

Introduction to Statistical Mechanics

- Statistical mechanics attempts to answer how microscopic behaviour of particles or small constituents leads to a particular macroscopic property of the material
- Statistical mechanics does not care about the actual motions or interactions of individual particles, but instead with the most probable behaviour of the individuals.

**Number of particles
of energy ϵ**

$$n(\epsilon) = g(\epsilon)f(\epsilon)$$

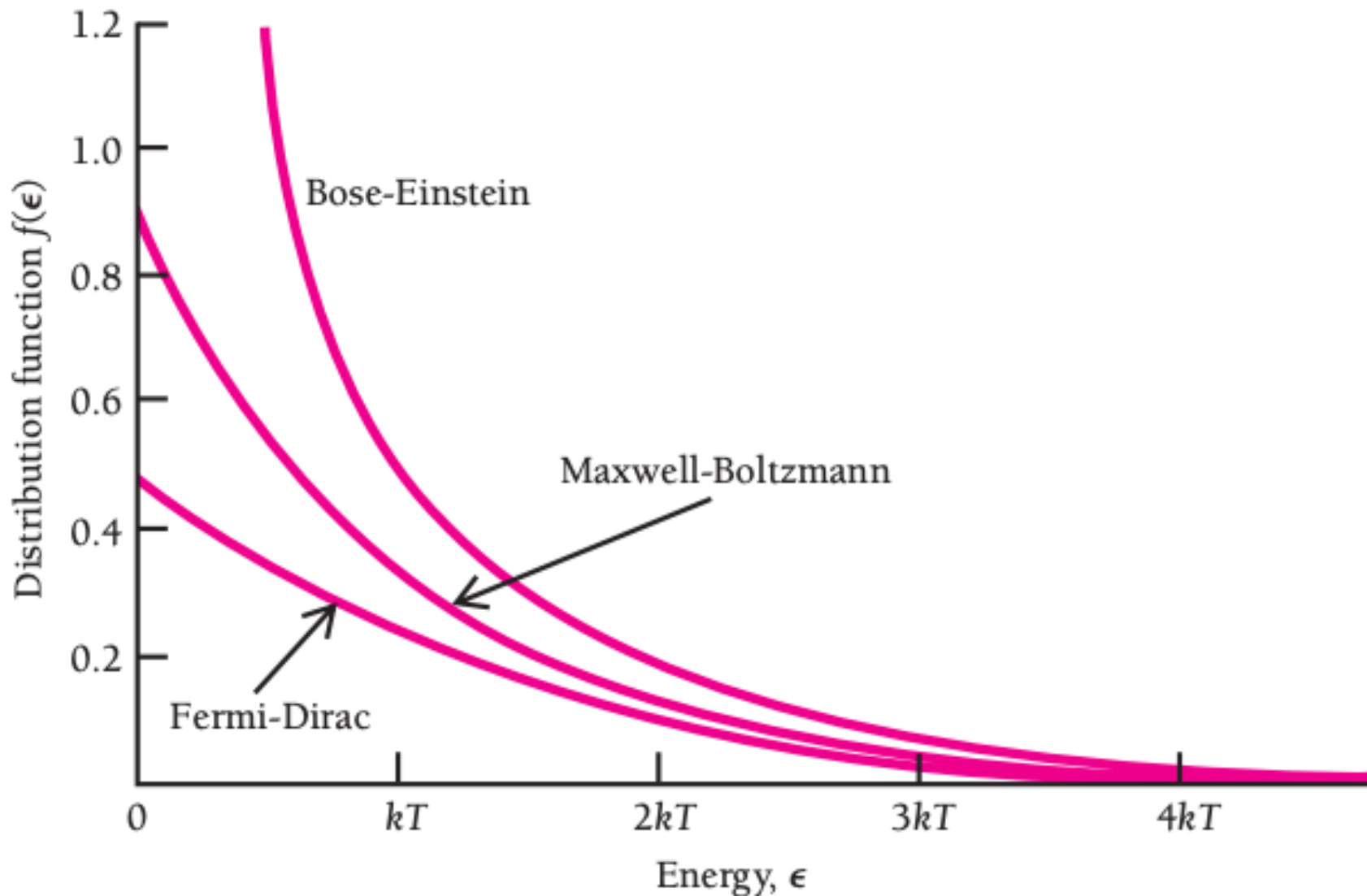
where $g(\epsilon)$ = number of states of energy ϵ
= statistical weight corresponding to energy ϵ
 $f(\epsilon)$ = distribution function
= average number of particles in each state of energy ϵ
= probability of occupancy of each state of energy ϵ

Statistical distributions



	Maxwell-Boltzmann	Bose-Einstein	Fermi-Dirac
Applies to systems of	Identical, distinguishable particles	Identical, indistinguishable particles that do not obey exclusion principle	Identical, indistinguishable particles that obey exclusion principle
Category of particles	Classical	Bosons	Fermions
Properties of particles	Any spin, particles far enough apart so wave functions do not overlap	Spin 0, 1, 2, . . . ; wave functions are symmetric to interchange of particle labels	Spin $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$; wave functions are antisymmetric to interchange of particle labels
Examples	Molecules of a gas	Photons in a cavity; phonons in a solid; liquid helium at low temperatures	Free electrons in a metal; electrons in a star whose atoms have collapsed (white dwarf stars)
Distribution function (number of particles in each state of energy ϵ at the temperature T)	$f_{MB}(\epsilon) = Ae^{-\epsilon/kT}$	$f_{BE}(\epsilon) = \frac{1}{e^{\alpha}e^{\epsilon/kT} - 1}$	$f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon-\epsilon_F)/kT} + 1}$
Properties of distribution	No limit to number of particles per state	No limit to number of particles per state; more particles per state than f_{MB} at low energies; approaches f_{MB} at high energies	Never more than 1 particle per state; fewer particles per state than f_{MB} at low energies; approaches f_{MB} at high energies

Statistical distributions



Statistical distributions

Maxwell–Boltzmann Statistics: (Classical case)

How many distinct ways can we put the 2 identical particles into the 2 states?

Single Particle State	1	2

	AB	
		AB
	A	B
	B	A

- Particles are distinguishable so let's label them A and B
- Any number of particles can be in any state
- A total of 4 states of the system as a whole

Total number of ways in which N_i particles can be distributed in g_i quantum states:

$$W_i = \frac{(g_i)^{N_i}}{(N_i)!}$$

The total number of ways of distributing N_1 particles in g_1 states, N_2 particles in g_2 states and so on, will be:

$$W = W_1 W_2 W_3 \dots$$

Statistical distributions

Bose-Einstein Statistics: (Quantum mechanical case)

Single Particle State

1

2

AA

AA

A

A

- Particles are indistinguishable both particles are labelled A
- Any number of particles can be in one state
- A total of 3 states of the system as a whole
- 2/3 of the states have the particles bunched in the same state and 1/3 of the states have them in separate states.

Total number of ways in which N_i particles of energy E_i can be distributed in g_i states:

$$W_i = \frac{(N_i + g_i - 1)!}{(N_i)! (g_i - 1)!}$$

The total number of ways of distributing N_1 particles in g_1 states, N_2 particles in g_2 states and so on, will be:

$$W = W_1 W_2 W_3 \dots\dots\dots$$

Statistical distributions

Fermi-Dirac Statistics: (Quantum mechanical case)

Single Particle State

1

2

A

A

- Particles are indistinguishable both particles are labelled A
- A total of 1 states of the system as a whole
- None of the states have the particles bunched up; the Pauli exclusion principle forbids that.

Total number of ways in which N_i fermions can be distributed in g_i quantum states:

$$W_i = \frac{(g_i)!}{(N_i)! (g_i - N_i)!} = C(g_i, N_i)$$

The total number of ways of distributing N_1 particles in g_1 states, N_2 particles in g_2 states and so on, will be:

$$W = W_1 W_2 W_3 \dots$$

Maxwell-Boltzmann Statistics (Classical Statistics)

Maxwell-Boltzmann
distribution function

$$f_{MB}(\epsilon) = Ae^{-\epsilon/kT}$$

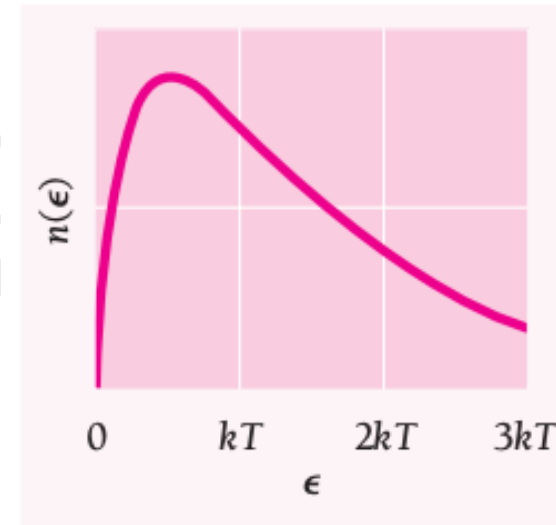
Boltzmann's
constant

$$k = 1.381 \times 10^{-23} \text{ J/K} = 8.617 \times 10^{-5} \text{ eV/K}$$

Maxwell-Boltzmann

$$n(\epsilon) = Ag(\epsilon)e^{-\epsilon/kT}$$

Maxwell-Boltzmann energy distribution for the molecules of an ideal gas. The average molecular energy is $3/2 kT$.



Molecular energies in an ideal gas (M-B Statistics)

Number of molecules with energies between ϵ and $\epsilon + d\epsilon$

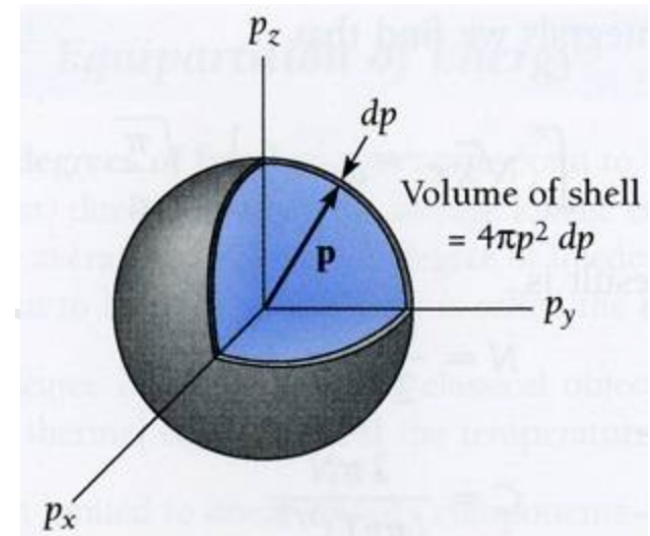
$$n(\epsilon) d\epsilon = [g(\epsilon) d\epsilon] [f(\epsilon)] = Ag(\epsilon) e^{-\epsilon/kT} d\epsilon$$

$$p = \sqrt{2m\epsilon} = \sqrt{p_x^2 + p_y^2 + p_z^2}$$

Number of momentum states

$$g(p) dp = Bp^2 dp$$

$$g(\epsilon) d\epsilon = Bp^2 dp$$



Because

$$p^2 = 2m\epsilon \quad \text{and} \quad dp = \frac{m d\epsilon}{\sqrt{2m\epsilon}}$$

Molecular energies in an ideal gas (M-B Statistics)

Number of energy
states

$$g(\epsilon) d\epsilon = 2m^{3/2} B \sqrt{\epsilon} d\epsilon$$

The number of molecules with energies between ϵ and $d\epsilon$ is therefore

$$n(\epsilon) d\epsilon = C \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon$$

where $C(= 2m^{3/2} AB)$ is a constant to be evaluated.

Normalization

$$N = \int_0^{\infty} n(\epsilon) d\epsilon = C \int_0^{\infty} \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon$$

Molecular energies in an ideal gas (M-B Statistics)

$$\int_0^{\infty} \sqrt{x} e^{-ax} dx = \frac{1}{2a} \sqrt{\frac{\pi}{a}}$$

Here $a = 1/kT$, and the result is

$$N = \frac{C}{2} \sqrt{\pi} (kT)^{3/2}$$

$$C = \frac{2\pi N}{(\pi kT)^{3/2}}$$

and, finally,

**Molecular energy
distribution**

$$n(\epsilon) d\epsilon = \frac{2\pi N}{(\pi kT)^{3/2}} \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon$$

Average Molecular Energy

$$E = \int_0^{\infty} \epsilon n(\epsilon) d\epsilon = \frac{2\pi N}{(\pi kT)^{3/2}} \int_0^{\infty} \epsilon^{3/2} e^{-\epsilon/kT} d\epsilon$$

Making use of the definite integral

$$\int_0^{\infty} x^{3/2} e^{-ax} dx = \frac{3}{4a^2} \sqrt{\frac{\pi}{a}}$$

we have

**Total energy of N
gas molecules**

$$E = \left[\frac{2\pi N}{(\pi kT)^{3/2}} \right] \left[\frac{3}{4} (kT)^2 \sqrt{\pi kT} \right] = \frac{3}{2} NkT$$

The average energy of an ideal-gas molecule is E/N , or

**Average molecular
energy**

$$\bar{\epsilon} = \frac{3}{2} kT$$

Distribution of molecular speeds

$$\epsilon = \frac{1}{2}mv^2 \quad d\epsilon = mv \, dv$$

**Molecular-speed
distribution**

$$n(v) \, dv = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT} \, dv$$

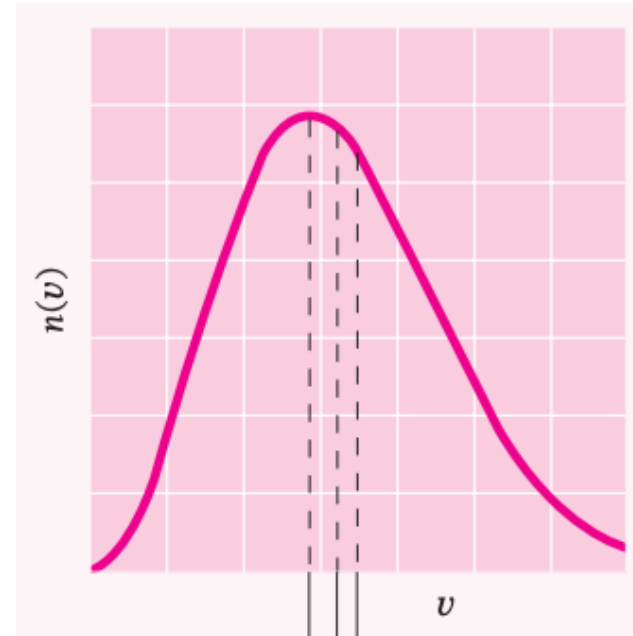
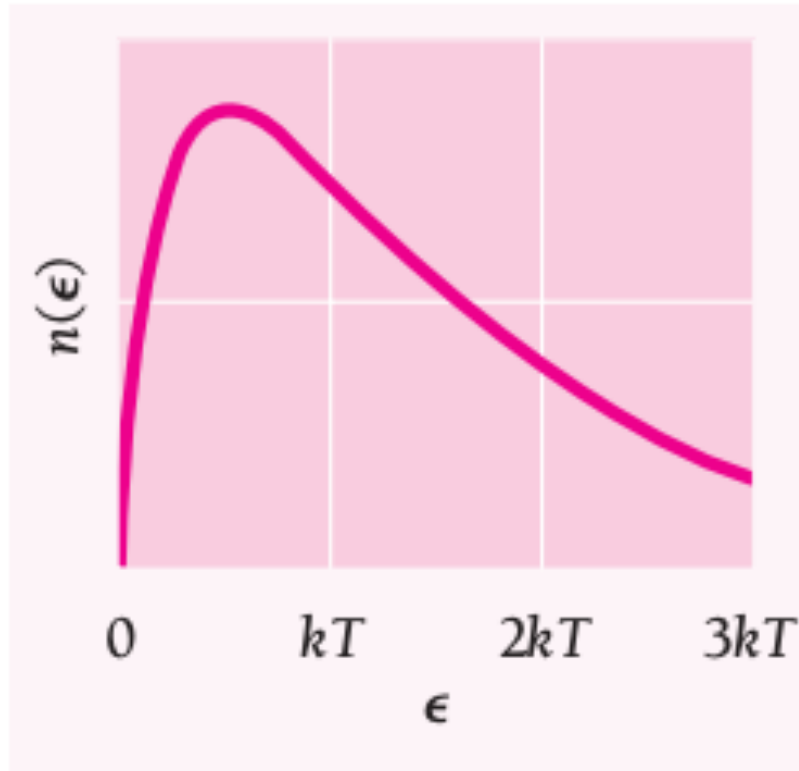
RMS speed

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}}$$

**Most probable
speed**

$$v_p = \sqrt{\frac{2kT}{m}}$$

M-B distribution of molecular energy and speeds



$\sqrt{v^2} = \text{root-mean-square speed} = \sqrt{3kT/m}$
 $\bar{v} = \text{average speed} = \sqrt{8kT/\pi m}$
 $v_p = \text{most probable speed} = \sqrt{2kT/m}$

Equipartition of Energy

- “The average energy per degree of freedom of any classical object that is a member of a system of such objects in thermal equilibrium at the temperature T is $1/2 kT$.”

$$\frac{1}{2} m \overline{v_x^2} = \frac{1}{2} m \overline{v_y^2} = \frac{1}{2} m \overline{v_z^2} = \frac{1}{2} kT$$

- A rigid diatomic molecule has five degrees of freedom, one each for motions in the x , y , and z directions and two for rotations about axes perpendicular to its symmetry axis.
- A 1D harmonic oscillator has two degrees of freedom, one that corresponds to its kinetic energy $1/2 m v_x^2$ and the other to its potential energy $1/2 K(\Delta x)^2$, where K is the force constant. Each oscillator in a system of them in thermal equilibrium accordingly has a total average energy of $2(1/2 kT) = kT$ (quantization is disregarded!)

Symmetric and anti-symmetric wavefunctions

For a system of two particles, 1 and 2, one of which is in state a and the other in state b. When the particles are distinguishable there are two possibilities for occupancy of the states

$$\psi_I = \psi_a(1)\psi_b(2)$$

$$\psi_{II} = \psi_a(2)\psi_b(1)$$

Bosons

$$\psi_B = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)]$$

[Symmetric wavefunctions]

Fermions

$$\psi_F = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)]$$

[Anti-symmetric wavefunctions]

If both particles are in the same state

$$\psi_M = \psi_a(1)\psi_a(2)$$

Distinguishable particles

$$\psi_M^* \psi_M = \psi_a^*(1)\psi_a^*(2)\psi_a(1)\psi_a(2)$$

Symmetric and anti-symmetric wavefunctions

$$\psi_B = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_a(2) + \psi_a(1)\psi_a(2)] = \frac{2}{\sqrt{2}} \psi_a(1)\psi_a(2) = \sqrt{2}\psi_a(1)\psi_a(2)$$

Bosons

$$\psi_B^* \psi_B = 2\psi_a^*(1)\psi_a^*(2)\psi_a(1)\psi_a(2) = 2\psi_M^* \psi_M$$

Fermions

$$\psi_F = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_a(2) - \psi_a(1)\psi_a(2)] = 0$$

- In a system of bosons, the presence of a particle in a certain quantum state increases the probability that other particles are to be found in the same state
- In a system of fermions, the presence of a particle in a certain state prevents any other particles from being in that state

Fermi-Dirac Distribution

Fermi energy

$$\epsilon_F = -\alpha kT$$

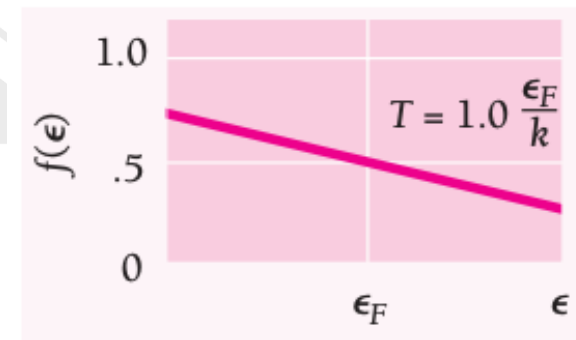
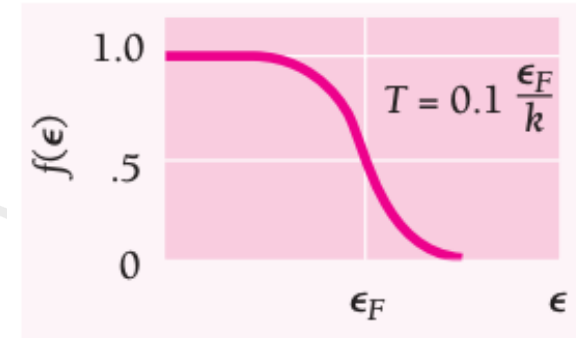
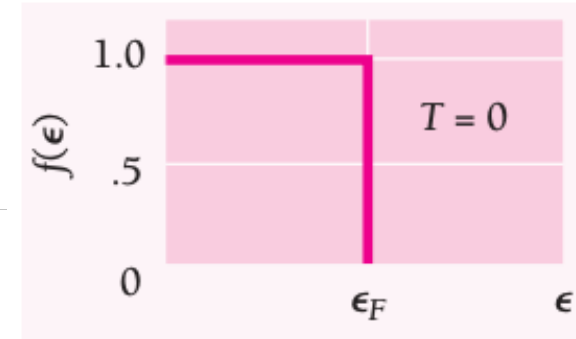
Fermi-Dirac

$$f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon - \epsilon_F)/kT} + 1}$$

$$T = 0, \epsilon < \epsilon_F: \quad f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon - \epsilon_F)/kT} + 1} = \frac{1}{e^{-\infty} + 1} = \frac{1}{0 + 1} = 1$$

$$T = 0, \epsilon > \epsilon_F: \quad f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon - \epsilon_F)/kT} + 1} = \frac{1}{e^{\infty} + 1} = 0$$

- At $T = 0$, all the energy states up to the Fermi energy ϵ_F are occupied
- At a low temperature ($kT < \epsilon_F$), some fermions will leave states just below ϵ_F and move into states just above ϵ_F
- At a higher temperature, fermions from any state below ϵ_F may move into states above ϵ_F



Planck's radiation law

$$\epsilon_n = nh\nu, \quad n = 0, 1, 2, 3, \dots$$

Using Maxwell Boltzmann statistics: _____

$$\bar{\epsilon} = \frac{h\nu}{e^{h\nu/kT} - 1}$$

**Planck radiation
formula**

$$u(\nu) d\nu = \bar{\epsilon} G(\nu) d\nu = \frac{8\pi h}{c^3} \frac{\nu^3 d\nu}{e^{h\nu/kT} - 1}$$

While Planck got the right formula, his derivation is seriously flawed from the perspective of quantum harmonic oscillators inside the cavity with energies $\epsilon_n = (n + \frac{1}{2}) h\nu$, $n = 0, 1, 2, 3, \dots$

Planck's radiation law (B-E Statistics)

$$\epsilon_n = \left(n + \frac{1}{2}\right) h\nu, \quad n = 0, 1, 2, 3, \dots$$

EM waves inside the cavity is equivalent to photon gas, average number of photons $f(\nu)$ in each state of energy $h\nu$ is given by BE distribution. Since number of photons inside the cavity are not fixed, $\alpha = 0$

Photon distribution function

$$f(\nu) = \frac{1}{e^{h\nu/kT} - 1}$$

$$u(\nu) d\nu = h\nu G(\nu) f(\nu) d\nu = \frac{8\pi h}{c^3} \frac{\nu^3 d\nu}{e^{h\nu/kT} - 1}$$

Atomic Specific Heat

Classical internal
energy of solid

$$E = 3N_0kT = 3RT$$

where $R = N_0k = 8.31 \times 10^3 \text{ J/Kmol} \cdot \text{K} = 1.99 \text{ kcal/kmol} \cdot \text{K}$

Specific heat at
constant volume

$$c_V = \left(\frac{\partial E}{\partial T} \right)_V$$

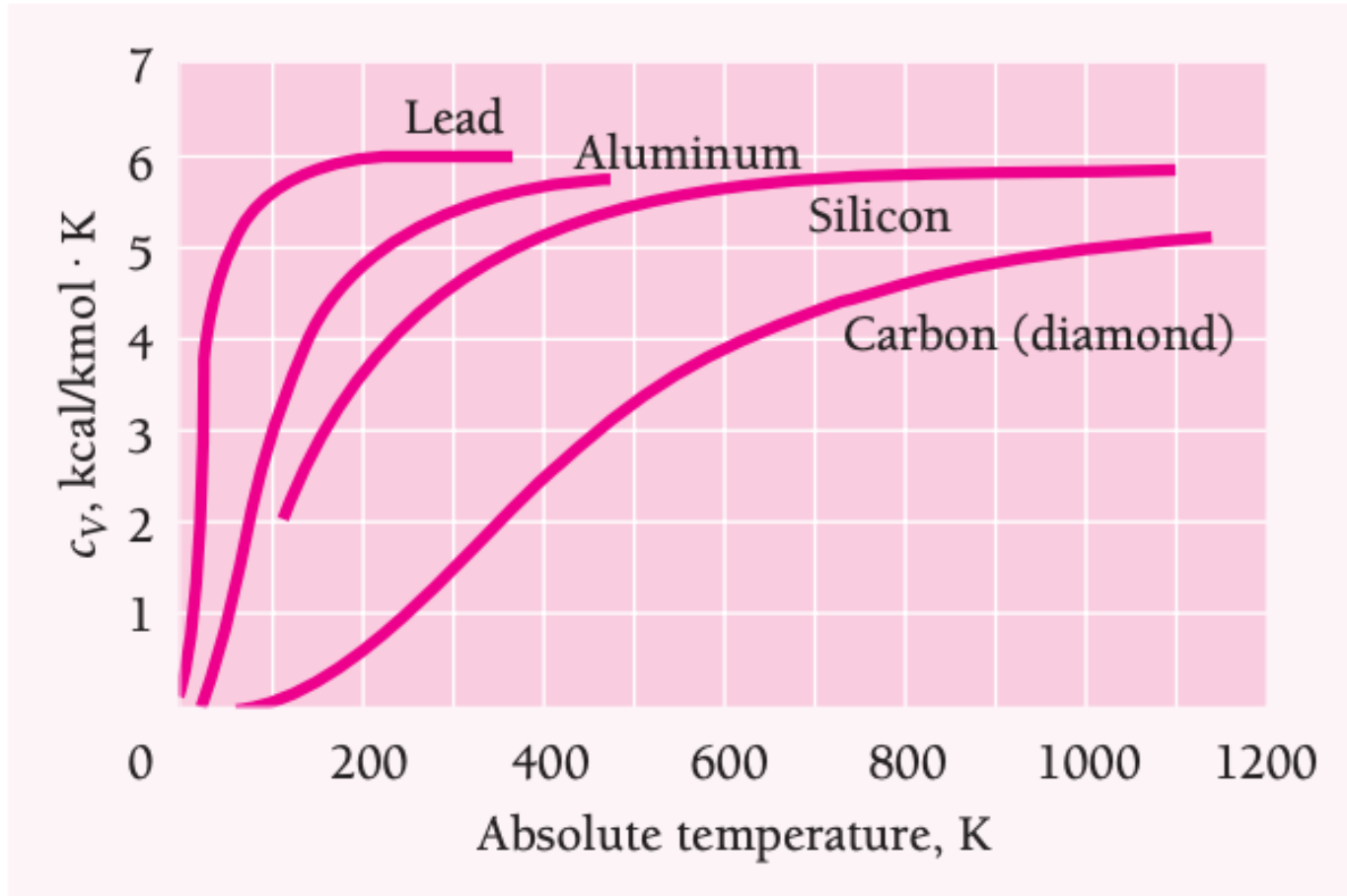
and so here

Dulong-Petit law

$$c_V = 3R = 5.97 \text{ kcal/kmol} \cdot \text{K}$$

Dulong-Petit law fails for certain light elements such as B, Be and C, for which C_V is 3.34, 3.85, and 1.46 kcal/kmol·K, respectively at 20°C

Specific Heat in Solids



Specific heats of all solids drop sharply at low temperatures and approach 0 as $T \rightarrow 0$ K

Specific Heat in Solids (Einstein's Quantum theory)

Average energy
per oscillator

$$\bar{\epsilon} = h\nu f(\nu) = \frac{h\nu}{e^{h\nu/kT} - 1}$$

Internal energy
of solid

$$E = 3N_0\bar{\epsilon} = \frac{3N_0h\nu}{e^{h\nu/kT} - 1}$$

Einstein specific
heat formula

$$c_V = \left(\frac{\partial E}{\partial T} \right)_V = 3R \left(\frac{h\nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}$$

- At high temperatures, $h\nu \ll kT$, $C_V \approx 3R$, the Dulong-Petit value
- At low temperatures, $h\nu \gg kT$, $C_V \approx 3R \left(\frac{h\nu}{kT} \right)^2 e^{-\frac{h\nu}{kT}}$
- While the agreement is reasonably good at $T \rightarrow 0$ K, experimentally $C_V \propto T^3$ at low temperatures

Free electron gas (F-D Statistics)

$$j_x = \frac{2L}{\lambda} = 1, 2, 3, \dots = \text{number of half-wavelengths in } x \text{ direction}$$

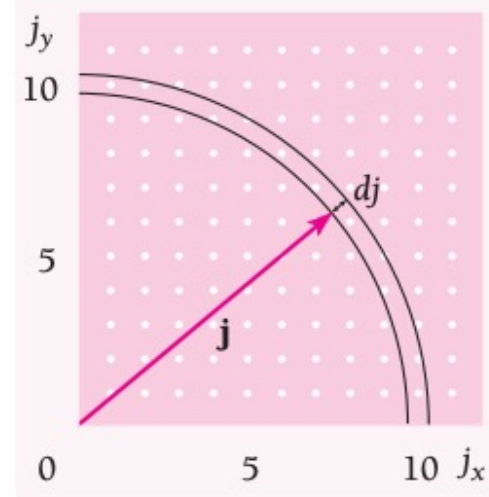
$$j_y = \frac{2L}{\lambda} = 1, 2, 3, \dots = \text{number of half-wavelengths in } y \text{ direction}$$

$$j_z = \frac{2L}{\lambda} = 1, 2, 3, \dots = \text{number of half-wavelengths in } z \text{ direction}$$

**Standing waves
in a cubic cavity**

$$j_x^2 + j_y^2 + j_z^2 = \left(\frac{2L}{\lambda} \right)^2$$

$$\begin{aligned} j_x &= 0, 1, 2, \dots \\ j_y &= 0, 1, 2, \dots \\ j_z &= 0, 1, 2, \dots \end{aligned}$$



**Number of
standing waves**

$$g(j) dj = (2)(\frac{1}{8})(4\pi j^2 dj) = \pi j^2 dj$$

$$j = \frac{2L}{\lambda} = \frac{2Lp}{h} = \frac{2L\sqrt{2m\epsilon}}{h} \quad dj = \frac{L}{h} \sqrt{\frac{2m}{\epsilon}} d\epsilon$$

**Number of
electron states**

$$g(\epsilon) d\epsilon = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \sqrt{\epsilon} d\epsilon$$

Free electron gas (F-D Statistics)

$$N = \int_0^{\epsilon_F} g(\epsilon) d\epsilon = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \int_0^{\epsilon_F} \sqrt{\epsilon} d\epsilon = \frac{16\sqrt{2}\pi V m^{3/2}}{3h^3} \epsilon_F^{3/2}$$

Fermi energy

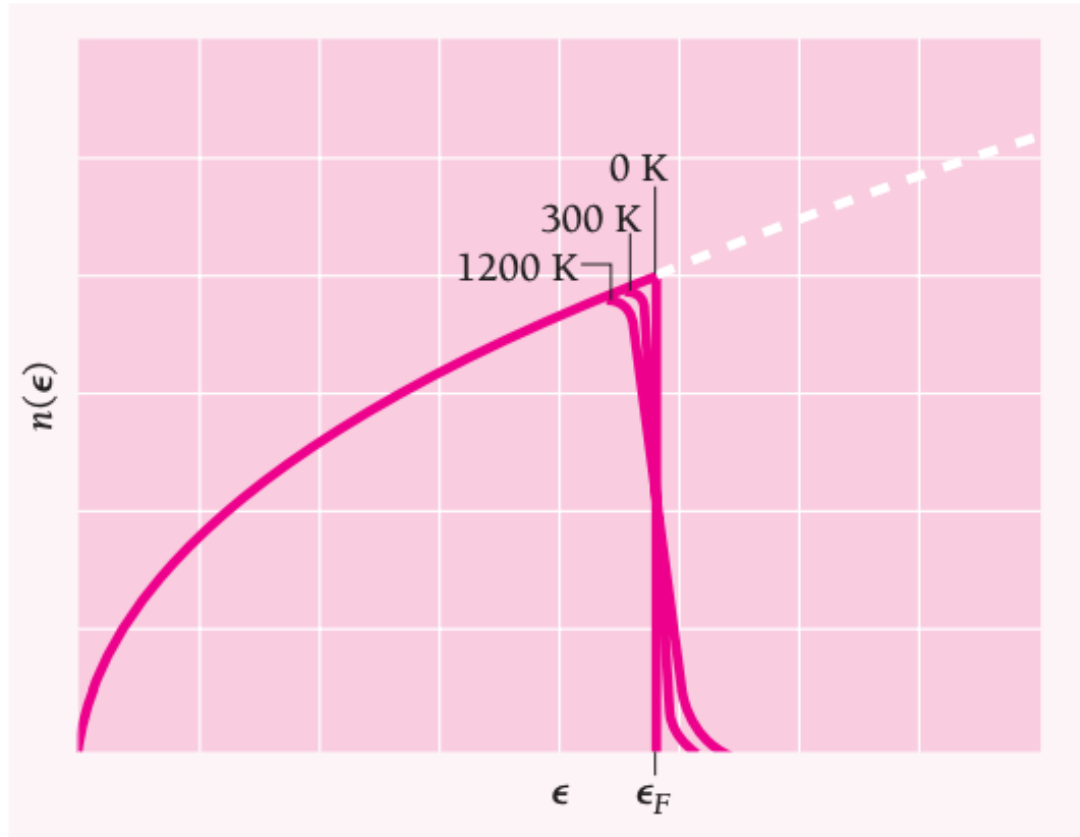
$$\epsilon_F = \frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{2/3}$$

$$n(\epsilon) d\epsilon = g(\epsilon) f(\epsilon) d\epsilon = \frac{(8\sqrt{2}\pi V m^{3/2}/h^3) \sqrt{\epsilon} d\epsilon}{e^{(\epsilon - \epsilon_F)/kT} + 1}$$

Electron energy distribution

$$n(\epsilon) d\epsilon = \frac{(3N/2) \epsilon_F^{-3/2} \sqrt{\epsilon} d\epsilon}{e^{(\epsilon - \epsilon_F)/kT} + 1}$$

Free electron gas (F-D Statistics)



- When the metal is heated, only those electrons occupying energy levels near ϵ_F absorb additional energy and move to higher energy levels.
- At room temperature, only 1% of the electrons absorb energy and their contribution to the specific heat is of the order of $10^{-2} R$

Free electron gas (F-D Statistics)

$$E_0 = \int_0^{\epsilon_F} \epsilon n(\epsilon) d\epsilon$$

Since at $T = 0$ K all the electrons have energies less than or equal to the Fermi energy ϵ_F , we may let

$$e^{(\epsilon - \epsilon_F)/kT} = e^{-\infty} = 0$$

and

$$E_0 = \frac{3N}{2} \epsilon_F^{-3/2} \int_0^{\epsilon_F} \epsilon^{3/2} d\epsilon = \frac{3}{5} N \epsilon_F$$

**Average electron
energy at $T = 0$**

$$\bar{\epsilon}_0 = \frac{3}{5} \epsilon_F$$

Electronic Specific Heat (F-D Statistics)

$$E_e = \frac{3}{2} N_0 kT = \frac{3}{2} RT$$

$$c_{Ve} = \left(\frac{\partial E_e}{\partial T} \right)_V = \frac{3}{2} R$$

$$c_V = 3R + \frac{3}{2} R = \frac{9}{2} R$$

Electron specific
heat

$$c_{Ve} = \frac{\pi^2}{2} \left(\frac{kT}{\epsilon_F} \right) R$$

Electronic Specific Heat (F-D Statistics)

- The failure of the free electrons in a metal to contribute appreciably to its specific heat is linked to their energy distribution.
- Electrons in a metal do not contribute to its specific heat except at very high and very low temperatures
- At room temperature, only 1% of the electrons absorb energy and their contribution to the specific heat is of the order of $10^{-2} R$
- The dominance of the atomic specific heat C_V in a metal over the electronic specific heat is pronounced over a wide temperature range.
- At very low temperatures, C_{Ve} becomes significant because $C_V \propto T^3$ whereas $C_{Ve} \propto T$. At very high temperatures C_V has leveled out at about $3R$ while C_{Ve} has continued to increase, and the contribution of C_{Ve} to the total specific heat is then detectable.

Bose-Einstein Condensation

Theoretical development:

1924- Bose develops the statistical distribution of non-interacting bosons. This distribution is the famous Bose-Einstein statistics.

1924- Einstein shows that a non-interacting Bosonic gas will flood the ground state below a critical temperature, the Bose-Einstein condensation temperature.

The challenge was to achieve a cold enough gas without it becoming a liquid or solid first.

1995- Accomplished by Eric Cornell, Carl Wieman, and their co-workers in Colorado using a gas of Rb atoms.

Requirements for a BEC

- The transition to BEC occurs below a critical temperature, which for a uniform 3D gas consisting of non-interacting particles is given by:

$$T_c = \left(\frac{n}{\zeta(3/2)} \right)^{2/3} \frac{2\pi\hbar^2}{mk_B} \approx 3.3125 \frac{\hbar^2 n^{2/3}}{mk_B}$$

Where T_c = Critical temperature, n = particle density, m = mass per Boson, ζ = Riemann zeta function, $\zeta(3/2) \approx 2.6124$

- At $T < T_c$, fraction of Bosons to condensate:

$$\frac{\langle n_0 \rangle}{N} = 1 - \left(\frac{T}{T_c} \right)^{3/2}$$

- At sufficiently low temperatures, the thermal de Broglie wavelength is greater than the mean spacing between particles and the wave packet overlap to a great extent

Experimental Confirmation of BEC, 1995

Science 269, pp. 198-201 (1995)

Observation of Bose-Einstein Condensation in a Dilute Atomic Vapor

M. H. Anderson, J. R. Ensher, M. R. Matthews, C. E. Wieman,*
E. A. Cornell

A Bose-Einstein condensate was produced in a vapor of rubidium-87 atoms that was confined by magnetic fields and evaporatively cooled. The condensate fraction first appeared near a temperature of 170 nanokelvin and a number density of 2.5×10^{12} per cubic centimeter and could be preserved for more than 15 seconds. Three primary signatures of Bose-Einstein condensation were seen. (i) On top of a broad thermal velocity distribution, a narrow peak appeared that was centered at zero velocity. (ii) The fraction of the atoms that were in this low-velocity peak increased abruptly as the sample temperature was lowered. (iii) The peak exhibited a nonthermal, anisotropic velocity distribution expected of the minimum-energy quantum state of the magnetic trap in contrast to the isotropic, thermal velocity distribution observed in the broad uncondensed fraction.

Bose-Einstein Condensation

- The atoms were first cooled and trapped by six intersecting beams of laser light, which slows the atoms and thereby cool the assembly as well as pushing the atoms together and away from the warm walls of the chamber.
- To get the assembly still colder, the lasers were turned off and a magnetic field held the slower atoms together while allowing the faster ones to escape.
- When the temperature was down to under 10^{-7} K—a tenth of a millionth of a degree above absolute zero—about 2000 rubidium atoms came together in a Bose-Einstein condensate $10\text{ }\mu\text{m}$ long that lasted for 10 s

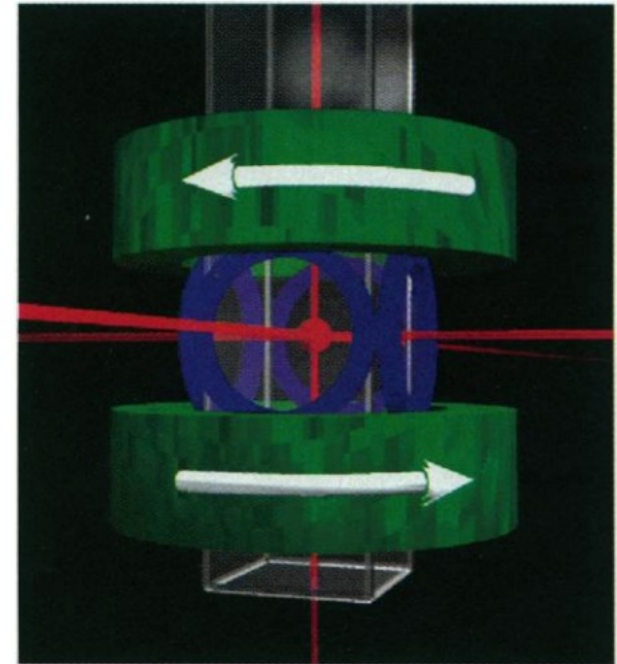
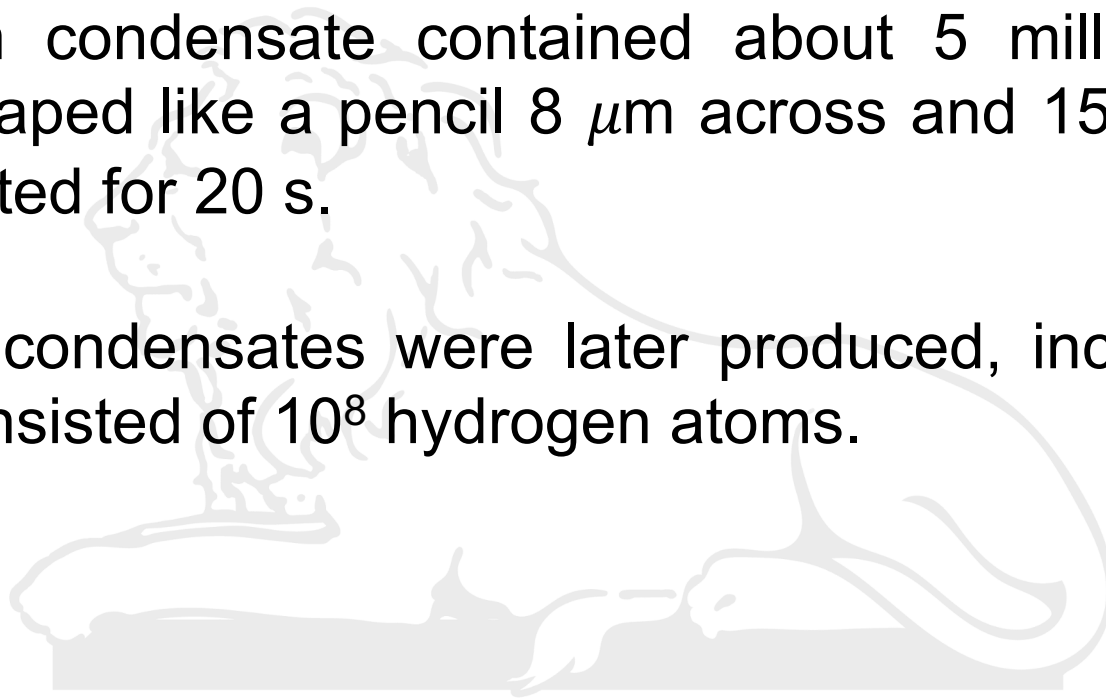


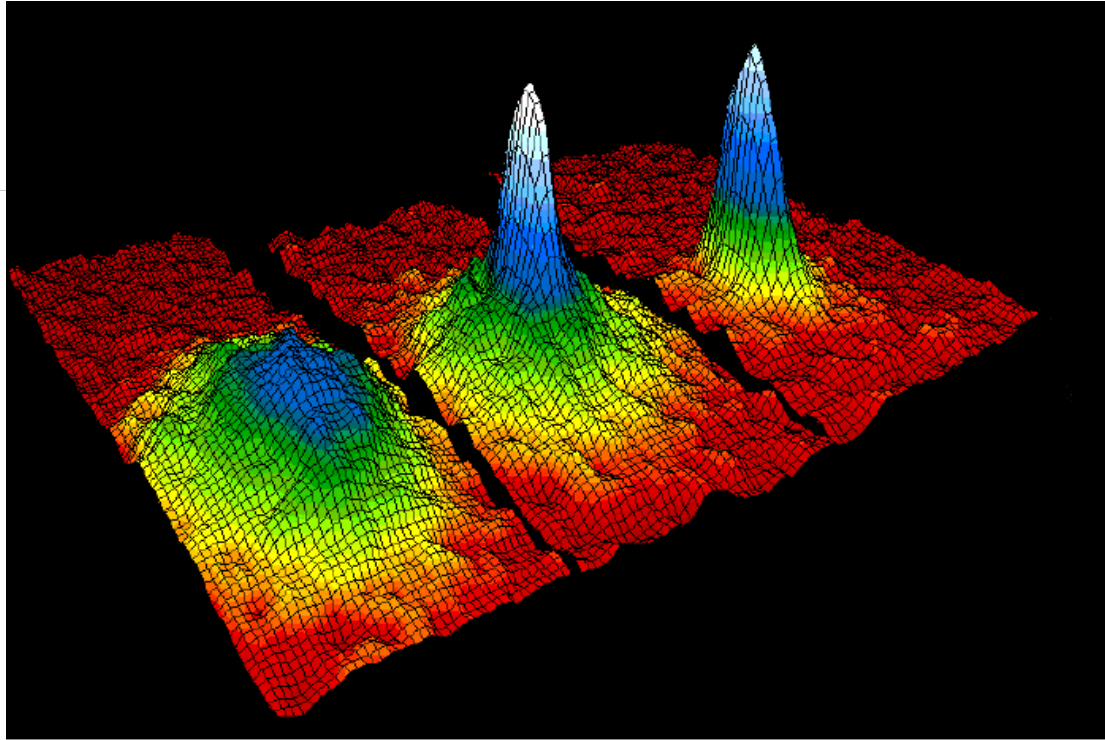
Fig. 1. Schematic of the apparatus. Six laser beams intersect in a glass cell, creating a magneto-optical trap (MOT). The cell is 2.5 cm square by 12 cm long, and the beams are 1.5 cm in diameter. The coils generating the fixed quadrupole and rotating transverse components of the TOP trap magnetic fields are shown in green and blue, respectively. The glass cell hangs down from a steel chamber (not shown) containing a vacuum pump and rubidium source. Also not shown are coils for injecting the rf magnetic field for evaporation and the additional laser beams for imaging and optically pumping the trapped atom sample.

Bose-Einstein Condensation

- Sodium condensate contained about 5 million atoms, was shaped like a pencil $8\text{ }\mu\text{m}$ across and $150\text{ }\mu\text{m}$ long, and lasted for 20 s.
- Larger condensates were later produced, including one that consisted of 10^8 hydrogen atoms.

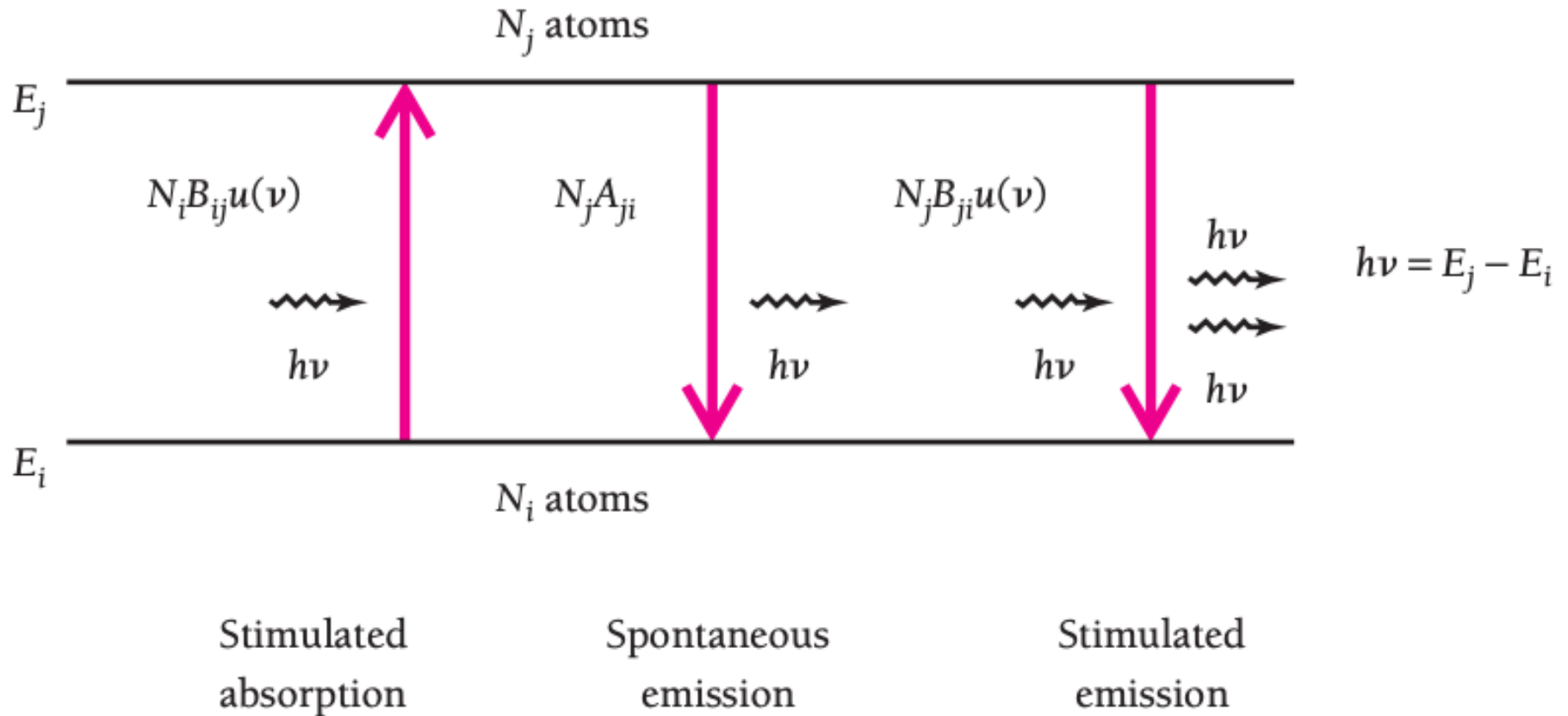


Bose-Einstein Condensation



Velocity-distribution data confirming the discovery of a new phase of matter, the Bose-Einstein condensate, out of a gas of rubidium-87 atoms. The artificial colors indicate the number of atoms at each velocity, with red being the fewest and white being the most.

Absorption and emission of radiation



Number of atoms
that absorb photons

$$N_{i \rightarrow j} = N_i B_{ij} u(\nu)$$

Absorption and emission of radiation

Number of atoms
that emit photons

$$N_{j \rightarrow i} = N_j [A_{ji} + B_{ji} u(\nu)]$$

$$N_{i \rightarrow j} = N_j [A_{ji} + B_{ji} u(\nu)]$$

$$N_i B_{ij} u(\nu) = N_j [A_{ji} + B_{ji} u(\nu)]$$

$$\left(\frac{N_i}{N_j} \right) \left(\frac{B_{ij}}{B_{ji}} \right) u(\nu) = \frac{A_{ji}}{B_{ji}} + u(\nu)$$

$$u(\nu) = \frac{A_{ji}/B_{ji}}{\left(\frac{N_i}{N_j} \right) \left(\frac{B_{ij}}{B_{ji}} \right) - 1}$$

Absorption and emission of radiation

$$N_i = Ce^{-E_i/kT}$$

$$N_j = Ce^{-E_j/kT}$$

$$\frac{N_i}{N_j} = e^{-(E_i - E_j)/kT} = e^{(E_j - E_i)/kT} = e^{h\nu/kT}$$

$$u(\nu) = \frac{A_{ji}/B_{ji}}{\left(\frac{B_{ij}}{B_{ji}}\right)e^{h\nu/kT} - 1}$$

$$B_{ij} = B_{ji} \quad \longrightarrow \quad \frac{A_{ji}}{B_{ji}} = \frac{8\pi h\nu^3}{c^3}$$

Absorption and emission of radiation

- Stimulated emission does occur and its probability for a transition between two states is equal to the probability for absorption.
- Probability of spontaneous and stimulated emission increases rapidly with the energy difference between the two states.
- Under ordinary conditions at thermal equilibrium, $N_j < N_i$, an incident photon is more likely to be absorbed than to cause emission.
- The situation in which the number of atoms in the higher energy state exceeds that in the lower state ($N_j > N_i$) is known as population inversion (LASER action)
- Stimulated emissions are further encouraged by increasing the radiation density $u(\nu)$ of the stimulated radiation