The Three Distribution Functions

1. Overview

Distribution function

$\downarrow$

equilibrium, function of temperature

Table

2. Maxwell - Boltzmann distribution

N distinguishable

$N!$

N_i ϵ_i $W_{\{N_i\}} = \frac{N!}{N_1!\,N_2!\cdots N_k!}$

$\downarrow$ Stirling approximation
Lagrange multiplier

$$f_{MB}(\epsilon) = A\,e^{-\epsilon/kT}$$

$\downarrow$

Maxwell - Boltzmann distribution.

3. Bosons and Fermions

4. Bose - Einstein distribution

derivation.

5. Fermi - Dirac distribution.

6. Ideal Bose - Einstein Gas

$\mu \rightarrow$ chemical potential

$\updownarrow$

α Lagrange multiplier

Bose - Einstein condensation.

${}^4He$, ${}^3He$

Superfluidity

6A Photon Gas, Planck's distribution

7. Ideal Fermi Gas

Fermi Energy

Thermal excitation

Applications

Example : conduction electrons in a metal
liquid ${}^3He$
neutron stars

Band structure

Kronig - Penny model , Bloch theorem.

Metals, Insulators , Semi - conductors

分類：
編號： 12-14
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The Three Statistical Distribution Functions

	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 $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$; 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)	$f_{MB}(\epsilon) = Ae^{-\epsilon/kT}$	$f_{BE}(\epsilon) = \dfrac{1}{e^{\alpha}e^{\epsilon/kT} - 1}$	$f_{FD}(\epsilon) = \dfrac{1}{e^{(\epsilon-\epsilon_F)/kT} + 1}$
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

Chapter 12

Statistical Physics

Experiments in physics :

Probe the properties of the individual constituents of a system.

Study the average properties of a large system.

Key concepts

One uses statistical method to deduce the macroscopic properties at thermal equilibrium from the distribution of the totel energy of the system among its numerous constituent particles

This energy distribution function $f(E_i)$ is defined as the probability that a state of energy E_i is occupied.

Microstate : a description of the system wherein the state of every particles is identified.

The macrostate is less detailed characterization of the system; it specifies only the number of particles that occupy a given state

Classical statistical physics is based on the following fundamental postulates :

(i) The particles of the system are identical but distinguishable

(ii) There is no restriction on the number of particles that may occupy a particular energy state.

(iii) At thermal equilibrium, the distribution of particles among the accessible energy states is the most probable distribution consistent with prescribed constraints such as total energy and total number of particles

(iv) Every microstate of the system has equal a priori probability.

The derivation of the Maxwell-Boltzmann distribution

Want to find $\{N_i\}$ that makes $W_{\{N_i\}}$ maximum under the restriction

$$\sum_{i=1}^{k} N_i = N \quad , \quad \sum_{i=1}^{k} N_i \epsilon_i = E$$

$$W_{\{N_i\}} = \frac{N!}{N_1!\,N_2!\,\cdots\cdots\,N_k!}$$

It is useful to take

$$\ln W = \ln N! - \sum_{i=1}^{k} \ln N_i!$$

Stirling approximation.

$$\ln N! \simeq N \ln N - N$$

$$\ln W = N \ln N - N - \left(\sum_{i=1}^{k} N_i \ln N_i - \sum_{i=1}^{k} N_i\right)$$

$$= N \ln N - \sum_{i=1}^{k} N_i \ln N_i \qquad \left(\sum_{i=1}^{k} N_i = N\right)$$

$$\delta \ln W = -\sum_{i=1}^{k} \left(\ln N_i \,\delta N_i + N_i \frac{\delta N_i}{N_i}\right) = 0$$

Constraint $\sum_{i=1}^{k} N_i = N \Rightarrow \sum_{i=1}^{k} \delta N_i = 0$

$$\sum_{i=1}^{k} N_i \epsilon_i = E \Rightarrow \sum_{i=1}^{k} \epsilon_i \delta N_i = 0$$

Introduce the Lagrange multiplier λ, μ

$$\sum_{i=1}^{k} (\ln N_i + \lambda + \mu \epsilon_i)\, \delta N_i = 0$$

With the presence of Lagrange multiplier λ, μ δN_i can be treated as independent

$$\Rightarrow \quad \ln N_i + \lambda + \mu \epsilon_i = 0$$

$$\underset{\downarrow}{N_i} = e^{-\lambda - \mu \epsilon_i}$$

$$f_{MB}(\epsilon_i) \underset{\downarrow}{=} e^{-\lambda - \mu \epsilon_i} = A e^{-\mu \epsilon_i}$$

Maxwell - Boltzmann distribution

Emission lines from Stellar Hydrogen.

Ground state $E_1 = -13.6\,eV$ $g_1 = 2$

First excited state $E_2 = -3.4\ eV$ $g = 8$

Second excited state $E_3 = -1.51\,eV$ $g = 18$

$$\frac{n_2}{n_1} = \frac{g_2 A e^{-E_2/k_B T}}{g_1 A\, e^{-E_1/k_B T}} = \frac{g_2}{g_1} e^{(E_1 - E_2)/k_B T}$$

At $T = 300K$ $k_B T \sim \frac{1}{40}\ eV$

$$\frac{n_2}{n_1} \sim 4 e^{-395}$$

$\frac{n_3}{n_1}$ is even smaller

$\Rightarrow$ essentially all atoms are in the ground state at 300K

At 20 000 K

$$\frac{n_2}{n_1} = 0.0107$$

$$\frac{n_3}{n_1} = 0.00807$$

$$\frac{S(3 \to 1)}{S(2 \to 1)} = \frac{n_3\, P(3-1)}{n_2\, P(2-1)}$$

$$\frac{S(3 \to 2)}{S(2 \to 1)} = \frac{n_3}{n_2} \frac{P(3 \to 2)}{P(2 \to 1)}$$

Assume $P(2 \to 1) = P(3 \to 1) = P(3 \to 2)$

$$\frac{S(3 \to 1)}{S(2 \to 1)} = 0.75\,, \qquad \frac{S(3 \to 2)}{S(2 \to 1)} = 0.75$$

polarization $= \dfrac{n\uparrow - n\downarrow}{n\uparrow + n\downarrow}$

$H = -\vec{\mu} \cdot \vec{B}$

$= g_e \frac{e}{2m_e} \vec{S} \cdot \vec{B}$

$= g_e \frac{e}{2m_e} S_z B$ $\quad\vec{B}$ is along z direction

$= g_e \frac{e\, m_s}{2m_e} \hbar B$

$n_\uparrow = A e^{-\frac{g_e \overset{\frac{1}{2}}{\overset{\shortparallel}{m_s}} \hbar}{2m_e} \hbar B}$

$n_\downarrow = A e^{-g_e \frac{(-\frac{1}{2})\hbar}{2m_e} B}$

Large polarization

Large B, small T.

Question of degeneracy

↓

there are g_i state with the same energy ϵ_i

$$W_{\{N_i\}} = N! \prod_{i=1}^{k} \frac{(g_i)^{N_i}}{N_i!} \qquad \text{No restriction.}$$

$$N_i \Rightarrow A g_i e^{-\beta \epsilon_i}$$

$$\sum N_i = N, \quad \sum N_i \epsilon_i = E$$

$\Rightarrow$ the generalization is obvious.

$n_i = g_i f_{MB} = g_i A e^{-\epsilon_i \beta}$

$\Sigma n_i = N$

Discrete → continuous

$g_i \Rightarrow g(\epsilon)$

$f_{MB} \Rightarrow A e^{-\epsilon\beta}$

$n_i \rightarrow g_i f_{MB} \longrightarrow n(\epsilon)\,d\epsilon = g(\epsilon) f_{MB}(\epsilon)\,d\epsilon$

$\Sigma n_i = N \qquad \frac{N}{V} = \int_0^\infty n(\epsilon)\,d\epsilon = \int_0^\infty g(\epsilon) f_{MB}(\epsilon)\,d\epsilon$

↓

Maxwell - Boltzmann distribution.

↓

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

Spin Classification

One essential parameter for classification of particles is their "spin" or ~~intrinsic angular momentum~~. Half-integer spin ~~fermions~~ are constrained by the ~~Pauli exclusion principle~~ whereas integer spin ~~bosons~~ are not. The ~~electron~~ is a fermion with ~~electron spin~~ 1/2.

The spin classification of particles determines the nature of the ~~energy distribution~~ in a collection of the particles. Particles of integer spin obey ~~Bose-Einstein statistics~~, whereas those of half-integer spin behave according to ~~Fermi-Dirac statistics~~.

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~~HyperPhysics~~***** ~~Quantum Physics~~ ***** ~~Particles~~

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Fermions

Fermions are particles which have half-integer ~~spin~~ and therefore are constrained by the ~~Pauli exclusion principle~~. Particles with integer spin are called ~~bosons~~. Fermions include ~~electrons~~, ~~protons~~, ~~neutrons~~. The wavefunction which describes a collection of fermions must be antisymmetric with respect to the exchange of identical particles, while the wavefunction for a collection of bosons is symmetric.

The fact that electrons are fermions is foundational to the buildup of the periodic table of the elements since there can be only one electron for each state in an atom (only one electron for each possible set of quantum numbers). The fermion nature of electrons also governs the behavior of ~~electrons in a metal~~ where at low temperatures all the low energy states are filled up to a level called the ~~Fermi energy~~. This filling of states is described by ~~Fermi-Dirac statistics~~.

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Bosons

Bosons are particles which have integer ~~spin~~ and which therefore are not constrained by the ~~Pauli exclusion principle~~ like the half-integer spin ~~fermions~~. The energy distribution of bosons is described by ~~Bose-Einstein statistics~~. The wavefunction which describes a collection of bosons must be symmetric with respect to the exchange of identical particles, while the wavefunction for a collection of fermions is antisymmetric.

At low temperatures, bosons can behave very differently than fermions because an unlimited number of them can collect into the same energy state. The collection into a single state is called condensation, or ~~Bose-Einstein condensation~~. It is responsible for the phenomenon of ~~superfluidity~~ in ~~liquid helium~~. Coupled particles can also act effectively as bosons. In the ~~BCS Theory~~ of ~~superconductivity~~, coupled pairs of electrons act like bosons and condense into a state which demonstrates zero electrical resistance.

Bosons include ~~photons~~ and the characterization of photons as particles with frequency-dependent energy given by the ~~Planck relationship~~ allowed Planck to apply Bose-Einstein statistics to explain the ~~thermal radiation~~ from a hot cavity.

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Chapter 16

Quantum Statistics

Maxwell - Boltzmann distribution ⇒ distinguishable particles

Bose - Einstein distribution ⇒ indistinguishable particles to which the exclusion principle does not apply i.e. particles with integral spin.

Fermi - Dirac distribution ⇒ indistinguishable particles to which the exclusion principle does apply, i.e., particles with half-integral spin.

Bose Einstein statistics.

All quantum states are assumed to have equal a priori probabilities.

n_i number of particles having energy u_i
g_i number of states that have energy u_i

n_i particle

For example $n_i = 5$ . . . . .
$g_i = 3$

Particles are indinguishable ⇒ there shall be grouped into g_i groups
↓
we want to calculate the number of ways this grouping can be done.
↓
we need 2 paritTitions

Example $\underbrace{\cdot\ \cdot}_{2} \mid \underbrace{\cdot\ \cdot}_{2} \mid \underbrace{\cdot}_{1}$

All together there are $\overbrace{n_i + g_i - 1}^{7}$ position

Number of ways of assign these 7! ways of assigning these 7 objects.
Permutation among particles is irrelevant ⇒ should be divided by 5!
Permutation among partitions is irrelevant. ⇒ should be divided by 2!.

$$\Rightarrow \frac{7!}{5!\,2!}$$

In general the number of ways to divide n_i particles into g_i states

$$= \frac{(n_i+g_i-1)!}{n_i!\,(g_i-1)!}$$

$$W_{\{n_i\},B.E.} = \prod \frac{(n_i+g_i-1)!}{n_i!\,(g_i-1)!}$$

Assume $n_i + g_i \gg 1$

$$\ln W = \sum\left[\ln(n_i+g_i)! - \ln n_i! - \ln(g_i-1)!\right]$$

$$\underset{\uparrow}{\simeq} \sum\left[(n_i+g_i)\ln(n_i+g_i) - (n_i+g_i) - n_i\ln n_i + n_i - (g_i-1)\ln g_i + g_i - 1\right]$$

$$\delta \ln W = \sum\left[(n_i+g_i)\frac{1}{n_i+g_i}\delta n_i + \ln(n_i+g_i)\delta n_i - n_i\frac{1}{n_i}\delta n_i - \ln n_i\,\delta n_i\right]$$

$$= \sum\left[\ln(n_i+g_i) - \ln n_i\right]\delta n_i = 0$$

Constraints.

$\sum \delta n_i = 0$ number of particles is conserved.

$\sum u_i\,\delta n_i = 0$ energy is conserved.

Use Lagrange multiplier method

$$\sum\left[\ln(n_i+g_i) - \ln n_i - \alpha - \beta u_i\right]\delta n_i = 0$$

$$\ln(n_i+g_i) - \ln n_i - \alpha - \beta u_i = 0$$

$$\ln\frac{n_i+g_i}{n_i} = \alpha + \beta u_i$$

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

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

Identify $\beta = \frac{1}{kT}$

$\Rightarrow$ $n_i = \dfrac{g_i}{e^{\alpha}e^{u_i/kT} - 1}$ Bose-Einstein distribution

Bose-Einstein Statistics

N_i particles is to be put into g_i degenerate states in the ith energy level ϵ_i

No restriction on the number of particles in each state

Number of ways to put g_i-1 dividing bar among N_i particles

Total number of possible permutations $(N_i+g_i-1)!$

The permutations among N_i particles is unimportant
The permutations among g_i-1 bar is unimportant.

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

$$\Rightarrow \quad W_{\{N_i\}} = \prod_i \frac{(N_i+g_i-1)!}{N_i!\,(g_i-1)!}$$

$$\ln W = \sum \Big[(N_i+g_i-1)\ln(N_i+g_i-1) - \cancel{(N_i+g_i-1)} - (N_i \ln N_i - \cancel{N_i}) - \big((g_i-1)\ln(g_i-1) - \cancel{(g_i-1)}\big)\Big]$$

$$= \sum \big[(N_i+g_i-1)\ln(N_i+g_i-1) - N_i \ln N_i - (g_i-1)\ln(g_i-1)$$

$$N_i,\ g_i \gg 1$$

$$\rightarrow \sum \big[(N_i+g_i)\ln(N_i+g_i) - N_i \ln N_i - g_i \ln g_i \big]$$

$$\delta \ln W = \sum \Big[\cancel{(N_i+g_i)}\frac{\delta N_i}{\cancel{N_i+g_i}} + \ln(N_i+g_i)\,\delta N_i - \cancel{N_i}\frac{\delta N_i}{\cancel{N_i}} - \ln N_i\,\delta N_i \Big]$$

$$= \sum \ln\left(\frac{N_i+g_i}{N_i}\right)\delta N_i = 0$$

$$-\alpha \qquad \sum \delta N_i = 0$$
$$-\beta \qquad \sum \epsilon_i\,\delta N_i = 0$$

$$\Rightarrow \quad \ln\frac{N_i+g_i}{N_i} = \alpha + \beta\epsilon_i$$

$$1 + \frac{g_i}{N_i} = e^{\alpha+\beta\epsilon_i}$$

$$N_i = \frac{g_i}{e^{\alpha+\beta\epsilon_i} - 1}$$

↓

Bose - Einstein distribution

· · | · · · | · · | · ·

Divide the particles into 4 cells ⇒ need 3 bars

| · · · · | · · · · | · ·

This means the first cell has no particles

No restriction on the number of particles in the cell.

↱ number need not to be conserved

If $\delta \sum N_i = 0$ constraint is removed

then

$$N_i = \frac{g_i}{e^{\beta \epsilon_i} - 1}$$

↓

Planck's distribution

Fermi-Dirac Statistics

N_i particles is to be put into g_i degenerate state

Each state can accommodate at most one particle.

$g_i \geq N_i$

The first particle has g_i possible choice
2nd 〃 has $g_i - 1$ possible choice
⋮
N_i th particle has $g_i - N_i + 1$ possible choice

The permutation among N_i particles is unimportant

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

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

$$W_{\{N_i\}} = \prod_i \frac{g_i!}{(g_i-N_i)!\,N_i!}$$

$$W = \prod_i \frac{g_i!}{(g_i-N_i)!\,N_i!}$$

$$\ln W = \sum \left[\ln g_i! - \ln N_i! - \ln (g_i - N_i)! \right]$$

$$= \sum \left[g_i \ln g_i - g_i - (N_i \ln N_i - N_i) - \left((g_i - N_i)\ln(g_i - N_i) - (g_i - N_i)\right)\right]$$

$$= \sum \left[g_i \ln g_i - N_i \ln N_i - (g_i - N_i) \ln (g_i - N_i)\right]$$

$$\delta \ln W = \sum \left[-\left(N_i \frac{1}{N_i} \delta N_i + \ln N_i \, \delta N_i\right) - \left[(g_i - N_i) \frac{1}{g_i - N_i} (-\delta N_i) + \ln (g_i - N_i)(-\delta N_i)\right]\right]$$

$$= \sum \left[-\cancel{\delta N_i} - \ln N_i \, \delta N_i + \cancel{\delta N_i} + \ln (g_i - N_i)\, \delta N_i \right] = 0$$

$$\downarrow$$

$$\delta \ln W = 0 \quad \Rightarrow \quad \sum \ln \left(\frac{g_i - N_i}{N_i} \right) \delta N_i = 0$$

$$-\alpha \qquad \sum \delta N_i = 0$$

$$-\beta \qquad \sum \epsilon_i \, \delta N_i = 0$$

$$\Rightarrow \quad \ln \left(\frac{g_i - N_i}{N_i} \right) - \alpha - \beta \epsilon_i = 0$$

$$\ln \frac{g_i - N_i}{N_i} = \alpha + \beta \epsilon_i$$

$$\downarrow$$

$$\frac{g_i - N_i}{N_i} = e^{\alpha + \beta \epsilon_i}$$

$$\frac{g_i}{N_i} = 1 + e^{\alpha + \beta \epsilon_i}$$

$$\frac{N_i}{g_i} = \frac{1}{e^{\alpha + \beta \epsilon_i} + 1}$$

$$\downarrow$$

Fermi-Dirac distribution

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Ideal Bose-Einstein Gas.

$$n(\epsilon)\,d\epsilon = g(\epsilon)\,d\epsilon\, f_{BE}(\epsilon)$$

$$f_{BE}(\epsilon) = \frac{1}{e^{\alpha}e^{\epsilon/kT}+1} = \frac{1}{e^{(\epsilon-\mu)/kT}-1}$$

μ = chemical potential

Identification of the Lagrange multiplier

β with $\frac{1}{kT}$

Calculation of $g(\epsilon)$ density of state

$\downarrow$

free particle in a box

$\downarrow$

same as before

$$n(\epsilon)d\epsilon = g\,\frac{2\pi}{h^3}(2m)^{3/2}\epsilon^{\frac{1}{2}}\,\frac{1}{e^{\alpha}e^{\epsilon/kT}-1}\,d\epsilon$$

$g = 2s+1$ is the spin degeneracy.

$\Rightarrow$ fundamental equation

α is again determined by the normalization condition.

$$n = \int g\,\frac{2\pi}{h^3}(2m)^{3/2}\epsilon^{\frac{1}{2}}\,\frac{1}{e^{\alpha}e^{\epsilon/kT}-1}\,d\epsilon$$

$$\frac{N}{V} = \int \frac{2\pi(2m)^{3/2}\epsilon^{\frac{1}{2}}d\epsilon}{h^3}\,\frac{1}{e^{(\epsilon-\mu)/kT}-1}$$

$\downarrow$

from this equation
one can calculate
μ
in term of N, V, T

The Ideal Bose Gas

$$n(\epsilon)\,d\epsilon = \frac{gV}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{\epsilon^{\frac{1}{2}}\,d\epsilon}{e^{(\epsilon-\mu)/kT}-1}$$

$g = (2S+1)$ is the spin degeneracy

$\mu \rightarrow$ chemical potential.

$$N = \frac{gV}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\epsilon^{\frac{1}{2}}\,d\epsilon}{e^{(\epsilon-\mu)/kT}-1} \qquad (A)$$

This is an integral equation
$\Rightarrow$ μ in term of T, V and N

When V, N fixed, μ is a function of T.

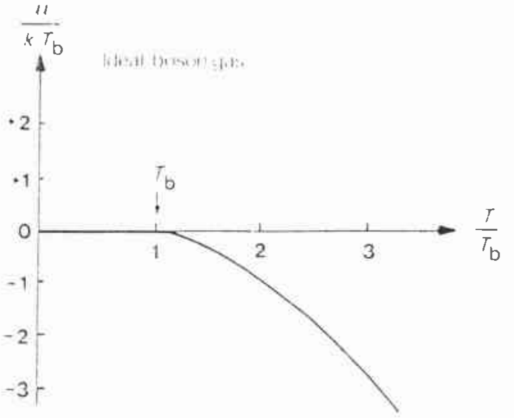

Figure 12.11—Variation of the chemical potential μ of an ideal boson gas with temperature. The Bose temperature T_b is given by equation (12.55). The chemical potential μ is always negative. It is virtually zero up to the Bose temperature. As T increases above T_b, μ gets more and more negative. [Adapted with permission from *Introductory Statistical Mechanics*, by R. E. Turner and D. S. Betts.]

Since the number of bosons in any particle state cannot be negative

$$e^{(\epsilon-\mu)/kT} > 1$$

$\Rightarrow$ $\epsilon > \mu$

$\Rightarrow$ the chemical potential of an ideal boson gas must always be less than the lowest single particle state.

Take the single particle ground state energy to be zero

$\Rightarrow \mu < 0$

Qualitative discussion of Bose-Einstein condensation

There exists a $\underset{\substack{\downarrow \\ \text{boson temperature}}}{T_b} = \frac{3.31\hbar^2}{mk}\left(\frac{N}{gV}\right)^{2/3}$

$\Rightarrow$ $T > T_b$, and $T < T_b$ exhibit different behavior

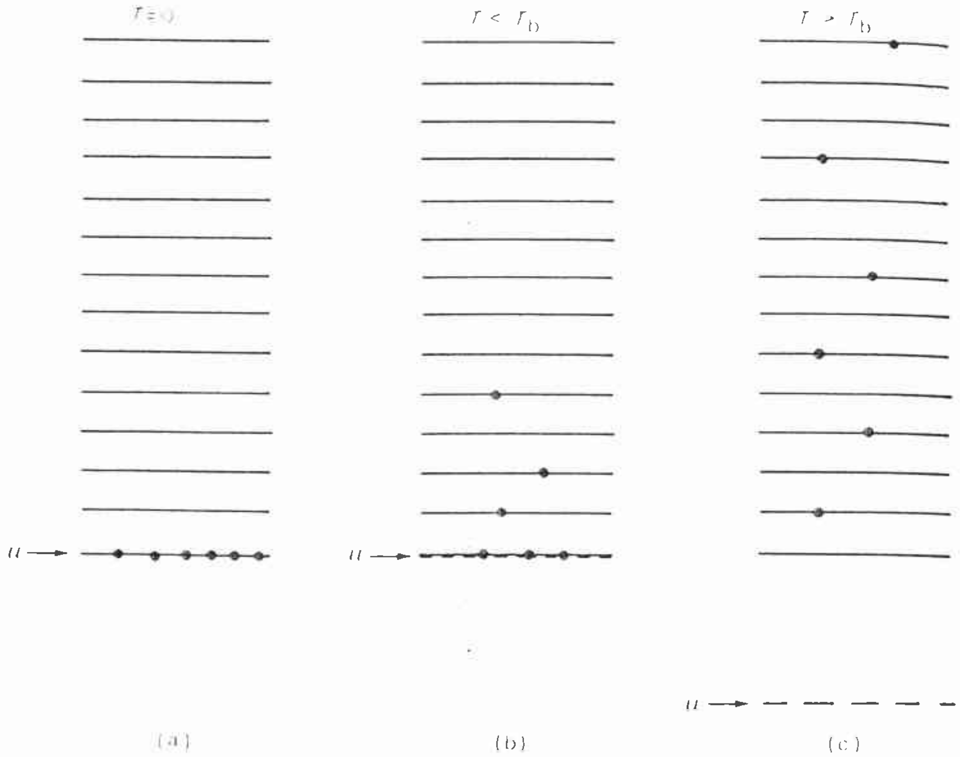

Figure 12.9.—A simple system consisting of 6 identical bosons of spin zero. (a) At $T = 0$ all the bosons are in the single particle ground state. (b) When $T > 0$ but $T < T_b$, where the Bose temperature T_b is given by equation (12.55), some of the bosons are in excited single particle states, but a significant fraction of the bosons are still in the single particle ground state. (c) When $T > T_b$, there are very few, if any, bosons in the single particle ground state. The case when $b(\varepsilon) \ll 1$ for all the single particle states corresponds to the classical limit.

The value of the chemical potential μ is shown in each case: (a) At $T = 0$, μ is equal to the energy of the lowest energy single particle state. In the text, this energy is chosen as the zero of the energy scale, in which case $\mu = 0$ at $T = 0$. (b) When $T < T_b$, μ is only fractionally less than the energy of the lowest energy single particle state. (c) As T increases above T_b, μ gets more and more negative.

Take the single particle ground state as zero of our energy scale.

$\Rightarrow \mu < 0$

Define $x = \epsilon / kT$

$$\frac{N}{V} = \frac{1}{4\pi^2}\left(\frac{2mkT}{\hbar^2}\right)\int_0^\infty \frac{\sqrt{x}\,dx}{e^x e^{-\mu/kT} - 1}$$

As $\frac{N}{V}$ is fixed, T decrease, the integral must increase $\Rightarrow$ $e^{-\mu/kT}$ must decrease

$\Rightarrow$ μ must decrease in magnitude

At $T = T_c = T_b \Rightarrow \mu = 0$

↓

the normalization condition can be met.

At $T < T_b$, $\mu = 0$

At $\mu = 0$, the RHS is fixed to be

$$\frac{N_c(T)}{V} = \frac{1}{4\pi^2}\left(\frac{2mkT}{\hbar^2}\right)\int_0^\infty \frac{\sqrt{x}\,dx}{e^x - 1}$$

$$= \frac{1}{4\pi^2}\left(\frac{2mkT}{\hbar^2}\right)^{3/2} \cdot 2.31$$

$N_c(T) < N$

↓

the normalization condition cannot be met

↓

real difficulty.

$N = N_0 + N_c$

↳ condense into ground state

$\mu \simeq 0$ for $T \leq T_b$

$\Rightarrow \quad N_{ex} = N\left(\frac{T}{T_b}\right)^{3/2}$ at $T = T_b$ $N_{ex} = N$

$N_0 = N\left[1 - \left(\frac{T}{T_b}\right)^{3/2}\right]$

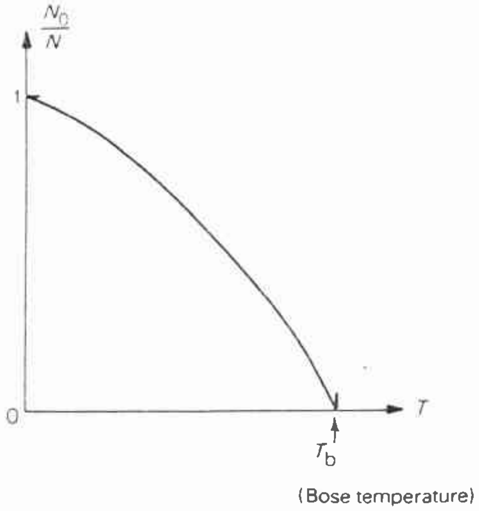

Figure 12.13—The variation with absolute temperature T of the ratio of the number N_0 of bosons in the single particle ground state to N, the total number of bosons, for temperatures below the Bose temperature.

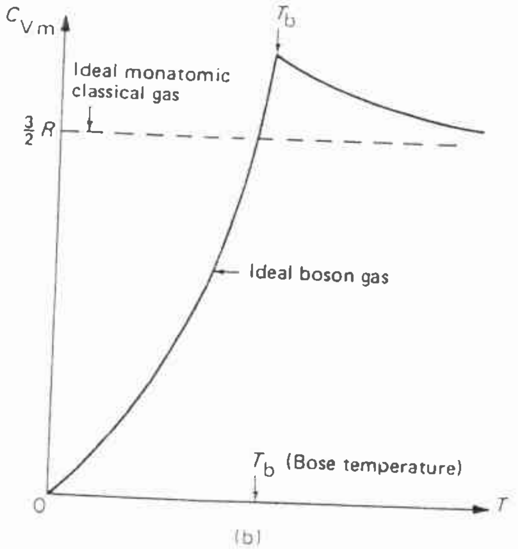

Figure 12.12—Behaviour of an ideal Boson gas. (a) The variations of the energy U and the pressure p with absolute temperature T are shown. (b) The variation of the molar heat capacity $C_{V,m}$ with absolute temperature T is shown. There is a cusp in the curve at the Bose temperature T_b, where T_b is given by equation (12.55). At high temperatures $C_{V,m}$ tends to the classical value of $3R/2$. (Adapted with permission from *Statistical Mechanics and Properties of Matter* by E. S. R. Gopal, Ellis Horwood Ltd., Chichester.)

Liquid Helium

Kamerlingh Onnes worked for many years to liquify the element which persisted as a gas to the lowest temperature. Using liquid air to produce liquid hydrogen and then the hydrogen to jacket the liquification apparatus, he produced about 60 cubic centimeters of liquid helium on July 10, 1908. Its boiling point was found to be 4.2 K. Onnes received the Nobel Prize in 1913 for his low temperature work leading to this achievement.

When helium is cooled to a critical temperature of 2.17 K (called its ~~lambda point~~), a remarkable discontinuity in heat capacity occurs, the liquid density drops, and a fraction of the liquid becomes a zero viscosity "~~superfluid~~". Superfluidity arises from the fraction of helium atoms which has condensed to the lowest possible energy.

An important application of liquid helium has been in the study of ~~superconductivity~~ and for the applications of ~~superconducting magnets~~.

~~Liquid helium working range~~

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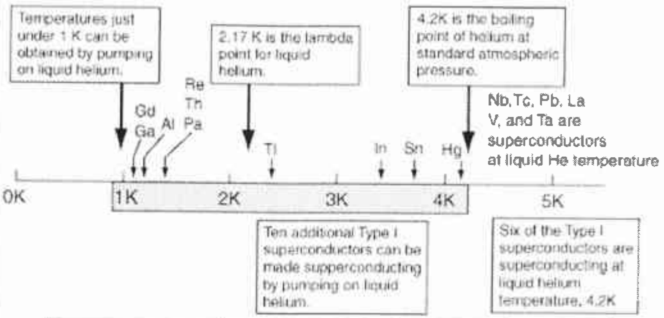
Liquid Helium Working Range



~~Liquid helium~~ ~~Lambda point~~ ~~Superconductors~~

~~Index~~

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~~HyperPhysics~~***** ~~Quantum Physics~~

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Superfluidity

A remarkable transition occurs in the properties of ~~liquid helium~~ at the temperature 2.17K, called the "~~lambda point~~" for helium. Part of the liquid becomes a "superfluid", a zero ~~viscosity~~ fluid which will move rapidly through any pore in the apparatus.

A vacuum container which seemed to be leak tight could suddenly leak helium rapidly as the superfluid moved out through a microscopic hole. A vertical tube could produce a fountain effect as the superfluid moved up the walls and out the top.

In 1938, F. London proposed a "two-fluid" model to explain the behavior of the liquid: normal liquid and the superfluid fraction consisting of those atoms which have "condensed" to the ground state and make no contribution to the entropy or heat capacity of the liquid. This condensed fraction is the standard example of ~~Bose-Einstein condensation~~.

Another remarkable characteristic of the the superfluid is its very high heat conductivity, 30 times that of copper!

~~Application in IRAS Satellite~~

~~Index~~

Reference:
~~Blatt~~

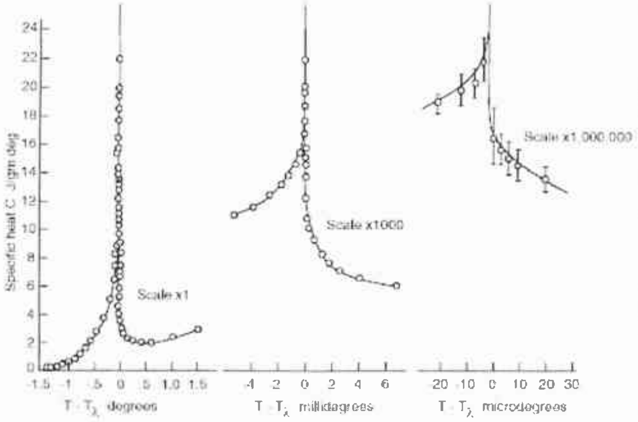
~~HyperPhysics~~***** ~~Quantum Physics~~

R Nave

Lambda Point for Liquid Helium

When helium is cooled to a critical temperature of 2.17 K , a remarkable discontinuity in heat capacity occurs, the liquid density drops, and a fraction of the liquid becomes a zero viscosity "~~superfluid~~". It is called the lambda point because the shape of the specific heat curve is like that Greek letter. Superfluidity arises from the fraction of helium atoms which has condensed to the lowest possible energy by a process called ~~Bose-Einstein condensation~~.

When helium is cooled to a critical temperature of 2.17 K , a remarkable discontinuity in heat capacity occurs, the liquid density drops, and a fraction of the liquid becomes a zero viscosity "~~superfluid~~". It is called the lambda point because the shape of the specific heat curve is like that Greek letter. Superfluidity arises from the fraction of helium atoms which has condensed to the lowest possible energy by a process called ~~Bose-Einstein condensation~~.



Specific heat data from ~~Buckingham and Fairbank~~, 1961, p. 138.

~~Liquid helium working range~~

~~Index~~

Reference: ~~Blatt~~

~~HyperPhysics~~***** ~~Quantum Physics~~ *R Nave* ~~Go Back~~

Bose-Einstein Condensation

In 1924 Einstein pointed out that ~~bosons~~ could "condense" in unlimited numbers into a single ground state since they are governed by ~~Bose-Einstein statistics~~ and not constrained by the ~~Pauli exclusion principle~~. Little notice was taken of this curious possibility until the anomalous behavior of ~~liquid helium~~ at low temperatures was studied carefully.

When helium is cooled to a critical temperature of 2.17 K, a remarkable discontinuity in heat capacity occurs, the liquid density drops, and a fraction of the liquid becomes a zero viscosity "~~superfluid~~". Superfluidity arises from the fraction of helium atoms which has condensed to the lowest possible energy.

A condensation effect is also credited with producing ~~superconductivity~~. In the ~~BCS Theory~~, pairs of electrons are coupled by lattice interactions, and the pairs (called ~~Cooper pairs~~) act like bosons and can condense into a state of zero electrical resistance.

The conditions for achieving a Bose-Einstein condensate are quite extreme. The participating particles must be considered to be identical, and this is a condition that is difficult to achieve for whole atoms. The condition of ~~indistinguishability~~ requires that the ~~deBroglie wavelengths~~ of the particles overlap significantly. This requires extremely low temperatures so that the deBroglie wavelengths will be long, but also requires a fairly high particle density to narrow the gap between the particles.

Since the 1990s there has been a surge of research into Bose-Einstein condensation since it was discovered that Bose-Einstein condensates could be formed with ultra-cold atoms. The use of ~~laser cooling~~ and the trapping of ultra-cold atoms with ~~magnetic traps~~ has produced temperatures in the nanokelvin range. Cornell and Wieman along with Ketterle of MIT received the 2001 Nobel Prize in Physics "for the achievement of Bose-Einstein condensation in dilute gases of alkali atoms, and for early fundamental studies of the properties of the condensates". Cornell and Wieman led an active group at the University of Colorado, Boulder which has produced Bose-Einstein condensates with ~~rubidium atoms~~. Other groups at MIT, Harvard and Rice have been very active in this rapidly advancing field.

Bose-Einstein Condensation.

In a gas of non-interacting bosons at a certain transition temperaction below which a substantial fraction of total number of particles in the system will occupy the single eigenstate of the lowest energy

↓

ground state

↓

Einstein condensation

The key is the behavior of μ at low temperature

$$f(\epsilon, kT) = \frac{1}{e^{(\epsilon-\mu)/kT}-1}$$

μ is the chemical potential

The ground state energy is taken to be zero

$$f(0, k_B T) = \frac{1}{e^{-\mu/\tau}-1}$$

$k_B T \to 0$, the occupancy of the ground state

$$\lim_{\tau \to 0} f(0,\tau) = \lim_{\tau \to 0} \frac{1}{e^{-\mu/\tau}-1}$$

$$\simeq \frac{1}{1-\frac{\mu}{\tau}-1} \to -\frac{\tau}{\mu}$$

$\frac{\mu}{\tau}$ must be small, otherwise the total number cannot be large

$$N = -\frac{\tau}{\mu} \Rightarrow \mu = -\frac{\tau}{N} \quad \text{as } \tau \to 0$$

$$\lambda \equiv e^{\mu/\tau} = 1 + \frac{\mu}{\tau} \sim 1 - \frac{1}{N} \quad \text{as } \tau \to 0$$

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

$$N = N_0(\tau) + \int_0^\infty d\epsilon\, g(\epsilon) f(\epsilon, \tau)$$

$N_0(\tau)$ ↓ number of atoms in the ground state at temperature τ

↓ condensed phase

integral ↓ normal phase

excludes the atoms in the ground state since $g(\epsilon)=0$ at $\epsilon=0$

$$N_0(\tau) = \frac{1}{e^{-\mu/\tau}-1} = \frac{1}{\lambda^{-1}-1}$$

$$N_e(\tau) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty d\epsilon \; \frac{\epsilon^{1/2}}{\lambda^{-1}e^{\epsilon/\tau}-1}$$

Let $x \equiv \epsilon/\tau$

$$N_e(\tau) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\tau^{3/2}\int_0^\infty \frac{x^{1/2}}{\lambda^{-1}e^{x}-1}\,dx$$

Take $\lambda = 1$

$$\int_0^\infty \frac{x^{\frac{1}{2}}}{e^{x}-1}dx = \int_0^\infty \frac{x^{\frac{1}{2}}e^{-x}}{1-e^{-x}}$$

$$= \sum_{s=1}^{\infty}\int_0^\infty dx\, x^{\frac{1}{2}}e^{-sx}$$

$y = sx$

$$= \left(\sum_{s=1}^{\infty} s^{-3/2}\right)\int_0^\infty dy\, y^{\frac{1}{2}}e^{-y}$$

$$= 1.306\,\pi^{1/2}$$

$$N_e = \frac{1.306V}{4}\left(\frac{2m\tau}{\pi\hbar^2}\right)^{3/2} = 2.612\, n_Q V$$

$$N_e/N \simeq 2.612\, n_Q/n$$

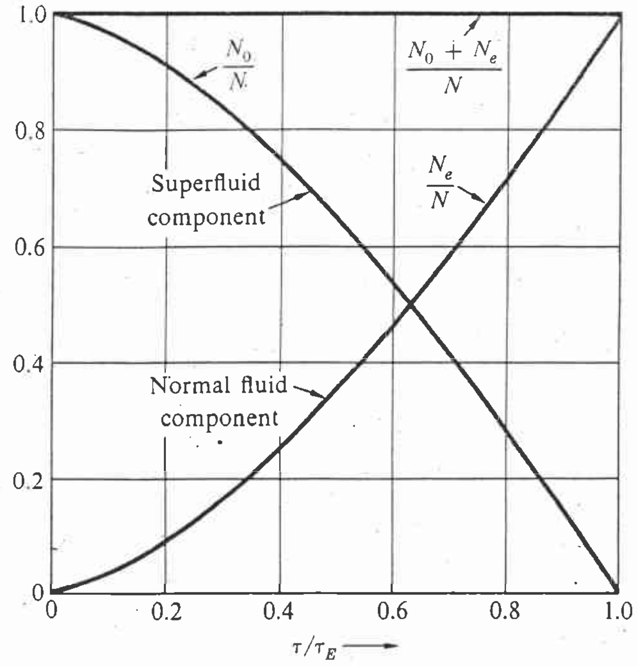
τ_E = temperature $N_e(\tau_E) = N$

$$\Rightarrow \quad \tau_E \equiv \frac{2\pi\hbar^2}{m}\left(\frac{N}{2.612V}\right)^{2/3}$$

$$\frac{N_e}{N} \simeq \left(\frac{\tau}{\tau_E}\right)^{3/2}$$

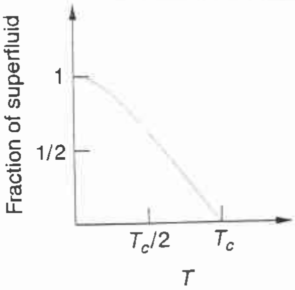
$$N_0 = N - N_e = N\left[1-\left(\frac{\tau}{\tau_E}\right)^{3/2}\right]$$

For liquid He $\Rightarrow$ $T_E = 3.1\,K$



Condensed boson gas: temperature dependence of the proportion N_0/N of atoms in the ground orbital and of the proportion N_e/N of atoms in all excited orbitals. We have labeled the two components as normal and superfluid to agree with the customary description of liquid helium.

Relate to the two-fluid model of F. London.



Graph of the fraction of superfluid in a sample of liquid helium as a function of temperature.

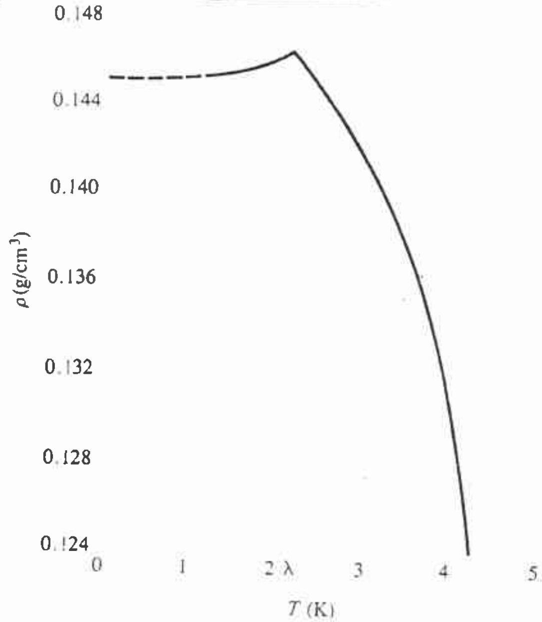


Figure 11.6 The density of liquid helium as a function of temperature. Note the discontinuity at T_λ = 2.17 K.

The Bose-Einstein Condensation

Liquid He

1908 Kamerlingh Onnes liquid He

1924 Kamerlingh Onnes and J. Bok

↓

density of liquid helium vs temperture

cusp in the temperature at 2.17 K

1928 W. H. Keesom and M. Wolfke

discontinuity of the curve

⇒ indication of phase transition.

He I liquid above 2.17 K

He II liquid below 2.17 K

λ - point

1938 F. London → two fluid model

$$\rho = \rho_s + \rho_n$$

As the temperature is lowered from the lambda point, the fraction consisting of the superfluid increases and that of the normal fluid decreases until, at absolute zero, only the superfluid remain.

The superfluid corresponds to the helium atoms being in the lowest possible quantum state, the ground state.

These atoms are not excited to higher states, so the superfluid cannot contribute to viscosity.

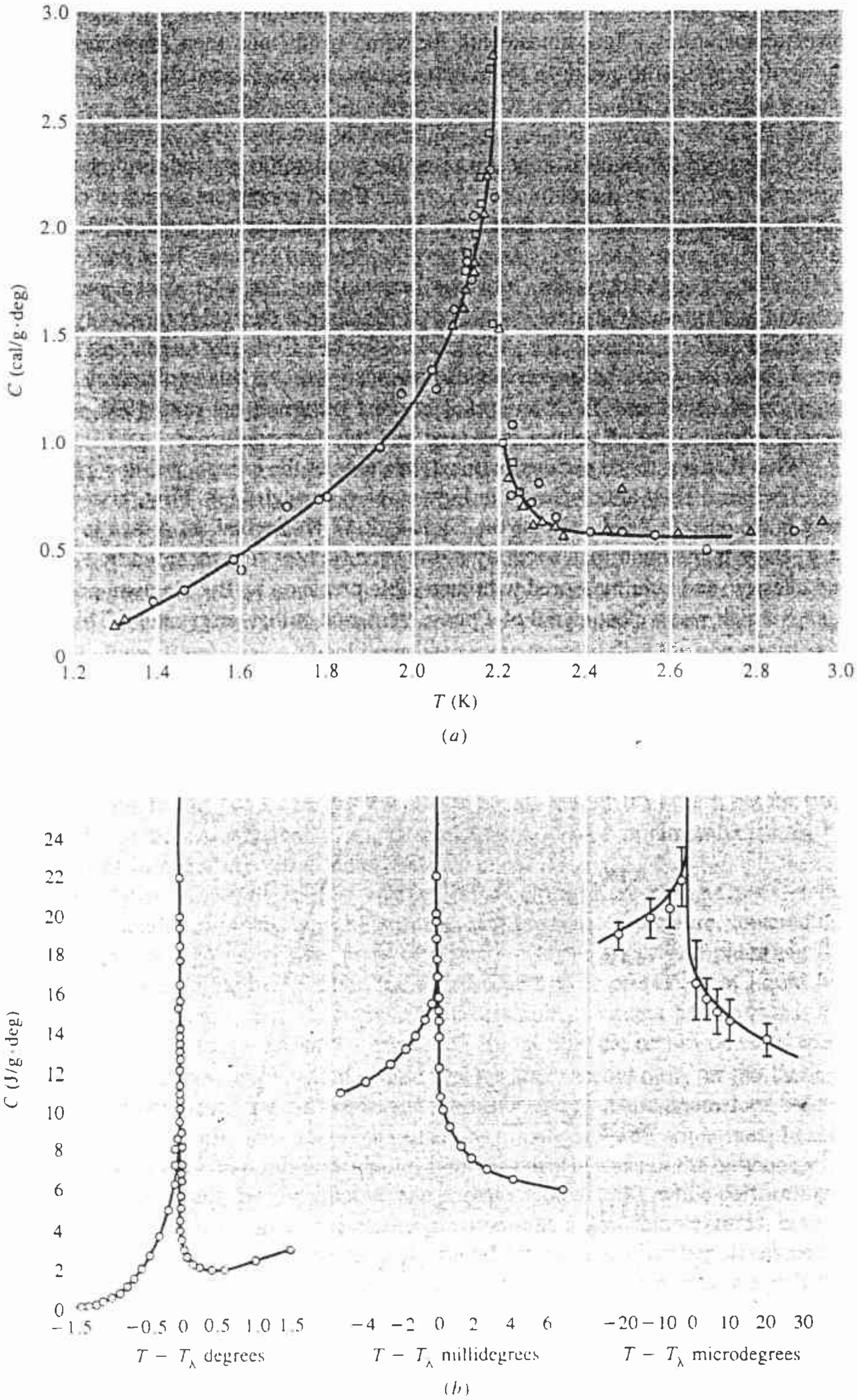


Figure 11.7 The specific heat of liquid helium near the λ transition to the superfluid phase. (*a*) Results of early measurements. (*b*) Data obtained by Buckingham and Fairbank in 1961; note that the data points near T_λ are separated by only a few microkelvins.

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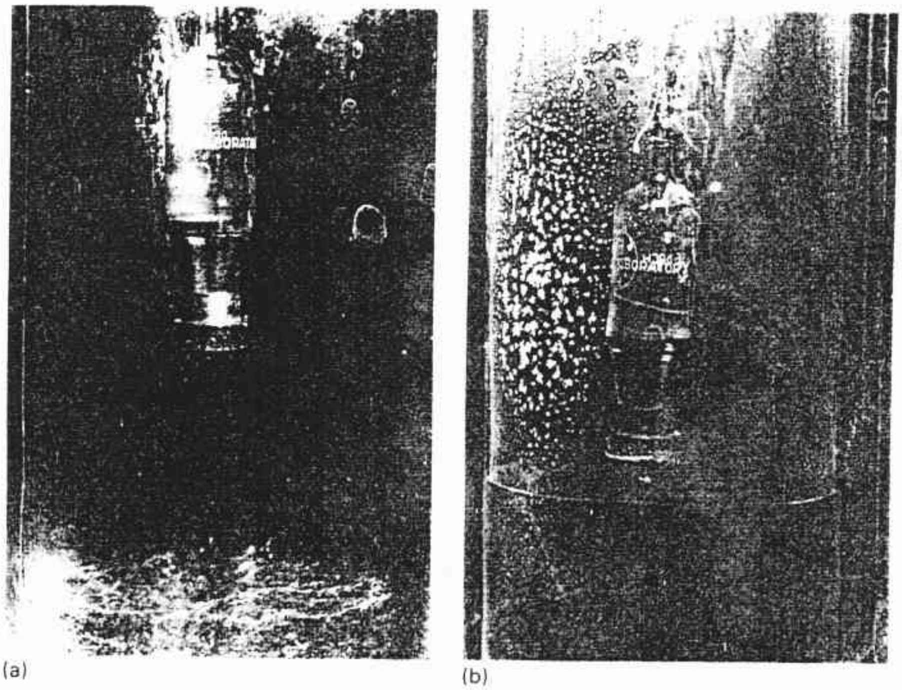

Figure 11.8 Liquid helium and the porous-plug experiment. (*a*) Above the λ transition, the liquid helium is seen to boil vigorously and the liquid inside the small container sealed with a porous plug of jeweler's rouge does not escape. (*b*) Below the λ transition, the liquid is quiescent and flows through the porous plug. *(Kurt Mendelssohn,* The Quest for Absolute Zero, *Wiley, New York, 1977, p. 242; Physics Photographic Unit, University of Oxford.)*

Superfluid ^3He $(2p, 1n; 2e^-)$

Physicists thought for a long time that ^3He could not form a superfluid, since its nucleus consists of two protons and a neutron. It thus has ½ - integer spin and obeys Fermi - Dirac statistics, which prohibits such particles from sharing the same energy state.

However, early in 1970s Lee, Osheroff, and Richardson showed that when cooled to 2.7 mK the spins of pairs of ^3He can align parallel, creating, in effect, a boson of spin 1 and enabling the liquid to condense to a sperfluid state

Two additional superfluid states were subsequently discovered a spin 0 state (antiparallel spins) at 1.8 mK and a second spin 1 state that is created when an external field aligns the spins of ^3He pairs

The three scientists received the 1996 Nobel prize for their discovery.

Comments on superconductivity

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編號： 12-23
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Carl Wieman and Eric Cornell

(born 1951 and 1961, both American)

A Bose–Einstein condensate in a gas was first achieved on planet Earth at 10:54 a.m., June, 5, 1995, in the laboratory of Wieman(left) and Cornell(right) on the campus of the University of Colorado at Boulder. The original experimental apparatus is now at the Smithsonian Institution. Along with MIT physicist, Wolfgang Ketterle, Wieman and Cornell were awarded the 2001 Nobel Prize in physics for their experimental work. A dedicated teacher, Wieman now splits his time between research and developing innovative ways of teaching freshman physics.

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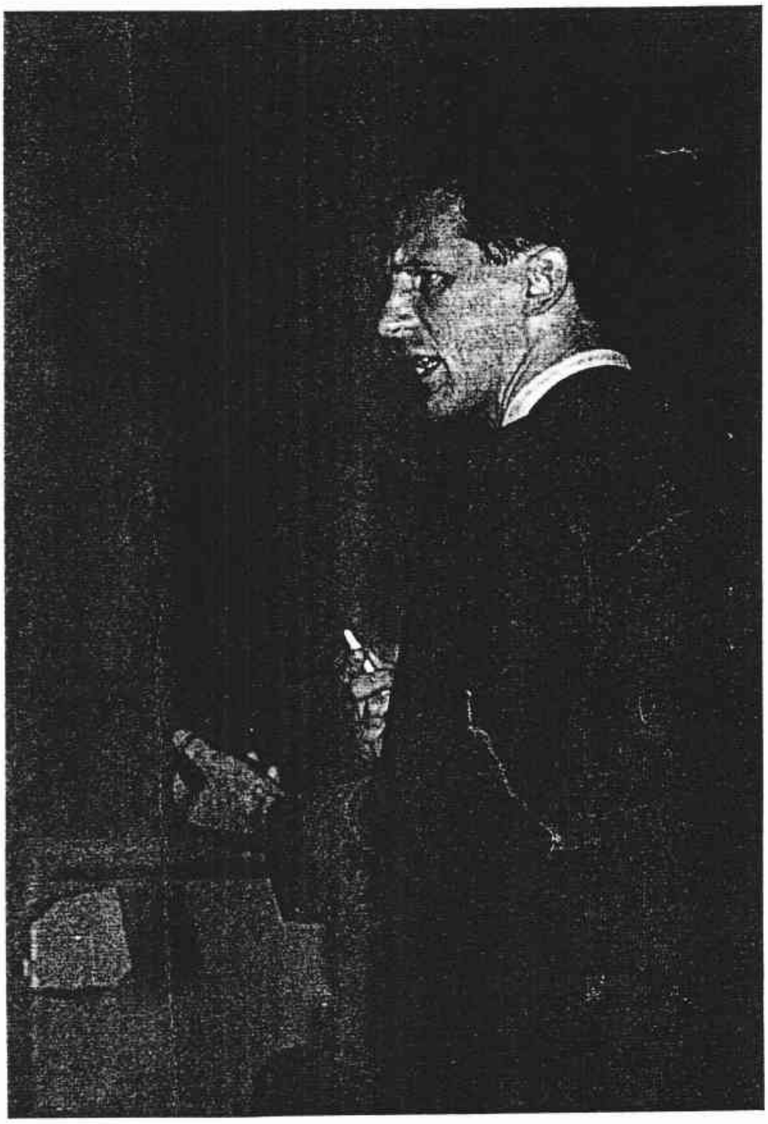

Wolfgang Ketterle

The BEC in a gas was first achieved at 10^{54} am June 5, 1995

With W. Ketterle, C. Wieman and E. Cornell won the 2001 Nobel prize in Physics.

Theoretical work

Einstein

London

Landau

Tisza

Bogoliubov

Penrose

Onsager

Feynman

Lee, Yang, Huang

Beliaev and Pitaevskii

Challenges.

- The identification of an atomic system which would stay gaseous all the way to the BEC transition.
- The development of cooling and trapping technique to reach the required regime of temperature and density.

The Photon Gas :

Treating the electromagnetic radiation in a cavity as a collection of photons.

Photons are bosons (with spin 1)

However, photon number is not constant

Photons are continuously being created (emitted by the cavity) and destroyed (absorbed by the cavity)

$\Rightarrow$ $\Sigma \delta N_i = 0$ constraint equation needs not be imposed

Follow the same procedure as before, we have

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

$$n_{ph}(\epsilon) = g_{ph}(\epsilon) f_{ph}(\epsilon)$$

$$= \frac{g_{ph}(\epsilon)}{e^{\epsilon/kT} - 1}$$

$$g_{ph}(\epsilon)\, d\epsilon = \frac{8\pi \nu^2 d\nu}{c^3} V$$

$$= \frac{8\pi V \epsilon^2 d\epsilon}{c^3 h^3}$$

$\epsilon = h\nu$ has been used

$$\underset{\substack{\downarrow \\ \text{energy density}}}{u(\epsilon)}\, d\epsilon = \frac{8\pi \epsilon^3 d\epsilon}{c^3 h^3 (e^{\epsilon/kT} - 1)} = \frac{\epsilon\, g_{ph}(\epsilon) f_{ph}(\epsilon)\, d\epsilon}{V}$$

$$u(\nu)\, d\nu = \frac{8\pi \nu^2}{c^3} \frac{h\nu\, d\nu}{e^{h\nu/kT} - 1}$$

Planck's formula.

Bose's original work.

Cosmic Blackground radiation.

$T = 2.7\ K$

$\Rightarrow$ want to find the photons per unit volume in the universe.

$$n_{ph}(\epsilon) = \frac{g_{ph}(\epsilon)}{e^{\epsilon/kT}-1}$$

$$\frac{N}{V} = \frac{1}{V}\int_0^\infty n_{ph}(\epsilon)\,d\epsilon$$

$$= \frac{1}{V}\int_0^\infty \frac{g_{ph}(\epsilon)\,d\epsilon}{e^{\epsilon/kT}-1}$$

$$= \int_0^\infty \frac{8\pi\epsilon^2 d\epsilon}{(ch)^3(e^{\epsilon/kT}-1)}$$

$$= \frac{8\pi(kT)^3}{(ch)^3}\int_0^\infty \frac{\left(\frac{\epsilon}{kT}\right)^2 \frac{d\epsilon}{kT}}{e^{\epsilon/kT}-1}$$

Let $x = \frac{\epsilon}{kT}$

$$\frac{N}{V} = 8\pi\left(\frac{kT}{ch}\right)^3 \underbrace{\int \frac{x^2 dx}{e^x-1}}_{2.40}$$

$$\frac{N}{V} = 8\pi\left(\frac{1.38\cdot10^{-23}J/K \times 2.7K}{3\cdot10^8 m/s\cdot 6.63\cdot10^{-34}Js}\right)^3\cdot 2.40$$

$$= \underline{3.97\cdot10^8\ photons/m^3}$$

2.3.8. Derivation of the Kronig-Penney model

The solution to Schrödinger's equation for the Kronig-Penney potential previously shown in Figure 2.3.3 and discussed in section 2.3.2.1 is obtained by assuming that the solution is a Bloch function, namely a traveling wave solution of the form, e^{ikx}, multiplied with a periodic solution, $u(x)$, which has the same period as the periodic potential. The total wavefunction is therefore of the form:

$$\Psi(x) = u(x)e^{ikx} \tag{2.3.18}$$

where $u(x)$ is the periodic function as defined by $u(x) = u(x + a)$, and $k(x)$ is the wave number. Rewriting the wavefunction in such form allows the simplification of the Schrödinger equation, which we now apply to region I, between the barriers where $V(x) = 0$ and region II, the barrier region where $V(x) = V_0$:

In region I, Schrödinger's equation becomes:

$$\frac{d^2u_I(x)}{dx^2} + 2ik\frac{du_I(x)}{dx} + (\beta^2 - k^2)u_I(x) = 0 \text{ for } 0 < x < a\text{-}b \tag{2.3.19}$$

with

$$\beta = \frac{2\pi}{h}\sqrt{2mE} \tag{2.3.20}$$

While in region II, it becomes:

$$\frac{d^2u_{II}(x)}{dx^2} + 2ik\frac{du_{II}(x)}{dx} - (k^2 + \alpha^2)u_{II}(x) = 0 \text{ for } a\text{-}b < x < a \tag{2.3.21}$$

with

$$\alpha = \frac{2\pi}{h}\sqrt{2m(V_0 - E)} \tag{2.3.22}$$

The solution to equations (2.3.6) and (2.3.8) are of the form:

$$u_I(x) = (A\cos\beta x + B\sin\beta x)e^{-ikx} \text{ for } 0 < x < a\text{-}b \tag{2.3.23}$$

$$u_{II}(x) = (C\cosh\alpha x + D\sin\alpha x)e^{-ikx} \text{ for } a\text{-}b < x < a \tag{2.3.24}$$

Since the potential, $V(x)$, is finite everywhere, the solutions for $u_I(x)$ and $u_{II}(x)$ must be continuous as well as their first derivatives. Continuity at $x = 0$ results in:

$$u_I(0) = u_{II}(0) \text{ so that } A = C \tag{2.3.25}$$

and continuity at $x = a\text{-}b$ combined with the requirement that $u(x)$ be periodic results in:

$$u_I(a-b) = u_{II}(-b) \tag{2.3.26}$$

so that

$$(A\cos\beta(a-b) + B\sin\beta(a-b))e^{-ik(a-b)} = (C\cosh\alpha b - D\sinh\alpha b)e^{ikb} \tag{2.3.27}$$

Continuity of the first derivative at $x = 0$ requires that:

$$\left.\frac{du_I(x)}{dx}\right|_{x=0} = \left.\frac{du_{II}(x)}{dx}\right|_{x=0} \tag{2.3.28}$$

The first derivatives of $u_I(x)$ and $u_{II}(x)$ are:

$$\frac{du_I(x)}{dx} = (A\beta\sin\beta x - B\beta\cos\beta x)e^{-ikx} - ik(A\cos\beta x + B\sin\beta x)e^{-ikx} \tag{2.3.29}$$

$$\frac{du_{II}(x)}{dx} = (C\alpha\sinh\alpha x + D\alpha\cosh\alpha x)e^{-ikx} - ik(C\cosh\alpha x + D\sinh\alpha x)e^{-ikx} \tag{2.3.30}$$

so that (2.3.15) becomes:

$$-B\beta - ikA = D\alpha - ikC \tag{2.3.31}$$

Finally, continuity of the first derivative at $x = a\text{-}b$, again combined with the requirement that $u(x)$ is periodic, results in:

$$\left.\frac{du_I(x)}{dx}\right|_{x=a-b} = \left.\frac{du_{II}(x)}{dx}\right|_{x=-b} \tag{2.3.32}$$

so that

$$\begin{aligned}&(A\beta\sin\beta(a-b) - B\beta\cos\beta(a-b))e^{-ik(a-b)}\\&-ik(A\cos\beta(a-b) + B\sin\beta(a-b))e^{-ik(a-b)}\\&=(-C\alpha\sinh\alpha b + D\alpha\cosh\alpha b)e^{ikb} - ik(C\cosh\alpha b - D\sinh\alpha b)e^{ikb}\end{aligned} \tag{2.3.33}$$

This equation can be simplified using equation (2.3.14) as:

$$(A\beta\sin\beta(a-b) - B\beta\cos\beta(a-b)) = (-C\alpha\sinh\alpha b + D\alpha\cosh\alpha b)e^{ika} \tag{2.3.34}$$

As a result we have four homogenous equations, (2.3.12), (2.3.14), (2.3.18), and (2.3.21), with four unknowns, A, B, C, and D, for which there will be a solution if the determinant of this set of equations is zero, or:

$$\begin{vmatrix} 1 & 0 & -1 & 0 \\ 0 & \beta & 0 & \alpha \\ \cos\beta(a-b) & \sin\beta(a-b) & -\cosh\alpha b\exp ika & \sinh\alpha b\exp ika \\ \beta\sin\beta(a-b) & -\beta\cos\beta(a-b) & \alpha\sin\alpha b\exp ika & -\alpha\cosh\alpha b\exp ika \end{vmatrix} = 0 \qquad (2.3.35)$$

The first row of the determinant represents equation (2.3.12), the second row is obtained by combining (2.3.18) and (2.3.12), the third row represents equation (2.3.14) and the fourth row represents equation (2.3.21). This determinant can be rewritten as two determinants, each with three rows and column, while replacing cos$\beta(a\text{-}b)$ by β_c, sin$\beta(a\text{-}b)$ by β_s, coshαb e^{ika} by α_c and sinhαb e^{ika} by α_s, which results in:

$$\begin{vmatrix} \beta & 0 & \alpha \\ \beta_s & -\alpha_c & \alpha_s \\ -\beta\beta_c & \alpha\alpha_s & -\alpha\alpha_c \end{vmatrix} = \begin{vmatrix} 0 & \beta & \alpha \\ \beta_c & \beta_s & \alpha_s \\ \beta\beta_s & -\beta\beta_c & -\alpha\alpha_c \end{vmatrix} \qquad (2.3.36)$$

Working out the determinants and using $\beta_c^2 + \beta_s^2 = 1$, and $\alpha_c^2 - \alpha_s^2 = e^{2ika}$, one finds:

$$(\alpha^2 - \beta^2)\sinh\alpha b\sin\beta(a-b)\exp ika + 2\alpha\beta\cosh\alpha b\cos\beta(a-b)\exp ika = \alpha\beta(1+ \qquad (2.3.37)$$

And finally, substituting β_c, β_s, α_c and α_s:

$$\cos ka = F = \frac{\alpha^2 - \beta^2}{2\alpha\beta}\sinh\alpha b\sin\beta(a-b) + \cosh\alpha b\cos\beta(a-b) \qquad (2.3.38)$$

where e^{ika} + e^{-ika} was replaced by 2cos *ka*.

A further simplification is obtained as the barrier width, *b*, is reduced to zero while the barrier height, V_0, is increased to infinity in such manner that the product, bV_0, remains constant and the potential becomes a delta function train at $x = a$ and repeated with a period of *a*, namely $bV_0\delta(x - b - na)$ where n is an integer. As *b* approaches zero, sinhαb approaches αb. Equation (2.3.25) then reduces to:

$$\cos ka = F = P\frac{\sin\beta a}{\beta a} + \cos\beta a \qquad (2.3.39)$$

with

$$\beta = \frac{\sqrt{2mE}}{\hbar} \text{ and } P = \frac{mV_0ba}{\hbar^2} \qquad (2.3.40)$$

6.21 Intro to Band Structure

Quantum mechanics is essential to describe the properties of solid materials, just as it is for lone atoms and molecules. One well-known example is superconductivity, in which current flows without any resistance. The complete absence of any resistance cannot be explained by classical physics, just like superfluidity cannot for fluids.

But even *normal* electrical conduction simply cannot be explained without quantum theory. Consider the fact that at ordinary temperatures, typical metals have electrical resistivities of a few times 10^{-8} ohm-m (and up to a hundred thousand times less still at very low temperatures), while Wikipedia lists a resistance for teflon of up to 10^{24} ohm-m. (Teflon's "one-minute" resistivity can be up to 10^{19} ohm-m.) That is a difference in resistance between the best conductors and the best insulators by over thirty orders of magnitude!

There is simply no way that classical physics could even begin to explain it. As far as classical physics is concerned, all of these materials are quite similar combinations of positive nuclei and negative electrons.

Consider an ordinary sewing needle. You would have as little trouble supporting its tiny 60 mg weight as a metal has conducting electricity. But multiply it by 10^{30}. Well, don't worry about supporting its weight. Worry about the entire earth coming up over your ears and engulfing you, because the needle now has ten times the mass of the earth. That is how widely different the electrical conductivities of solids are.

Only quantum mechanics can explain why it is possible, by making the electron energy levels discrete, and more importantly, by grouping them together in "bands."

Key Points

- Even excluding superconductivity, the electrical conductivities of solids vary enormously.

6.21.1 Metals and insulators

To understand electrical conduction in solids requires consideration of their electron energy levels.

Typical energy spectra are sketched in figure 6.19. The spectrum of a free-electron gas, noninteracting electrons in a box, is shown to the left. The energy $E^{\rm p}$ of the single-particle states is shown along the vertical axis. The energy levels allowed by quantum mechanics start from zero and reach to infinity. The energy levels are spaced many orders of magnitude more tightly together than the hatching in the figure can indicate. For almost all practical purposes, the energy levels form a continuum. In the ground state, the electrons fill the lowest of these energy levels, one electron per state. In the figure, the occupied states are shown in red. For a macroscopic system, the number of electrons is practically speaking infinite, and so is the number of occupied states.

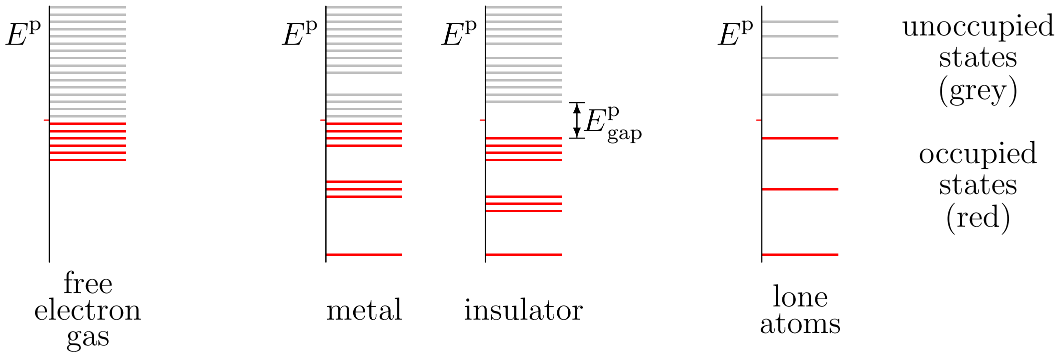

Figure 6.19: Sketch of electron energy spectra in solids at absolute zero temperature. (No attempt has been made to picture a density of states). Far left: the free-electron gas has a continuous band of extremely densely spaced energy levels. Far right: lone atoms have only a few discrete electron energy levels. Middle: actual metals and insulators have energy levels grouped into densely spaced bands separated by gaps. Insulators completely fill up the highest occupied band.

However, the free-electron gas assumes that there are no forces on the electrons. Inside a solid, this would only be true if the electric charges of the nuclei and fellow electrons would be homogeneously distributed throughout the entire solid. In that case the forces come equally from all directions and cancel each other out perfectly. In a true solid, forces from different directions do tend to cancel each other out, but this is far from perfect. For example, an electron very close to one particular nucleus experiences a strong attraction from that nucleus, much too strong for the rest of the solid to cancel.

The diametrical opposite of the free-electron gas picture is the case that the atoms of the solid are spaced so far apart that they are essentially lone atoms. In that case, of course, the "solid" would not physically be a solid at all, but a thin gas. Lone atoms do not have a continuum of electron energy levels, but discrete ones, as sketched to the far right in figure 6.19. One basic example is the hydrogen spectrum shown in figure 4.8. Every lone atom in the system has the exact same discrete energy levels. Widely spaced atoms do not conduct electricity, assuming that not enough energy is provided to ionize them. While for the free-electron gas conduction can be achieved by moving a few electrons to slightly higher energy levels, for lone atoms there *are no* slightly higher energy levels.

When the lone atoms are brought closer together to form a true solid, however, the discrete atomic energy levels broaden out into bands. In particular, the outer electrons start to interact strongly with surrounding atoms. The different forms that these interactions can take produce varying energies, causing initially equal electron energies to broaden into bands. The result is sketched in the middle of figure 6.19. The higher occupied energy levels spread out significantly. (The inner atomic electrons, having the most negative net energies, do not interact significantly with different atoms, and their energy levels do not broaden much. This is not just because these electrons are farther from the surrounding atoms, but also because the inner electrons have much greater kinetic and potential energy levels to start with.)

For metals, conduction now becomes possible. Electrons at the highest occupied energy level, the Fermi energy, can be moved to slightly higher energy levels to provide net motion in a particular direction. That is just like they can for a free-electron gas as discussed in the previous section. The net motion produces a current.

Insulators are different. As sketched in figure 6.19, they completely fill up the highest occupied energy band. That filled band is called the "valence band." The next higher and empty band is called the "conduction band."

Now it is no longer possible to prod electrons to slightly higher energy levels to create net motion. There are no slightly higher energy levels available; all levels in the valence band are already filled with electrons.

To create a state with net motion, some electrons would have to be moved to the conduction band. But that would require large amounts of energy. The minimum energy required is the difference between the top of the valence band and the bottom of the conduction band. This energy is appropriately called the "band gap" energy $E^{\rm p}_{\rm gap}$. It is typically of the order of electron volts, comparable to atomic potentials for outer electrons. That is in turn comparable to ionization energies, a great amount of energy on an atomic scale.

Resistance is determined for voltages low enough that Ohm's law applies. Such voltages do not provide anywhere near the energy required to move electrons to the conduction band. So the electrons in an insulator are stuck. They cannot achieve net motion at all. And without net motion, there is no current. That makes the resistance infinite. In this way the band gaps are responsible for the enormous difference in resistance between metals and insulators.

Note that a normal applied voltage will not have a significant effect on the band structure. Atomic potential energies are in terms of eV or more. For the applied voltage to compete with that would require a voltage drop comparable to volts *per atom*. On a microscopic scale, the applied potential does not change the states.

Key Points

- ⚷ Quantum mechanics allows only discrete energy levels for the electrons in a solid, and these levels group together in bands with gaps in between them.
- ⚷ If the electrons fill the spectrum right up to a gap between bands, the electrons are stuck. It will require a large amount of energy to activate them to conduct electricity or heat. Such a solid is an insulator at absolute zero temperature.
- ⚷ The filled band is called the valence band, and the empty band above it the conduction band.

6.21.2 Typical metals and insulators

If a material completely fills up its valence band with electrons, it is an insulator. But what materials would do that? This subsection gives a few rules of thumb.

One important rule is that the elements towards the left in the periodic table figure 5.8 are metals. A relatively small group of elements towards the right are nonmetals.

Consider first the alkali metals found in group I to the far left in the table. The lone atoms have only one valence electron per atom. It is in an atomic “s” state that can hold two electrons, chapter 5.9.4. Every spatial state, including the s state, can hold two electrons that differ in spin.

Now if the lone atoms are brought closer together to form a solid, the spatial states change. Their energy levels broaden out into a band. However, the total number of states does not change. One spatial state per atom stays one spatial state per atom. Since each spatial state can hold two electrons, and there is only one, the band formed from the s states is only half filled. Therefore, like the name says, the alkali metals are metals.

In helium the spatial 1s states are completely filled with the two electrons per atom. That makes solid helium an insulator. It should be noted that helium is only a solid at very low temperatures and very high pressures. The atoms are barely held together by very weak Van der Waals forces.

The alkaline metals found in group II of the periodic table also have two valence electrons per atom. So you would expect them to be insulators too. However, like the name says, the alkaline metals are metals. What happens is that the filled band originating from the atomic s states merges with an empty band originating from the atomic p states. That produces a partially filled combined band.

This does not apply to helium because there are no 1p states. The lowest empty energy states for helium are the 2s ones. Still, computations predict that helium will turn metallic at extremely high pressures. Compressing a solid has the primary effect of increasing the kinetic energy of the electrons. Roughly speaking, the kinetic energy is inversely proportional to the square of the electron spacing, compare the Fermi energy (6.16). And increasing the kinetic energy of the electrons brings them closer to a free-electron gas.

A case resembling that of helium is ionic materials in which the ions have a noble-gas electron structure. A basic example is salt, sodium chloride. These materials are insulators, as it takes significant energy to take apart the noble-gas electron configurations. See however the discussion of ionic conductivity later in this section.

Another case that requires explanation is hydrogen. Like the alkali metals, hydrogen has only one valence electron per atom. That is not enough to fill up the energy band resulting from the atomic 1s states. So you would expect solid hydrogen to be a metal. But actually, hydrogen is an insulator. What happens is that the energy band produced by the 1s states splits into two. And the lower half is completely filled with electrons.

The reason for the splitting is that in the solid, the hydrogen atoms combine pairwise into molecules. In an hydrogen molecule, there are not two separate spatial 1s states of equal energy, chapter 5.2. Instead, there is a lowered-energy *two-electron* spatial state in which the two electrons are symmetrically shared. There is also a raised-energy *two-electron* spatial state in which the two electrons are antisymmetrically shared. So there are now two energy levels with a gap in between them. The two electrons occupy the lower-energy symmetric state with opposite spins. In the solid, the hydrogen molecules are barely held together by weak Van der Waals forces. The interactions between the molecules are small, so the two molecular energy levels broaden only slightly into two thin bands. The gap between the filled symmetric states and the empty antisymmetric ones remains.

Note that sharing electrons in pairs involves a nontrivial interaction between the two electrons in each pair. The truth must be stretched a bit to fit it within the band theory idea of noninteracting electrons. Truly noninteracting electrons would have the spatial states of the hydrogen molecular *ion* available to them, chapter 4.6. Here the lower energy state is one in which a single electron is symmetrically shared between the atoms. And the higher energy state is one in which a single electron is antisymmetrically shared. In the model of noninteracting electrons, both electrons occupy the lower-energy single-electron spatial state, again with opposite spins. One problem with this picture is that the single-electron states do not take into account where the other electron is. There is then a significant chance that both electrons can be found around the same atom. In the correct two-electron state, the electrons largely avoid that. Being around the same atom would increase their energy, since the electrons repel each other.

Note also that using the actual hydrogen molecular ion states may not be the best approach. It might be better to account for the presence of the other electron approximately using some nuclear shielding approach like the one used for atoms in chapter 5.9. An improved, but still approximate way of accounting for the second electron would be to use a so-called "Hartree-Fock" method. More generally, the most straightforward band theory approach tends to work better for metals than for insulators. Alternative numerical methods exist that work better for insulators. At the time of writing there is no simple magic bullet that works well for every material.

Group IV elements like diamond, silicon, and germanium pull a similar trick as hydrogen. They are insulators at absolute zero temperature. However, their 4 valence electrons per atom are not enough to fill the merged band arising from the s and p states. That band can hold 8 electrons per atom. Like hydrogen, a gap forms within the band. First the s and p states are converted into hybrids, chapter 5.11.4. Then states are created in which electrons are shared symmetrically between atoms and states in which they are shared antisymmetrically. There is an energy gap between these states. The lower energy states are filled with electrons and the higher energy states are empty, producing again an insulator. But unlike in hydrogen, each atom is now bonded to four others. That turns the entire solid into essentially one big molecule. These materials are much stronger and more stable than solid hydrogen. Like helium, hydrogen is only a solid at very low temperatures.

It may be noted that under extremely high pressures, hydrogen might become metallic. Not only that, as the smallest atom of them all, and in the absence of 1p atomic states, metallic hydrogen is likely to have some very unusual properties. It makes metallic hydrogen the holy grail of high pressure physics.

It is instructive to examine how the band theory of noninteracting electrons accounts for the fact that hydrogen is an insulator. Unlike the discussion above, band theory does not actually look at the number of valence electrons *per atom.* For one, a solid may consist of atoms of more than one kind. In general, crystalline solids consist of elementary building blocks called "primitive cells" that can involve several atoms. Band theory predicts the solid to be a metal if the number of electrons *per primitive cell* is odd. If the number of electrons per primitive cell is even, the material may be an insulator. In solid hydrogen each primitive cell holds a complete molecule, so there are two atoms per primitive cell. Each atom contributes an electron, so the number of electrons per primitive cell is even. According to band theory, that allows hydrogen to be an insulator. In a similar way group V elements can fill up their valence bands with an odd number of valence electrons per atom. And like hydrogen, diamond, silicon, and germanium have two atoms per primitive cell, reflecting the gap that forms in the merged s and p bands.

Of course, that cannot be the complete story. It does not explain why atoms towards the right in the periodic table would group together into primitive cells that allow them to be insulators. Why don't the atoms to the left in the periodic table do the same? Why don't the alkali metals group together in two-atom molecules like hydrogen does? Qualitatively speaking, metals are characterized by valence electrons that are relatively loosely bound. Suppose you compare the size of the 2s state of a lithium atom with the spacing of the atoms in solid lithium. If you do, you find that on average the 2s valence electron is no closer to the atom to which it supposedly "belongs" than to the neighboring atoms. Therefore, the electrons are what is called "delocalized." They are not bound to one specific location in the atomic crystal structure. So they are not really interested in helping bond "their" particular atom to its immediate neighbors. On the other hand, to the right in the periodic table, including hydrogen and helium, the valence electrons are much more tightly held. To delocalize them would require that the atoms would be squeezed much more tightly together. That does not happen under normal pressures because it produces very high kinetic energy of the electrons.

Where hydrogen refuses to be a metal with one valence electron per atom, boron refuses to do so with three. However, boron is very ambivalent about it. It does not really feel comfortable with either metallic or covalent behavior. A bit of impurity can readily turn it metallic. That great sensitivity to impurity makes the element very hard to study. At the time of writing, it is believed that boron has a covalent ground state under normal pressures. The convoluted crystal structure is believed to have a unit cell with either 12 or 106 atoms, depending on precise conditions.

In group IV, tin is metallic above 13 °C, as white tin, but covalent below this temperature, as grey tin. It is often difficult to predict whether an element is a metal or covalent near the middle of the periodic table. Lead, of course, is a metal.

It should further be noted that band theory can be in error because it ignores the interactions between the electrons. "Mott insulators" and "charge transfer insulators" are, as the name says, insulators even though conventional band theory would predict that they are metals.

Key Points

- In the periodic table, the group I, II, and III elements are normally metals.
- Hydrogen and helium are nonmetals. Don't ask about boron.
- The group IV elements diamond, silicon, and germanium are insulators at absolute zero temperature.

6.21.3 Semiconductors

Temperature can have significant effects on electrical conduction. As the previous section noted, higher temperature decreases the conduction in metals, as there are more crystal vibrations that the moving electrons can get scattered by. But a higher temperature also changes which energy states the electrons occupy. And that can produce semiconductors.

Figure 6.19 showed which energy states the electrons occupy at absolute zero temperature. There are no electrons with energies above the Fermi level indicated by the red tick mark. Figure 6.20 shows how that changes for a nonzero temperature. Now random thermal motion allows electrons to reach energy levels up to roughly $k_{\rm B}T$ above the Fermi level. Here $k_{\rm B}$ is the Boltzmann constant and T the absolute temperature. This change in electron energies is described mathematically by the Fermi-Dirac distribution discussed earlier.

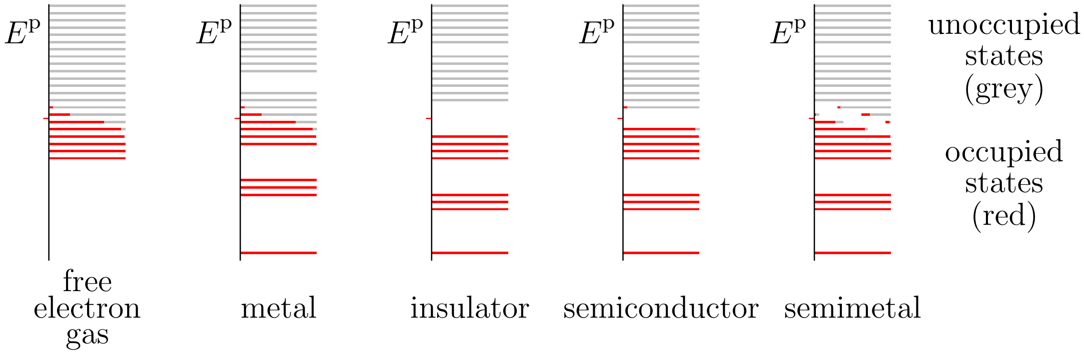

Figure 6.20: Sketch of electron energy spectra in solids at a nonzero temperature.

It does not make much difference for a free-electron gas or a metal. However, for an insulator it may make a dramatic difference. If the band gap is not too large compared to $k_{\rm B}T$, random thermal motion will put a few very lucky electrons in the previously empty conduction band. These electrons can then be prodded to slightly higher energies to allow some electric current to flow. Also, the created "holes" in the valence band, the states that have lost their electrons, allow some electric current. Valence band electrons can be moved into holes that have a preferred direction of motion from states that do not. These electrons will then leave behind holes that have the opposite direction of motion.

It is often more convenient to think of the moving holes instead of the electrons as the electric current carriers in the valence band. Since a hole means that a negatively charged electron is *missing,* a hole acts much like a positively charged particle would.

Because both the electrons in the conduction band and the holes in the valence band allow some electrical conduction, the original insulator has turned into what is called a "semiconductor."

The previous section mentioned that a classical picture of moving electrons simply does not work for metals. Their motion is much too much restrained by a lack of available empty energy states. However, the conduction band of semiconductors is largely empty. Therefore a classical picture works much better for the motion of the electrons in the conduction band of a semiconductor.

Key Points

- For semiconductors, conduction can occur because some electrons from the valence band are thermally excited to the conduction band.
- Both the electrons that get into the conduction band and the holes they leave behind in the valence band can conduct electricity.

6.21.4 Semimetals

One additional type of electron energy spectrum for solids should be mentioned. For a "semimetal," two distinct energy bands overlap slightly at the Fermi level. In terms of the simplistic spectra of figure 6.19, that would mean that semimetals are metals. Indeed they do allow conduction at absolute zero temperature. However, their further behavior is noticeably different from true metals because the overlap of the two bands is only small. One difference is that the electrical conduction of semimetals increases with temperature, unlike that of metals. Like for semiconductors, for semimetals a higher temperature means that there are more electrons in the upper band and more holes in the lower band. That effect is sketched to the far right in figure 6.20.

The classical semimetals are arsenic, antimony, and bismuth. Arsenic and antimony are not just semimetals, but also "metalloids," a group of elements whose chemical properties are considered to be intermediate between metals and nonmetals. But semimetal and metalloid are not the same thing. Semimetals do not have to consist of a single element. Conversely, metalloids include the semiconductors silicon and germanium.

A semimetal that is receiving considerable attention at the time of writing is graphite. Graphite consists of sheets of carbon atoms. A single sheet of carbon, called graphene, is right on the boundary between semimetal and semiconductor. A carbon nanotube can be thought of as a strip cut from a graphene sheet that then has its long edges attached together to produce a cylinder. Carbon nanotubes have electrical properties that are fundamentally different depending on the direction in which the strip is cut from the sheet. They can either be metallic or nonmetallic.

Key Points

- Semimetals have properties intermediate between metals and semiconductors.

6.21.5 Electronic heat conduction

The valence electrons in metals are not just very good conductors of electricity, but also of heat. In insulators electrons do not assist in heat conduction; it takes too much energy to excite them. However, atomic vibrations in solids can conduct heat too. For example, diamond, an excellent electrical insulator, is also an excellent conductor of heat. Therefore the differences in heat conduction between solids are not by far as large as those in electrical conduction. Because atoms can conduct significant heat, no solid material will be a truly superb thermal insulator. Practical thermal insulators are highly porous materials whose volume consists largely of voids.

Key Points

- Electrons conduct heat very well, but atoms can do it too.
- Practical thermal insulators use voids to reduce atomic heat conduction.

6.21.6 Ionic conductivity

It should be mentioned that electrons do not have an absolute monopoly on electrical conduction in solids. A different type of electrical conduction is possible in ionic solids. These solids consist of a mixture of positively and negatively charged ions. Positive ions, or “cations,” are atoms that have lost one or more electrons. Negative ions, or “anions,” are atoms that have absorbed one or more additional electrons. A simple example of a ionic solid is salt, which consists of Na^+ sodium cations and Cl^- chlorine anions. For ionic solids a small amount of electrical conduction may be possible due to motion of the ions. This requires defects in the atomic crystal structure in order to give the atoms some room to move.

Typical defects include “vacancies,” in which an atom is missing from the crystal structure, and “interstitials,” in which an additional atom has been forced into one of the small gaps between the atoms in the crystal. Now if a ion gets removed from its normal position in the crystal to create a vacancy, it must go somewhere. One possibility is that it gets squeezed in between the other atoms in the crystal. In that case both a vacancy and an interstitial have been produced at the same time. Such a combination of a vacancy and an interstitial is called a "Frenkel defect." Another possibility occurs in, for example, salt; along with the original vacancy, a vacancy for a ion of the opposite kind is created. Such a combination of two opposite vacancies is called a "Schottky defect." In this case there is no need to squeeze an atom in the gaps in the crystal structure; there are now equal numbers of ions of each kind to fill the surrounding normal crystal sites. Creating defects in Frenkel or Schottky pairs ensures that the complete crystal remains electrically neutral as it should.

Impurities are another important defect. For example, in salt a Ca^{2+} calcium ion might be substituted for a Na^+ sodium ion. The calcium ion has the charge of two sodium ions, so a sodium vacancy ensures electric neutrality of the crystal. In yttria-stabilized zirconia, (YSZ), oxygen vacancies are created in zirconia, ZrO_2, by replacing some Zr^{4+} zirconium ions with Y^{3+} yttrium ones. Calcium ions can also be used. The oxygen vacancies allow mobility for the oxygen ions. That is important for applications such as oxygen sensors and solid oxide fuel cells.

For salt, the main conduction mechanism is by natrium vacancies. But the ionic conductivity of salt is almost immeasurably small at room temperature. That is due to the high energy needed to create Schottky defects and for natrium ions to migrate into the natrium vacancies. Indeed, whatever little conduction there is at room temperature is due to impurities. Heating will help, as it increases the thermal energy available for both defect creation and ion mobility. As seen from the Maxwell-Boltzmann distribution discussed earlier, thermal effects increase exponentially with temperature. Still, even at the melting point of salt its conductivity is eight orders of magnitude less than that of metals.

There are however ionic materials that have much higher conductivities. They cannot compete with metals, but some ionic solids can compete with liquid electrolytes. These solids may be referred to as "solid electrolytes, "fast ion conductors," or "superionic conductors." They are important for such applications as batteries, fuel cells, and gas sensors. Yttria-stabilized zirconia is an example, although unfortunately only at temperatures around 1,000 °C. In the best ionic conductors, the crystal structure for one kind of ion becomes so irregular that these ions are effectively in a molten state. For example, this happens for the silver ions in the classical example of hot silver iodide. Throw in 25% of rubidium chloride and $RbAg_4Cl_5$ stays superionic to room temperature.

Crystal surfaces are also crystal defects, in a sense. They can enhance ionic conductivity. For example, nanoionics can greatly improve the ionic conductivity of poor ionic conductors by combining them in nanoscale layers.

Key Points

- In ionic solids, some electrical conduction may occur through the motion of the ions instead of individual electrons.
- It is important for applications such as batteries, fuel cells, and gas sensors.

6.22 Electrons in Crystals

A meaningful discussion of semiconductors requires some background on how electrons move through solids. The free-electron gas model simply assumes that the electrons move through an empty periodic box. But of course, to describe a real solid the box should really be filled with the countless atoms around which the conduction electrons move.

This subsection will explain how the motion of electrons gets modified by the atoms. To keep things simple, it will still be assumed that there is no direct interaction between the electrons. It will also be assumed that the solid is crystalline, which means that the atoms are arranged in a periodic pattern. The atomic period should be assumed to be many orders of magnitude shorter than the size of the periodic box. There must be many atoms in each direction in the box.

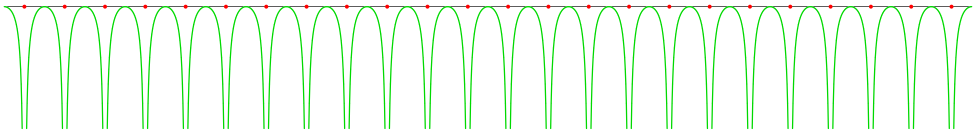

Figure 6.21: Potential energy seen by an electron along a line of nuclei. The potential energy is in green, the nuclei are in red.

The effect of the crystal is to introduce a periodic potential energy for the electrons. For example, figure 6.21 gives a sketch of the potential energy seen by an electron along a line of nuclei. Whenever the electron is right on top of a nucleus, its potential energy plunges. Close enough to a nucleus, a very strong attractive Coulomb potential is seen. Of course, on a line that does not pass exactly through nuclei, the potential will not plunge that low.

Kronig & Penney developed a very simple one-dimensional model that explains much of the motion of electrons through crystals. It assumes that the potential energy seen by the electrons is periodic on some atomic-scale period d_x. It also assumes that this potential energy is piecewise constant, like in figure 6.22. You might think of the regions of low potential energy as the immediate vicinity of the nuclei. This is the model that will be examined. The atomic