for Indistinguishable Particles

- For indistinguishable bosons there is no restriction on n_i , and the statistical weight can be derived by considering the problem of freely dividing the n_i particles between g_i available states.
- Following Guénault, if we represent particles by crosses and divisions between states by lines, this problem is equivalent to counting the number of distinct ways in which n_i identical crosses and $g_i - 1$ dividing lines can be arranged, e.g.:

An example for $n_i = 8$ and $g_i = 5$: this represents 1 particle in the first state, 2 in the second, 0 in the third, 3 in the fourth, and 2 in the last:



- The number of different arrangements is again given by the binomial theorem: $t_i = \frac{(g_i + n_i - 1)!}{n_i!(g_i - 1)!}$
- Since we will consider large systems, $t_i = \frac{(g_i + n_i - 1)!}{n_i!(g_i - 1)!} \approx \frac{(g_i + n_i)!}{n_i!g_i!}$ for large n_i, g_i

BOSONS

$$t_{BE}\{n_i\} = \prod_i \frac{(g_i + n_i)!}{n_i!g_i!}$$

(Bose-Einstein Statistics)

3.7 – Statistical Weight for “Dilute Gas”

- A “dilute gas” is defined as a system where there are many more available states than occupying particles, i.e. $g_i \gg n_i$
- An example of this is a low density gas (e.g. ideal gas at STP) but note that “dilute gas” can refer to any system where the occupancy is low (e.g. atoms in solid at room temperature). In fact many systems behave as dilute gases, but the *dilute gas approximation* breaks down for systems with high densities and/or low temperatures.
- In dilute gases the statistics are equivalent to that of distinguishable particles and the system is governed by Boltzmann Statistics (i.e. we recover the “classical” case).
- To find the dilute gas approximation, we can expand factorials for the Fermion statistical weight and cancel all the expanded $(g_i - n_i)!$ terms on the denominator with some on the numerator. We get

$$t_i = \frac{g_i!}{n_i!(g_i - n_i)!} = \frac{g_i(g_i - 1)(g_i - 2)\dots(2)(1)}{n_i!(g_i - n_i)(g_i - n_i - 1)(g_i - n_i - 2)\dots(2)(1)} = \frac{g_i(g_i - 1)(g_i - 2)\dots(g_i - n_i + 1)}{n_i!}$$

- Since $g_i \gg n_i$, the numbers on the numerator are very nearly the same, i.e. $g_i \approx (g_i - n_i + 1)$, giving

$$t_i \approx \frac{(g_i)^{n_i}}{n_i!}$$

DILUTE GAS $t_{DG}\{n_i\} = \prod_i \frac{(g_i)^{n_i}}{n_i!}$ **Boltzmann Statistics**

- The same result is obtained for this approximation by starting with Bose-Einstein statistical weight

3.8 – Determining Distributions

- We now know the statistical weights for the three cases of interest:

FERMIONS: $t_{FD}\{n_i\} = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!}$ **(Fermi-Dirac Statistics)**

BOSONS $t_{BE}\{n_i\} = \prod_i \frac{(g_i + n_i)!}{n_i! g_i!}$ **(Bose-Einstein Statistics)**

DILUTE GAS $t_{DG}\{n_i\} = \prod_i \frac{(g_i)^{n_i}}{n_i!}$ **Boltzmann Statistics**

- For each we can repeat exactly the same steps as covered in Section 2 to derive expressions for the average number of particles in each state (which we call the **distribution function, f**).

3.8 – Determining Distributions

EXAMPLE: Fermi-Dirac Statistics

- Determine the **most likely distribution**
- Take natural log of the statistical weight
- Use Stirling's approximation
 $\ln x! \approx x \ln x - x$, if $x \gg 1$
- Maximise by differentiating w.r.t. n_i and setting equal to zero
- System is isolated, N and U are constant allowing addition of
- Expression only = 0 for all possible changes to level populations n_i if

$$t_{FD}\{n_i\} = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!}$$

$$\ln t_{FD} = \sum_i (\ln g_i! - \ln n_i! - \ln(g_i - n_i)!)$$

$$\ln t_{FD} \approx \sum_i (g_i \ln g_i - n_i \ln n_i - (g_i - n_i) \ln(g_i - n_i))$$

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

$$0 = \alpha \sum_i dn_i \quad 0 = \beta \sum_i \varepsilon_i dn_i \quad \beta = -\frac{1}{k_B T}$$

$$\sum_i \left(\ln \left(\frac{g_i}{n_i} - 1 \right) + \alpha - \frac{\varepsilon_i}{k_B T} \right) dn_i = 0$$

$$\ln \left(\frac{g_i}{n_i} - 1 \right) + \alpha - \frac{\varepsilon_i}{k_B T} = 0$$

$$n_i = \frac{g_i}{\exp(-\alpha + \frac{\varepsilon_i}{k_B T}) + 1} = \frac{g_i}{C \exp(\frac{\varepsilon_i}{k_B T}) + 1}$$

3.8 Distribution Functions

- Similar method gives distributions for Bose-Einstein and dilute gas statistics. Overall distributions are

$$n_i = \frac{g_i}{C \exp\left(\frac{\varepsilon_i}{k_B T}\right) + \delta} \quad C = \exp(-\alpha)$$

FERMIONS: Fermi-Dirac Dist. $\delta = +1$

DILUTE GAS: Boltzmann Dist. $\delta = 0$

BOSONS: Bose-Einstein Dist. $\delta = -1$

- The average occupancy of states at a given energy is

$$f_i = \frac{n_i}{g_i} = \frac{1}{C \exp\left(\frac{\varepsilon_i}{k_B T}\right) + \delta}$$

Note that, for a dilute gas, the distribution is the same as that obtained earlier (Section 2) for distinguishable particles.

- For energy levels represented as continuous, the distribution is expressed as

$$f(\varepsilon) = \frac{1}{C \exp\left(\frac{\varepsilon}{k_B T}\right) + \delta}$$

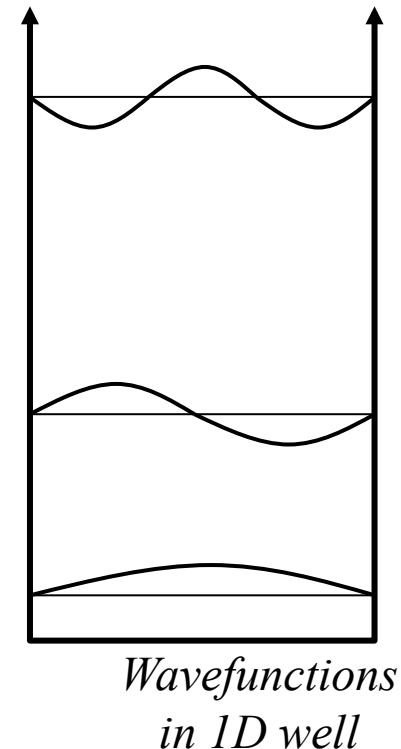
Section 4:

The density of states

- **Topics**
 - Calculating the density of states, including spin degeneracy, for infinite potential wells (2D/3D)
 - Representation of the density of states in terms of wavenumber, velocity, and energy
- **Objectives**
 - To be able to derive the density of states for simple potential wells
 - To understand how the density of states can be represented and be able to convert between different representations
 - To be able to account for spin degeneracy in the density of states

4.1 – Density of States (allowed k values)

- Recall (from Section 3) that $g(\varepsilon)d\varepsilon$ is the number of states with energy between ε and $\varepsilon+d\varepsilon$
- For a system of free particles enclosed in a volume V , we need to obtain an expression for the density of states $g(\varepsilon)d\varepsilon$ in order to find the distribution $n(\varepsilon)d\varepsilon$.
- We need the density of states regardless of which statistics apply:
 - a gas in a container (Boltzmann example)
 - electrons in a conductor/ semiconductor (Fermi-Dirac example)
 - or photons in a cavity (Bose-Einstein example)
- To calculate the density of states, we will find it useful to start by thinking of how the allowed quantum states can be described in terms of the particle wavevectors that specify them:
 - Wavenumber of a particle is given by $k = \frac{p}{\hbar} = \frac{2\pi}{\lambda}$ where p is momentum and λ is wavelength (recall wavefunctions in potential well from QM notes; see figure to right).
 - For 2D or 3D infinite square wells, we generalise the wavenumber to a wavevector, $\mathbf{k} = (k_x, k_y, k_z)$ where the three components describe the periodicity of the wavefunction in the x , y and z directions respectively



4.1 – Density of States (allowed k values)

We will usually need the density of states for a 3D box, but it is instructive first to consider 1D and 2D:

- One-Dimension

From the QM solution of a particle in a 1D box of size a , allowed values of k are

$$k = \frac{n\pi}{a}$$

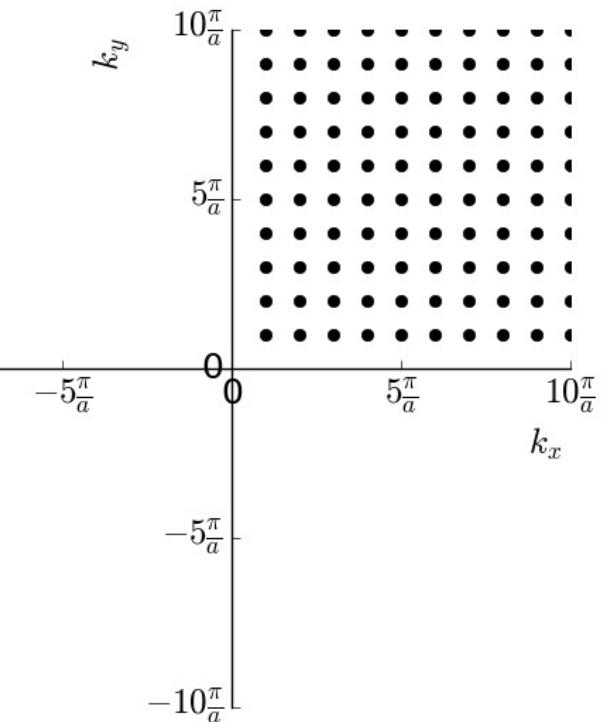
(where n is a positive integer): i.e. allowed values of k are spaced evenly at intervals of π/a (for $n \geq 1$).

- Two-Dimensions

For a particle in a 2D box of side a , the allowed values of k_x and k_y are

$$k_x = \frac{n_x \pi}{a} \text{ and } k_y = \frac{n_y \pi}{a}$$

(where n_x and n_y are both positive integers). So, in 2D, the allowed states form a regular “grid” in so-called “ k -space” (see diagram to right).



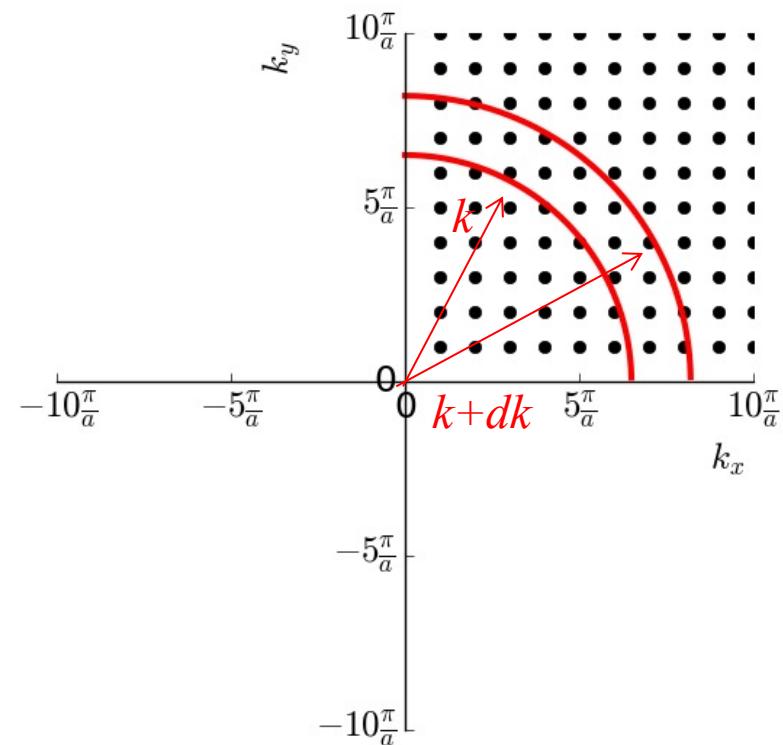
4.1 – Density of States (allowed k values)

- Two dimensions (cont.)

Working in k -space, we can calculate the density of states in terms of wavenumber $k = |\mathbf{k}| = (k_x^2 + k_y^2)^{1/2}$ from simple geometric considerations:

- There is one state for every area of $(\pi/a)^2$ in the $k_x k_y$ plane
- The area associated with the range between k and $k+dk$ is the area between the two red curves in the figure, which is given by $\frac{1}{2} \pi k dk$ ($= \frac{1}{4}$ “circumference times width”)
- So the number of states between k and $k+dk$ is

$$\begin{aligned} g(k)dk &= \frac{1}{2} \pi k dk / \left(\frac{\pi}{a}\right)^2 \\ &= \frac{a^2}{2\pi} k dk \end{aligned}$$



- This is the 2D density of states in k

4.1 – Density of States (allowed k values)

-Three dimensions

The 2D argument is readily extended to a 3D cubic box of side length a :

- The allowed values of $\mathbf{k} = (k_x, k_y, k_z)$ are now

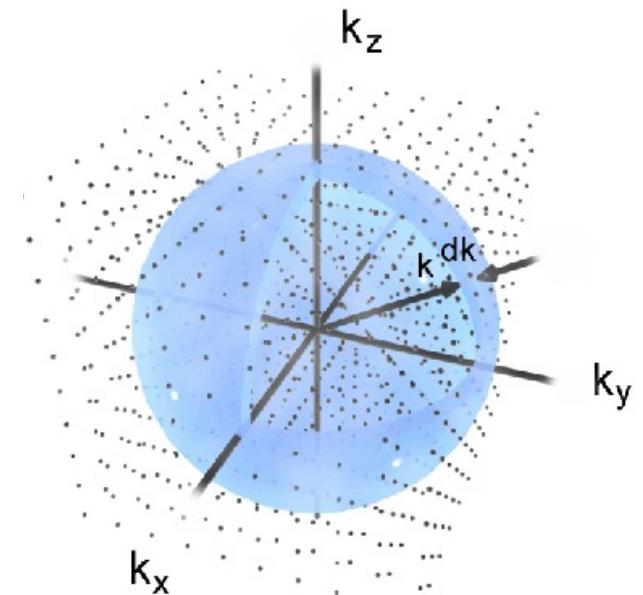
$$k_x = \frac{n_x \pi}{a}, k_y = \frac{n_y \pi}{a}, k_z = \frac{n_z \pi}{a}$$

- So we have one allowed state in each 3D k -space “volume” of $(\pi/a)^3$
- The volume in 3D k -space between k and $k+dk$ can be calculated from the surface area of a k -space sphere ($4\pi k^2$) and a factor of $1/8$ (all the states lie in the positive octant only). Thus the 3D density of states is

$$g(k)dk = \frac{1}{8} 4\pi k^2 dk / \left(\frac{\pi}{a}\right)^3$$

$$= \frac{a^3}{2\pi^2} k^2 dk$$

where $V = a^3$ is the volume of the box



4.2 – Density of States: other forms

- We have found that the density of states (in wavenumber) for a 3D box is:

$$g(k)dk = \frac{Vk^2}{2\pi^2} dk$$

- It is often useful to express the density of states in terms of other variables. To convert, we just need to know the relationship between k and the quantity we are interested in.
- For example, suppose we want to find the density of states expressed in particle velocity, $g(v)dv$

- For non relativistic particles, $v = \frac{p}{m} = \frac{\hbar k}{m}$ and so $dv = \frac{\hbar}{m} dk$. We can then substitute these forms:

$$g(k)dk = \frac{V}{2\pi^2} \left(\frac{mv}{\hbar}\right)^2 \frac{m}{\hbar} dk = \frac{V}{2\pi^2} \left(\frac{m}{\hbar}\right)^3 v^2 dv$$

- Since the number of states does not depend on whether we use velocity or wavenumber space to count them, the density of states in velocity, $g(v)$, is then given by

$$g(v)dv = g(k)dk = \frac{V}{2\pi^2} \left(\frac{m}{\hbar}\right)^3 v^2 dv$$

4.2 – Density of States: energy

- It is often particularly useful to work with the density of states in energy, $g(\varepsilon)d\varepsilon$
- Again, we obtain this from the density of states in wavenumber:

$$g(k)dk = \frac{Vk^2}{2\pi^2}dk$$

- Energy and wavenumber are related by

$$\varepsilon = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

so $d\varepsilon = \frac{\hbar^2}{m} k dk$, rearranging to $dk = \frac{m}{\hbar^2} \left(\frac{1}{k} \right) d\varepsilon = \frac{m}{\hbar^2} \left(\frac{\hbar^2}{2m\varepsilon} \right)^{1/2} d\varepsilon = \frac{1}{\hbar} \left(\frac{m}{2\varepsilon} \right)^{1/2} d\varepsilon$

- As before, the number of states does not depend on which quantity we use to count them, so

$$g(\varepsilon)d\varepsilon = g(k)dk = \frac{V}{2\pi^2} \left(\frac{2m\varepsilon}{\hbar^2} \right) \frac{1}{\hbar} \left(\frac{m}{2\varepsilon} \right)^{1/2} d\varepsilon$$

- Leading to the density of states, in energy, for a 3D volume:

$$g(\varepsilon)d\varepsilon = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{1/2} d\varepsilon$$

Note: We have derived this formula for a cube, but it is true for any enclosure of the same volume.

4.3 – Density of States: degeneracy factor

- So far, we have been counting states that differ in their spatial wavefunctions (i.e. allowed values of k) in a cubic box.
- If we have particles with spin S , then we must account for the additional degeneracy:
 - need to multiply by additional factor $G = 2S + 1$ to account for spin degeneracy (e.g. $G = 2$ for electrons)
- Including this factor, the 3D density of states in k and ε are:

$$g(k)dk = G \frac{V k^2}{2\pi^2} dk$$

$$g(\varepsilon)d\varepsilon = G \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{1/2} d\varepsilon$$

Section 5: Applications of Statistical Mechanics

- **Topics**

- Maxwell Boltzmann Speed Distribution
- Degeneracy Parameter
- Degenerate Gases, Fermi Level / Temperature
- Blackbody Radiation Distribution

- **Objectives**

To be able to

- derive the Maxwell-Boltzmann distribution and use it to determine properties of a dilute gas.
- determine when a system can be described as a dilute gas
- derive expressions for the Fermi energy and for average energy at low temperatures
- derive the Planck Blackbody formula

Section: main theme

Combining concepts from Section 3 and 4 leads to the main result that is the basis of Section 5, and indeed one of the most important conceptual expressions of this course: the number of particles in a system with energy between ε to $\varepsilon + d\varepsilon$ can be expressed as:

$$n(\varepsilon)d\varepsilon = f(\varepsilon) g(\varepsilon) d\varepsilon$$

where:

$f(\varepsilon)$ is the appropriate ***distribution function*** (i.e. fraction of states at energy ε) that will be occupied (Section 3)

$g(\varepsilon)$ is the appropriate ***density of states*** (Section 4)

5.1 – Distribution for a Dilute Gas

In Section 3, we noted that, for *distinguishable* particles (Section 1), if we consider a continuous distribution of energy states (i.e. the number of states with energies ε to $\varepsilon + d\varepsilon$ is given $g(\varepsilon)d\varepsilon$), then the number of particles with energy between ε to $\varepsilon + d\varepsilon$ is given by the classical Boltzmann distribution

$$n(\varepsilon)d\varepsilon = A \exp\left(-\frac{\varepsilon}{k_B T}\right) g(\varepsilon)d\varepsilon$$

where the normalisation constant A (which can also be written $A = N/Z$) is determined by the integral:

$$\int_0^\infty n(\varepsilon)d\varepsilon = N$$

and the partition function Z is also given by an integral:

$$Z = \frac{N}{A} = \int_0^\infty \exp\left(-\frac{\varepsilon}{k_B T}\right) g(\varepsilon)d\varepsilon$$

We have also shown in Section 3 that the Boltzmann factor $(\exp(-\varepsilon/k_B T))$ is recovered as the occupation probability for *indistinguishable* particles, in the dilute-gas limit. I.e. the *classical Boltzmann distribution* is a good approximation for dilute systems (indeed, for the dilute gas case, we can identify the constant C introduced at the end of Section 3 as $C = 1/A$).

5.1 – Distribution for a Dilute Gas

To evaluate the partition function we can substitute our expression for the density of states from Section 4: for particles with a spin degeneracy $G = 1$,

$$g(\varepsilon) d\varepsilon = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{1/2} d\varepsilon$$

Substituting this in the partition function integral above gives:

$$Z = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar} \right)^{3/2} \int_0^\infty \exp\left(-\frac{\varepsilon}{k_B T}\right) \varepsilon^{1/2} d\varepsilon$$

To evaluate this integral, use the substitution $\varepsilon = u^2$, $d\varepsilon = 2u du$

$$Z = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar} \right)^{3/2} \int_0^\infty u^2 \exp\left(-\frac{u^2}{k_B T}\right) du$$

5.1 – Distribution for a Dilute Gas

The integral encountered in Z can be found using the following standard integral result (see separate handout):

$$\text{For } I_n \equiv \int_0^\infty u^n \exp(-bu^2) du \quad , \quad I_2 = \frac{1}{4b} \left(\frac{\pi}{b} \right)^{1/2}$$

so with $b = 1/k_B T$

$$Z = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty u^2 \exp(-bu^2) du = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{k_B T}{4} (\pi k_B T)^{1/2}$$

$$Z = V \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} = V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2}$$

leading to, for the dilute-gas,

$$Z = V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2}$$

$$A = \frac{N}{Z} = \frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2}$$

5.1 – Distribution for dilute gas

Substituting our expressions for Z and $g(\varepsilon)d\varepsilon$, the dilute-gas distribution becomes

$$n(\varepsilon)d\varepsilon = \frac{N}{V} \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{3/2} \exp\left(-\frac{\varepsilon}{k_B T}\right) \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{1/2} d\varepsilon$$

$$n(\varepsilon)d\varepsilon = \frac{2N}{(k_B T)^{3/2}} \left(\frac{\varepsilon}{\pi} \right)^{1/2} \exp\left(-\frac{\varepsilon}{k_B T}\right) d\varepsilon$$

As we have done before, it is often convenient to convert this to an “occupation probability” by dividing by the total number of particles: i.e. the fraction of particle having an energy between ε and $\varepsilon + d\varepsilon$ is

$$p(\varepsilon)d\varepsilon = \frac{n(\varepsilon)d\varepsilon}{N} = \frac{2}{(kT)^{3/2}} \left(\frac{\varepsilon}{\pi} \right)^{1/2} \exp\left(-\frac{\varepsilon}{k_B T}\right) d\varepsilon$$

5.2 – Maxwell-Boltzmann Speed Distribution

The expressions formulated above can be easily converted from distribution in particle *energy* to distribution in particle *speed*. This gives rise to one of the most fundamental distributions in physics which underlies the entire kinetic theory of gasses: ***the Maxwell-Boltzmann Distribution.***

We start from the dilute gas $p(\varepsilon)d\varepsilon = \frac{2}{(kT)^{3/2}} \left(\frac{\varepsilon}{\pi}\right)^{1/2} \exp\left(-\frac{\varepsilon}{k_B T}\right) d\varepsilon$

Assuming non-relativistic particles, the energy and speed are related by

$$\varepsilon = \frac{1}{2}mv^2 \quad d\varepsilon = mvdv$$

Substituting these allows us to convert the distribution from energy to speed:

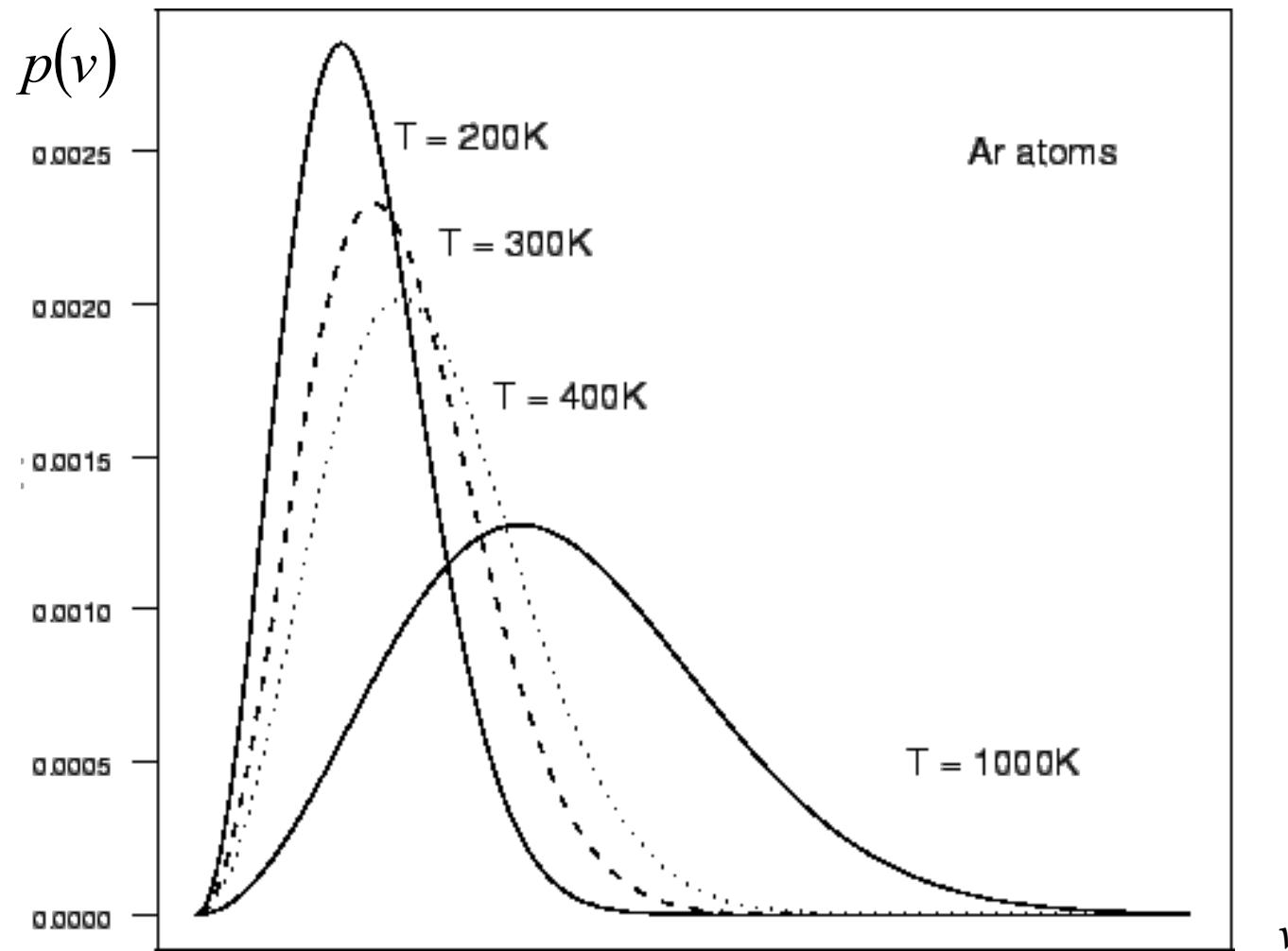
$$p(\varepsilon)d\varepsilon = \frac{2}{(k_B T)^{3/2}} \left(\frac{mv^2}{2\pi}\right)^{1/2} \exp\left(-\frac{mv^2}{2k_B T}\right) mv dv = p(v)dv$$

Rearranging to:

$$p(v)dv = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) dv$$

5.2 – Maxwell-Boltzmann Speed Distribution

$$p(v)dv = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) dv$$



5.2 – Maxwell-Boltzmann Speed Distribution

The Maxwell-Boltzmann speed distribution allows us to calculate how many particles have any particular speed in a dilute gas:

E.g. suppose we have 1 cubic metre of helium-4 gas at STP, how many particles have speed between 10 and 10.1 m/s?

The kinetic theory of gasses emerges from the MB distribution: calculation of pressure, viscosity etc. E.g. this theory is a necessary ingredient in our L2 lab Stern Gerlach experiment. See extra (**advanced**) handout for some important connections to thermal properties of gasses.

5.2 – Maxwell-Boltzmann Speed Distribution

The Maxwell-Boltzmann speed distribution allows us to calculate how many particles have any particular speed in a dilute gas:

E.g. suppose we have 1 cubic metre of helium-4 gas at STP, how many particles have speed between 10 and 10.1 m/s?

- For $T = 273 \text{ K}$, $v = 10 \text{ m/s}$ and $m = 4.003 \text{ amu}$, $p(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) = 1.9 \times 10^{-7} \text{ s m}^{-1}$
- So, for the velocity range $dv = 10.1 - 10 = 0.1 \text{ m/s}$, the fraction of particles in the range will be

$$p(v)dv = 1.9 \times 10^{-8}$$

- For an ideal gas, $PV = Nk_B T$ so the total number of particles in 1 cubic metre at STP is

$$N = 10^5 \text{ Pa} \times 1 \text{ m}^3 / k_B / 273 \text{ K} = 2.7 \times 10^{25}$$

- So the number of helium-4 particles in our volume with speed between 10 and 10.1 m/s is

$$N \times p(v)dv = 5 \times 10^{17}$$

The kinetic theory of gasses emerges from the MB distribution: calculation of pressure, viscosity etc. E.g. this theory is a necessary ingredient in our L2 lab Stern Gerlach experiment. See extra (**advanced**) handout for some important connections to thermal properties of gasses.

5.3 – When can I use the Boltzmann Distribution?

Recall that in our full treatment (Section 3), the Boltzmann distribution:

$$n(\varepsilon)d\varepsilon = A \exp\left(-\frac{\varepsilon}{k_B T}\right) g(\varepsilon) d\varepsilon$$

$$A = \frac{N}{V} \left(\frac{\hbar^2}{2\pi m k_B T} \right)^{3/2}$$

emerged from our dilute gas approximation: i.e. if we assumed $n(\varepsilon) \ll g(\varepsilon)$

Therefore it is evident from our final expression that for a **dilute gas** description to be appropriate necessitates $A \ll 1$

A is the degeneracy parameter which determines if the gas is “dilute” or “degenerate”

A system is said to be in a “degenerate state” if most of the levels are filled: this is why A is called the degeneracy parameter

5.3 – Degeneracy parameter: example

- For example consider Helium-4 gas again
 - At STP ($P = 10^5 \text{ Pa}$, $T = 273 \text{ K}$) number density is $\frac{N}{V} = \frac{P}{k_B T} = 2.65 \times 10^{25} \text{ m}^{-3}$ giving $A = 3.9 \times 10^{-6}$
 - If the gas is cooled to $T = 5 \text{ K}$ (1 atm), $A = 0.09$ which is still in the dilute gas regime.
 - However, when He becomes liquified Bose-Einstein statistics are needed (since ${}^4\text{He}$ atom is a boson)

5.3 – Physical Significance of Degeneracy Parameter

If we note that the kinetic energy of an ideal gas atom/molecule is $\varepsilon = \frac{p^2}{2m} = \frac{3}{2} k_B T$
then the degeneracy parameter can be written

$$A = \frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} = \frac{N}{V} \left(\frac{3}{2\pi} \frac{h^2}{p^2} \right)^{3/2} = 0.33 \frac{N}{V} \lambda^3$$

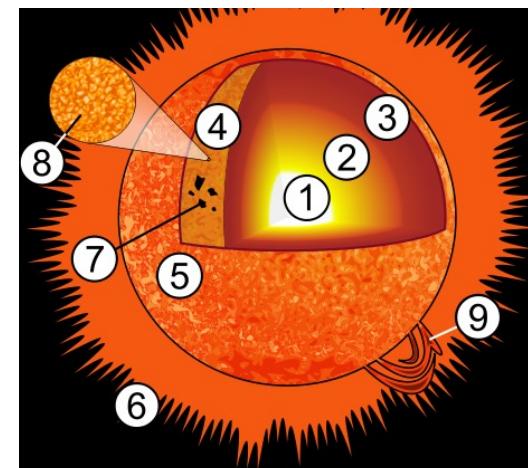
where λ is the de-Broglie wavelength

- λ^3 is quantum mechanically the volume within which the particle is localised
- So a high value of A indicates that there is high probability of the wavefunctions for neighbouring particles to overlap and hence the dilute gas approximation is not valid

5.4 – Fermi-Dirac Gases

- For a system of fermions (e.g. electrons), a dilute gas treatment cannot be used when at low temperatures and/or high densities (i.e. when the Degeneracy Parameter becomes large). Some examples of fermion “gasses” are given in the table below:

	Density (kg m ⁻³)	Temp (K)	Free electron density (m ⁻³)	Degeneracy Parameter A
Sun (corona)	10^{-16}	2×10^6	6×10^{10}	9×10^{-21}
Sun (core)	1.5×10^5	1.5×10^7	9×10^{31}	0.64
White Dwarf	10^9	10^7	3×10^{35}	4×10^3
Copper	8960	300	9×10^{28}	7200
Neutron Star (core)	10^{17}	10^7	6×10^{43} (neutrons)	10^7



5.4 – Fermi-Dirac Gasses: the Fermi Energy

- The Fermi-Dirac Distribution gives the fraction of states with an energy ε that are filled

$$f(\varepsilon) = \frac{1}{C \exp\left(\frac{\varepsilon}{k_B T}\right) + 1}$$

- The **Fermi Energy (or Fermi Level)** ε_F is defined as the energy at which $f(\varepsilon_F) = 0.5$. I.e.

$$0.5 = \frac{1}{C \exp\left(\frac{\varepsilon_F}{k_B T}\right) + 1}$$

which rearranges to give: $C = \exp\left(-\frac{\varepsilon_F}{k_B T}\right)$ i.e., the Fermi-Dirac distribution is often written as:

$$f(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - \varepsilon_F}{k_B T}\right) + 1}$$

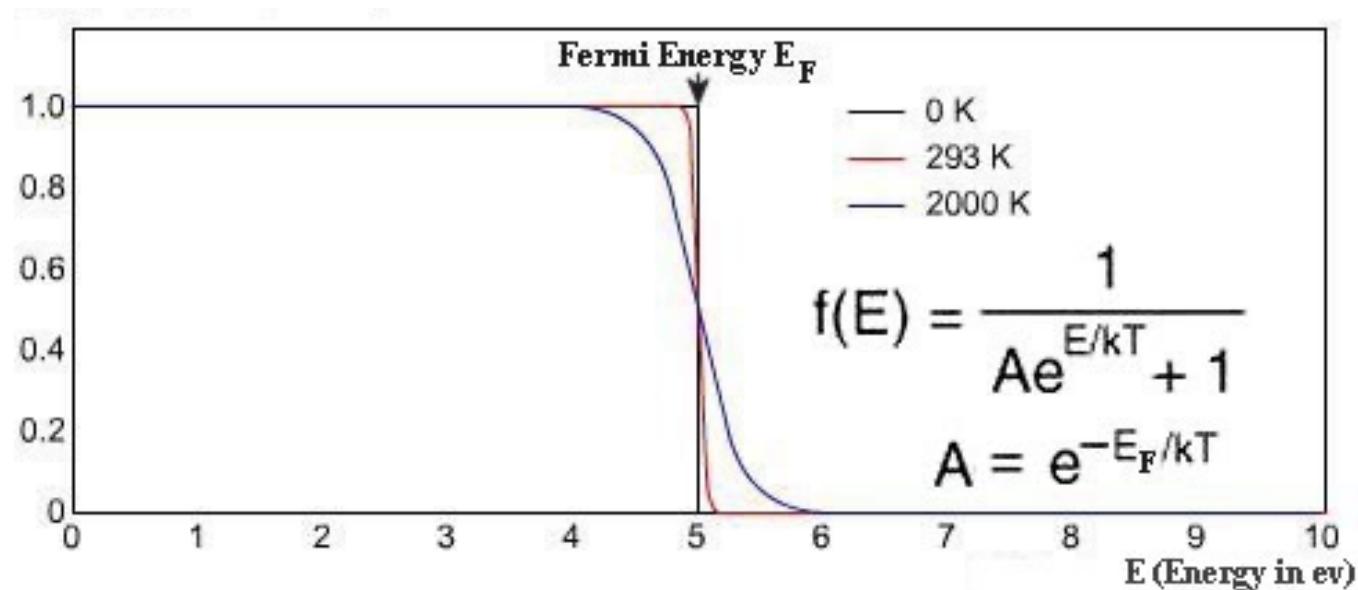
5.4 – Fermi-Dirac Gasses: the Fermi Energy

For the Fermi-Dirac distribution we can see that, as $T \rightarrow 0$,

- $f \approx 0$ for $\varepsilon > \varepsilon_F$
- $f \approx 1$ for $\varepsilon < \varepsilon_F$

$$f(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon - \varepsilon_F}{k_B T}\right) + 1}$$

I.e. as $T \rightarrow 0$, the levels are strongly “*degenerate*” (fully filled). In this case the Fermi level is the maximum energy a particle can possess.



Fermi-Dirac distribution for several temperatures

5.4 – Fermi-Dirac Gasses: the Fermi Energy

By considering the behaviour as $T \rightarrow 0$, we can determine a value for the Fermi level by recognising that all the states up to the Fermi level will be filled, and all above empty. I.e. for a total of N particles:

$$N = \int_0^{\infty} n(\varepsilon) d\varepsilon = \int_0^{\infty} f(\varepsilon) g(\varepsilon) d\varepsilon \approx \int_0^{\varepsilon_F} g(\varepsilon) d\varepsilon$$

We can now use our expression for the density of states (from Section 4) with e.g. a spin degeneracy of $G = 2$ (for electrons):

$$g(\varepsilon) d\varepsilon = \frac{GV}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{1/2} d\varepsilon$$

Using this we find

$$N = \int_0^{\varepsilon_F} \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{1/2} d\varepsilon = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \left[\frac{2}{3} \varepsilon^{3/2} \right]_0^{\varepsilon_F}$$

$$\boxed{\varepsilon_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3}}$$

5.4 – Fermi-Dirac Gasses: Fermi Temperature

We often work in terms of the Fermi temperature T_F , which is defined by

$$\epsilon_F = k_B T_F$$

Substituting this definition into our expression for the Fermi energy (see previous slide) gives:

$$T_F = \frac{\hbar^2}{2mk_B} \left(\frac{3\pi^2 N}{V} \right)^{2/3}$$

This provides a guide for determining if Boltzmann statistics can be used (i.e. dilute gas): we can express the degeneracy parameter A in terms of T_F

$$A = \frac{N}{V} \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{3/2} = \frac{8}{3\pi^{1/2}} \left(\frac{T_F}{T} \right)^{3/2} \approx 1.5 \left(\frac{T_F}{T} \right)^{3/2}$$

Therefore for temperatures

$T \gg T_F$, $A \ll 1$ it is a dilute gas and Boltzmann statistics can be used

$T < T_F$, $A > 1$ it is a degenerate gas and Fermi-Dirac statistics must be used

5.5 Fermi-Dirac “Degeneracy” Pressure

For a Fermi-Dirac gas as $T \rightarrow 0$, the average energy per particle U/N is

$$\frac{U}{N} = \frac{\int_0^\infty \varepsilon n(\varepsilon) d\varepsilon}{\int_0^\infty n(\varepsilon) d\varepsilon} = \frac{\int_0^{\varepsilon_F} \varepsilon g(\varepsilon) d\varepsilon}{\int_0^{\varepsilon_F} g(\varepsilon) d\varepsilon} = \frac{\int_0^{\varepsilon_F} \varepsilon^{3/2} d\varepsilon}{\int_0^{\varepsilon_F} \varepsilon^{1/2} d\varepsilon} = \frac{3}{5} \varepsilon_F$$

Thus, even at absolute zero the system has non-zero energy and the average energy is more than half the Fermi energy (this is because the density of states increases with energy).

For a weakly interacting gas, the total energy of the system is given by $P = \frac{2}{3} \frac{U}{V}$ (this result is derived in the handout on “Advanced Thermodynamics”).

Thus for an ideal Fermi-Dirac gas, as $T \rightarrow 0$ the system produces a “degeneracy pressure”

$$P = \frac{2}{5} \frac{N}{V} \varepsilon_F$$

This pressure is what stops White Dwarf and Neutron stars from collapsing under their own gravity. In contrast, a classical ideal gas would provide zero pressure as $T \rightarrow 0$.

5.6 Blackbody Radiation and the Planck Formula

For a system of photons enclosed in a cavity, the light emitted from a pinhole is known as blackbody radiation. The distribution of photons (in energy, frequency or wavelength) inside such a cavity is governed by the Planck “black body” formula.

At the very start of this module, you were introduced to the problem of the “ultraviolet catastrophe”, which was a challenge to Classical physics. We are now ready to appreciate the full quantum mechanical / statistical mechanical solution to that problem.



5.6 Photons: a special case!

Photons are spin-1 particles and (accordingly) bosons; they obey Bose-Einstein statistics.

However they are a special case: the photon is massless, which means that their total number is not fixed (only the total energy is fixed). This means that the Bose-Einstein distribution function needs to be slightly modified: the constant α (the Lagrange multiplier normally introduced to allow us to impose conservation of particle number) does not appear.

Photons are sometimes called “phoney bosons” because of the need for this adjustment.



5.6 Deriving the photon distribution function

The distribution function for photons can be derived using (almost!) the same method as the usual Bose-Einstein distribution:

- Start with the Boson statistical weight
- Take the logarithm
- Use Stirling's approximation
- Differentiate, and set to zero (to find max)
- Introduce the total energy constrain (but no constraint on particle number)
- Combine the derivative and the constraint

$$t_{BE}\{n_i\} = \prod_i \frac{(g_i + n_i)!}{n_i! g_i!}$$

$$\ln t_{BE} = \sum_i (\ln(g_i + n_i)! - \ln n_i! - \ln g_i!)$$

$$\ln t_{BE} \approx \sum_i ((g_i + n_i) \ln(g_i + n_i) - n_i \ln n_i - g_i \ln g_i)$$

$$d(\ln t_{BE}) = \sum_i \left(\ln \left(\frac{g_i + n_i}{n_i} \right) \right) dn_i = 0$$

$$0 = \beta \sum_i \varepsilon_i dn_i \quad \beta = -\frac{1}{k_B T} \quad \text{no } \alpha \text{ constant here}$$

$$\sum_i \left(\ln \left(\frac{g_i}{n_i} + 1 \right) - \frac{\varepsilon_i}{k_B T} \right) dn_i = 0$$

5.6 Deriving the photon distribution function

- (Copied from last slide)

$$\sum_i \left(\ln \left(\frac{g_i}{n_i} + 1 \right) - \frac{\varepsilon_i}{k_B T} \right) dn_i = 0$$

- Set coefficients to zero

$$\ln \left(\frac{g_i}{n_i} + 1 \right) - \frac{\varepsilon_i}{k_B T} = 0$$

- Rearrange to obtain the distribution function

$$n_i = \frac{g_i}{\exp(\frac{\varepsilon_i}{k_B T}) - 1}$$

$$f_i = \frac{n_i}{g_i} = \frac{1}{\exp(\frac{\varepsilon_i}{k_B T}) - 1}$$

- For continuous energies, this becomes

$$f(\varepsilon) = \frac{1}{\exp\left(\frac{\varepsilon}{k_B T}\right) - 1}$$

The distribution function differs from the usual Bose-Einstein case only in that there is no “C” normalisation constant (equivalent to the statement that $\alpha = 0$).

5.6 Blackbody Radiation – Planck Formula

In addition to the distribution function, to calculate the photon distribution we need the density of states:

$$g(k)dk = \frac{GVk^2}{2\pi^2} dk$$

Photons are have 2 possible polarisation states, therefore $G=2$.

For photons, it is convenient to work in wavelength and so we convert the density of states using the relationship between wavenumber and wavelength:

$$k = \frac{2\pi}{\lambda} \quad dk = -\frac{2\pi}{\lambda^2} d\lambda$$

yielding: $g(\lambda)d\lambda = \frac{8\pi V}{\lambda^4} d\lambda$ (ignore negative as only interested in magnitude)

5.6 Blackbody Radiation – Planck Formula

We can now calculate the distribution of photons in wavelength (using $\varepsilon = \frac{hc}{\lambda}$ for photons):

$$n(\lambda)d\lambda = f(\lambda)g(\lambda)d\lambda = \frac{1}{\exp\left(\frac{hc}{\lambda k_B T}\right) - 1} \frac{8\pi V}{\lambda^4} d\lambda$$

Usually, this result is not given in number of photons but in terms of energy per unit volume: $u(\lambda)d\lambda$

The conversion is easy since each photon has energy $\varepsilon = \frac{hc}{\lambda}$, thus:

$$u(\lambda)d\lambda = \frac{1}{V} \frac{hc}{\lambda} n(\lambda)d\lambda$$

$$u(\lambda)d\lambda = \frac{8\pi hc}{\lambda^5 \left(\exp\left(\frac{hc}{\lambda k_B T}\right) - 1 \right)} d\lambda$$

the Planck Blackbody formula

5.7: The ultraviolet catastrophe resolved

$$u(\lambda)d\lambda = \frac{8\pi hc}{\lambda^5 \left(\exp\left(\frac{hc}{\lambda k_B T}\right) - 1 \right)} d\lambda$$

- This Planck function obtained via our quantum/statistical treatment resolved the classical “ultraviolet catastrophe”: the energy density no longer diverges at short wavelengths (see figures on next slide).
- The classical form is, however, recovered in the long wavelength limit: i.e. for large λ we find the Rayleigh-Jeans law (this limit is reproduced by using $e^x \rightarrow 1 + x$ as $x \rightarrow 0$ to expand the exponential):

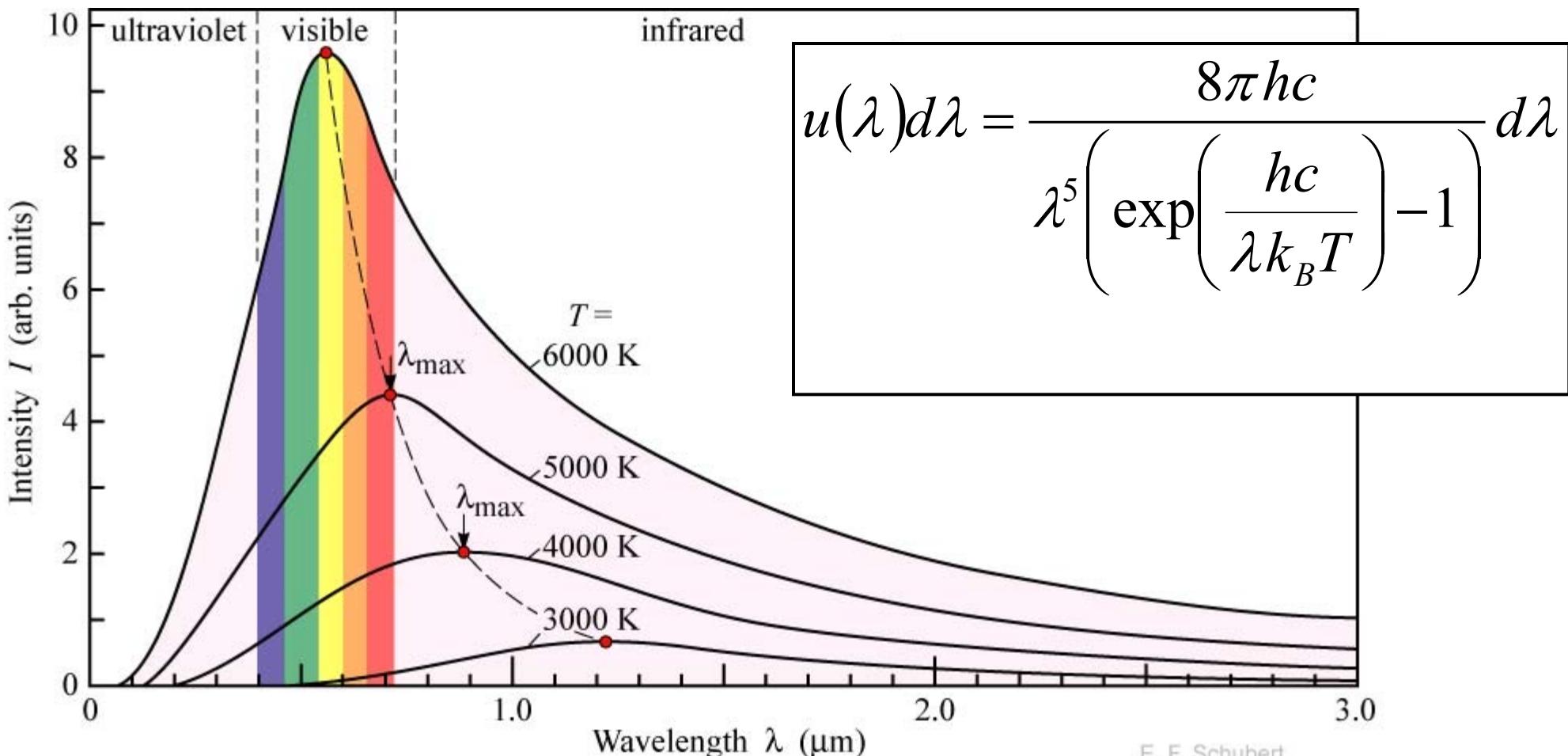
$$u(\lambda)d\lambda = \frac{8\pi k_B T}{\lambda^4} d\lambda$$

- We can also see that this result is recovered if there is no quantisation (i.e. $h \rightarrow 0$).

5.7 Blackbody Radiation – Wien's law

- Differentiating to obtain the wavelength of the maximum of this distribution yields **Wien's displacement law:**

$$\lambda_{MAX} T = \text{constant} = 2.90 \times 10^{-3} \text{ m.K}$$



5.7: Cosmic Microwave Background

- The blackbody radiation of the whole Universe (in microwave region) fits the Planck formula for a temperature of 2.725 K. This is the afterglow of the Big Bang and agrees well with models for the cooling of the Universe

