

## 9.1 STATISTICAL DISTRIBUTIONS

### *Three different kinds*

What statistical mechanics does is determine the most probable way in which a certain total amount of energy  $E$  is distributed among the  $N$  members of a system of particles in thermal equilibrium at the absolute temperature  $T$ . Thus we can establish how many particles are likely to have the energy  $\epsilon_1$ , how many to have the energy  $\epsilon_2$ , and so on.

The particles are assumed to interact with one another and with the walls of their container to an extent sufficient to establish thermal equilibrium but not so much that their motions are strongly correlated. More than one particle state may correspond to a certain energy  $\epsilon$ . If the particles are not subject to the exclusion principle, more than one particle may be in a certain state.

A basic premise of statistical mechanics is that the greater the number  $W$  of different ways in which the particles can be arranged among the available states to yield a particular distribution of energies, the more probable is the distribution. It is assumed that each state of a certain energy is equally likely to be occupied. This assumption is plausible but its ultimate justification (as in the case of Schrödinger's equation) is that the conclusions arrived at with its help agree with experiment.

The program of statistical mechanics begins by finding a general formula for  $W$  for the kind of particles being considered. The most probable distribution, which corresponds to the system's being in thermal equilibrium, is the one for which  $W$  is a maximum, subject to the condition that the system consists of a fixed number  $N$  of particles (except when they are photons or their acoustic equivalent called **phonons**) whose total energy is some fixed amount  $E$ . The result in each case is an expression for  $n(\epsilon)$ , the number of particles with the energy  $\epsilon$ , that has the form

Number of particles  
of energy  $\epsilon$

$$n(\epsilon) = g(\epsilon)f(\epsilon) \quad (9.1)$$

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

When a continuous rather than a discrete distribution of energies is involved,  $g(\epsilon)$  is replaced by  $g(\epsilon) d\epsilon$ , the number of states with energies between  $\epsilon$  and  $\epsilon + d\epsilon$ .

We shall consider systems of three different kinds of particles:

- 1 Identical particles that are sufficiently far apart to be distinguishable, for instance, the molecules of a gas. In quantum terms, the wave functions of the particles overlap to a negligible extent. The **Maxwell-Boltzmann distribution function** holds for such particles.
- 2 Identical particles of 0 or integral spin that cannot be distinguished one from another because their wave functions overlap. Such particles, called **bosons** in Chap. 7, do not obey the exclusion principle, and the **Bose-Einstein distribution function** holds for them. Photons are in this category, and we shall use Bose-Einstein statistics to account for the spectrum of radiation from a blackbody.
- 3 Identical particles with odd half-integral spin ( $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ ) that also cannot be distinguished one from another. Such particles, called **fermions**, obey the exclusion principle, and the **Fermi-Dirac distribution function** holds for them. Electrons are in this category, and we shall use Fermi-Dirac statistics to study the behavior of the free electrons in a metal that are responsible for its ability to conduct electric current.

## 9.2 MAXWELL-BOLTZMANN STATISTICS

*Classical particles such as gas molecules obey them*

The Maxwell-Boltzmann distribution function states that the average number of particles  $f_{MB}(\epsilon)$  in a state of energy  $\epsilon$  in a system of particles at the absolute temperature  $T$  is

**Maxwell-Boltzmann  
distribution function**

$$f_{MB}(\epsilon) = Ae^{-\epsilon/kT} \quad (9.2)$$

The value of  $A$  depends on the number of particles in the system and plays a role here analogous to that of the normalization constant of a wave function. As usual,  $k$  is Boltzmann's constant, whose value is

**Boltzmann's  
constant**

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

Combining Eqs. (9.1) and (9.2) gives us the number  $n(\epsilon)$  of identical, distinguishable particles in an assembly at the temperature  $T$  that have the energy  $\epsilon$ :

**Maxwell-  
Boltzmann**

$$n(\epsilon) = Ag(\epsilon)e^{-\epsilon/kT} \quad (9.3)$$



## Example 9.2

Obtain a formula for the populations of the rotational states of a rigid diatomic molecule.

### Solution

For such a molecule Eq. (8.9) gives the energy states in terms of the rotational quantum number  $J$  as

$$\epsilon_J = J(J + 1) \frac{\hbar^2}{2I}$$

More than one rotational state may correspond to a particular  $J$  because the component  $L_z$  in any specified direction of the angular momentum  $L$  may have any value in multiples of  $\hbar$  from  $J\hbar$  through 0 to  $-J\hbar$ , for a total of  $2J + 1$  possible values. Each of these  $2J + 1$  possible orientations of  $L$  constitutes a separate quantum state, and so

$$g(\epsilon) = 2J + 1$$

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If the number of molecules in the  $J = 0$  state is  $n_0$ , the normalization constant  $A$  in Eq. (9.3) is just  $n_0$ , and the number of molecules in the  $J = J$  state is

$$n_J = Ag(\epsilon)e^{-\epsilon/kT} = n_0(2J + 1)e^{-J(J+1)\hbar^2/kT}$$

In carbon monoxide, to give an example, this formula shows that the  $J = 7$  state is the most highly populated at 20°C. The intensities of the rotational lines in a molecular spectrum are proportional to the relative populations of the various rotational energy levels. Figure 8.22 shows the vibration-rotation band of CO for the  $v = 0 \rightarrow v = 1$  vibrational transition with lines identified according to the  $J$  value of the initial rotational level. The  $P$  and  $R$  branches both have their maxima at  $J = 7$ , as expected.

## 9.3 MOLECULAR ENERGIES IN AN IDEAL GAS

*They vary about an average of  $\frac{3}{2}kT$*

We now apply Maxwell-Boltzmann statistics to find the distribution of energies among the molecules of an ideal gas. Energy quantization is inconspicuous in the translational motion of gas molecules, and the total number of molecules  $N$  in a sample is usually very large. It is therefore reasonable to consider a continuous distribution of molecular energies instead of the discrete set  $\epsilon_1, \epsilon_2, \epsilon_3, \dots$ . If  $n(\epsilon) d\epsilon$  is the number of molecules whose energies lie between  $\epsilon$  and  $\epsilon + d\epsilon$ , Eq. (9.1) becomes

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

$$n(\epsilon) d\epsilon = [g(\epsilon) d\epsilon][f(\epsilon)] = Ag(\epsilon)e^{-\epsilon/kT} d\epsilon \quad (9.4)$$

The first task is to find  $g(\epsilon) d\epsilon$ , the number of states that have energies between  $\epsilon$  and  $\epsilon + d\epsilon$ . This is easiest to do in an indirect way. A molecule of energy  $\epsilon$  has a momentum  $\mathbf{p}$  whose magnitude  $p$  is specified by

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

Each set of momentum components  $p_x, p_y, p_z$  specifies a different state of motion. Let us imagine a **momentum space** whose coordinate axes are  $p_x, p_y, p_z$ , as in Fig. 9.1. The number of states  $g(p) dp$  with momenta whose magnitudes are between  $p$  and  $p + dp$  is proportional to the volume of a spherical shell in momentum space  $p$  in radius and  $dp$  thick, which is  $4\pi p^2 dp$ . Hence

### Number of momentum states

$$g(p) dp = Bp^2 dp \quad (9.5)$$

where  $B$  is some constant.

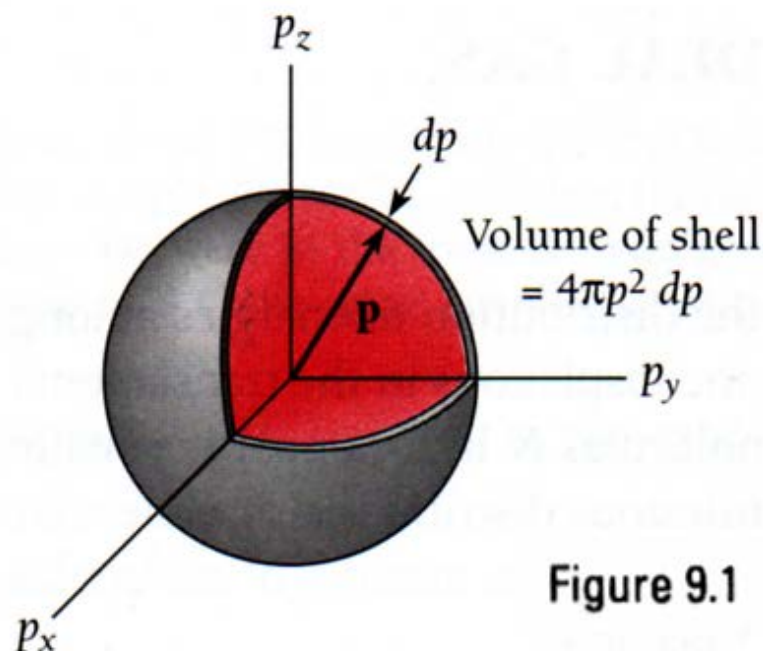


Figure 9.1



Since each momentum magnitude  $p$  corresponds to a single energy  $\epsilon$ , the number of energy states  $g(\epsilon) d\epsilon$  between  $\epsilon$  and  $\epsilon + d\epsilon$  is the same as the number of momentum states  $g(p) dp$  between  $p$  and  $p + dp$ , and so

$$g(\epsilon) d\epsilon = Bp^2 dp \quad (9.6)$$

Because

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

Eq. (9.6) becomes

**Number of energy states**

$$g(\epsilon) d\epsilon = 2m^{3/2} B \sqrt{\epsilon} d\epsilon \quad (9.7)$$

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

$$n(\epsilon) d\epsilon = C \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon \quad (9.8)$$

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

$$n(\epsilon) d\epsilon = Ag(\epsilon) e^{-\epsilon/kT} d\epsilon \quad (9.4)$$

To find  $C$  we make use of the normalization condition that the total number of molecules is  $N$ , so that

**Normalization** 
$$N = \int_0^{\infty} n(\epsilon) d\epsilon = C \int_0^{\infty} \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon \quad (9.9)$$

From a table of definite integrals we find that

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

Here  $a = 1/kT$ , and the result is 
$$N = \frac{C}{2} \sqrt{\pi} (kT)^{3/2}$$

$$C = \frac{2\pi N}{(\pi kT)^{3/2}} \quad (9.10)$$

and, finally,

**Molecular energy  
distribution**

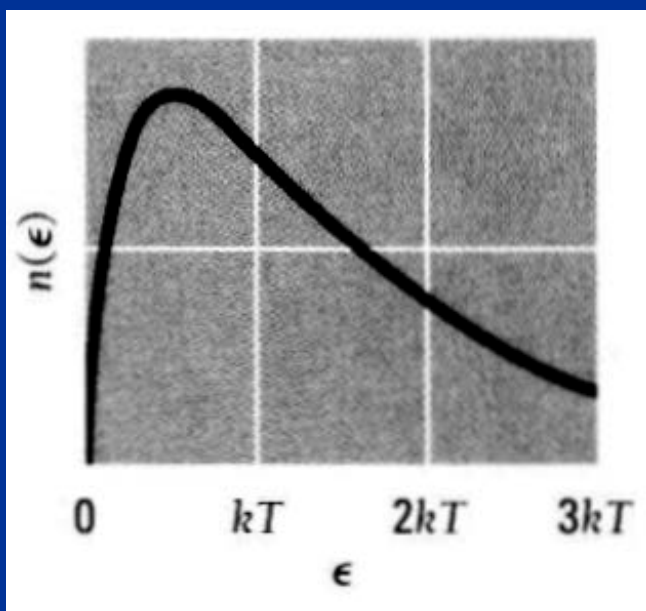
$$n(\epsilon) d\epsilon = \frac{2\pi N}{(\pi kT)^{3/2}} \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon \quad (9.11)$$

## Molecular energy distribution

$$n(\epsilon) d\epsilon = \frac{2\pi N}{(\pi kT)^{3/2}} \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon \quad (9.11)$$

This formula gives the number of molecules with energies between  $\epsilon$  and  $\epsilon + d\epsilon$  in a sample of an ideal gas that contains  $N$  molecules and whose absolute temperature is  $T$ .

Equation (9.11) is plotted in Fig. 9.2 in terms of  $kT$ . The curve is not symmetrical about the most probable energy because the lower limit to  $\epsilon$  is  $\epsilon = 0$  while there is, in principle, no upper limit (although the likelihood of energies many times greater than  $kT$  is small).



**Figure 9.2** Maxwell-Boltzmann energy distribution for the molecules of an ideal gas. The average molecular energy is  $\bar{\epsilon} = \frac{3}{2}kT$ .

## Average Molecular Energy

To find the average energy per molecule we begin by calculating the total internal energy of the system. To do this we multiply  $n(\epsilon) d\epsilon$  by the energy  $\epsilon$  and then integrate over all energies from 0 to  $\infty$ :

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

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**

$$E = \left[ \frac{2\pi N}{(\pi kT)^{3/2}} \right] \left[ \frac{3}{4} (kT)^2 \sqrt{\pi kT} \right] = \frac{3}{2} NkT \quad (9.12)$$

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

**Average molecular energy**

$$\bar{\epsilon} = \frac{3}{2} kT \quad (9.13)$$


which is independent of the molecule's mass: a light molecule has a greater average speed at a given temperature than a heavy one. The value of  $\bar{\epsilon}$  at room temperature is about 0.04 eV,  $\frac{1}{25}$  eV.



## *Equipartition of Energy*

A gas molecule has three **degrees of freedom** that correspond to motions in three independent (that is, perpendicular) directions. Since the average kinetic energy of the molecule is  $\frac{3}{2}kT$ , we can associate  $\frac{1}{2}kT$  with the average energy of each degree of freedom:  $\frac{1}{2}m\overline{v_x^2} = \frac{1}{2}m\overline{v_y^2} = \frac{1}{2}m\overline{v_z^2} = \frac{1}{2}kT$ . This association turns out to be quite general and is called the **equipartition theorem**:

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  $\frac{1}{2}kT$ .

Degrees of freedom are not limited to linear velocity components—each variable that appears squared in the formula for the energy of a particular object represents a degree of freedom. Thus each component  $\omega_i$  of angular velocity (provided it involves a moment of inertia  $I_i$ ) is a degree of freedom, so that  $\frac{1}{2}I_i\overline{\omega_i^2} = \frac{1}{2}kT$ . A rigid diatomic molecule of the kind described in Sec. 8.6 therefore 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.

$$n(\epsilon) d\epsilon = \frac{2\pi N}{(\pi kT)^{3/2}} \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon \quad (9.11)$$

## Distribution of Molecular Speeds

The distribution of molecular speeds in an ideal gas can be found from Eq. (9.11) by making the substitutions

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

The result for the number of molecules with speeds between  $v$  and  $v + dv$  is

**Molecular-speed  
distribution**

$$n(v) dv = 4\pi N \left( \frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT} dv \quad (9.14)$$

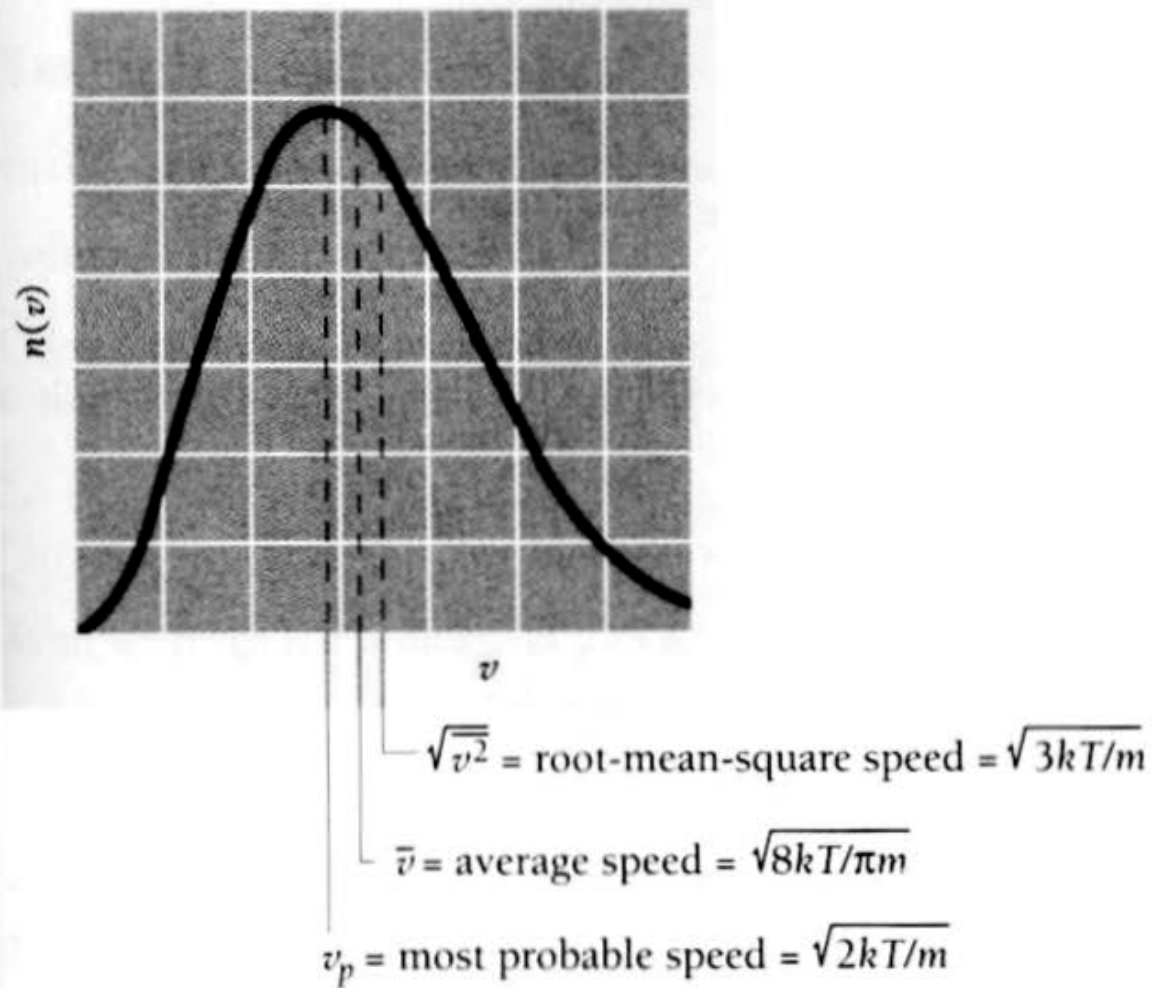
This formula, which was first obtained by Maxwell in 1859, is plotted in Fig. 9.3.

The speed of a molecule with the average energy of  $\frac{3}{2}kT$  is

**RMS speed**

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}} \quad (9.15)$$

since  $\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$ . This speed is denoted  $v_{\text{rms}}$  because it is the square root of the average of the squared molecular speeds—the root-mean-square speed—and is not the same as the simple arithmetical average speed  $\bar{v}$ .



**Figure 9.3** Maxwell-Boltzmann speed distribution.

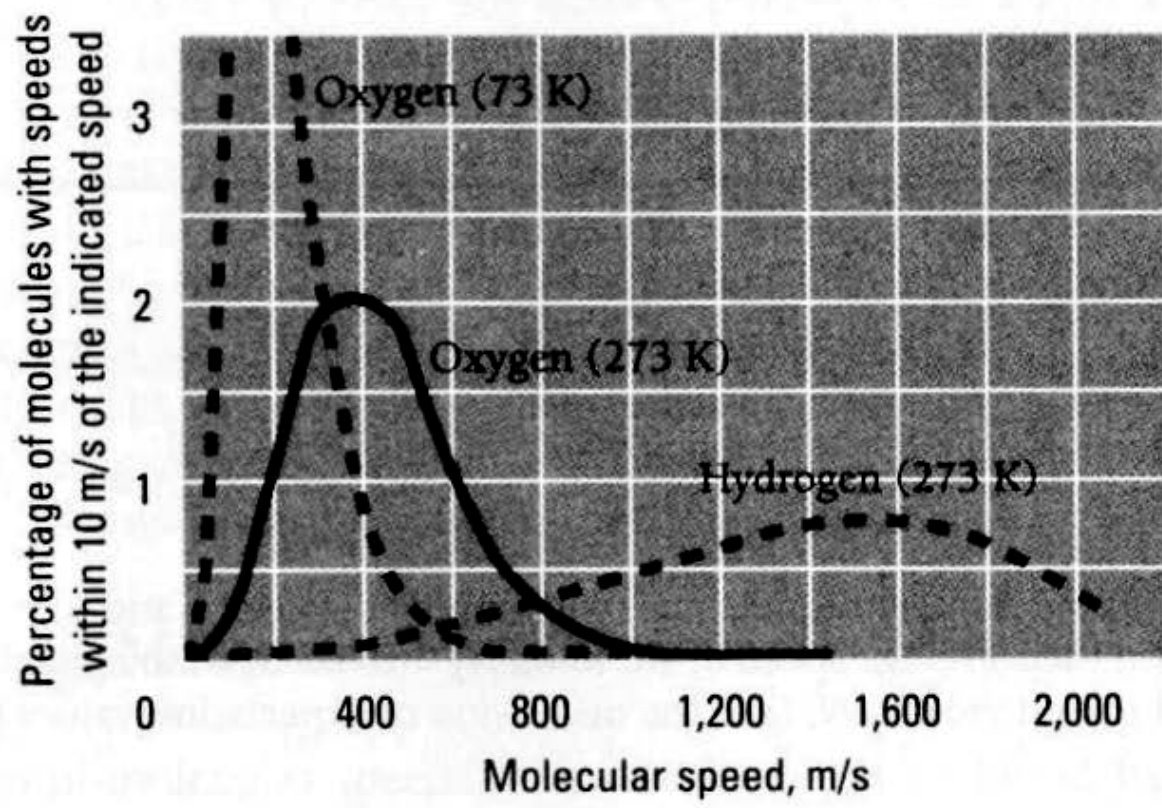
Because the speed distribution of Eq. (9.14) is not symmetrical, the most probable speed  $v_p$  is smaller than either  $\bar{v}$  or  $v_{\text{rms}}$ . To find  $v_p$ , we set equal to zero the derivative of  $n(v)$  with respect to  $v$  and solve the resulting equation for  $v$ . The result is

**Most probable  
speed**

$$v_p = \sqrt{\frac{2kT}{m}} \quad (9.16)$$

Molecular speeds in a gas vary considerably on either side of  $v_p$ . Figure 9.4 shows the distribution of speeds in oxygen at 73 K ( $-200^\circ\text{C}$ ), in oxygen at 273 K ( $0^\circ\text{C}$ ), and in hydrogen at 273 K. The most probable speed increases with temperature and decreases with molecular mass. Accordingly molecular speeds in oxygen at 73 K are on the whole less than at 273 K, and at 273 K molecular speeds in hydrogen are on the whole greater than in oxygen at the same temperature. The average molecular *energy* is the same in both oxygen and hydrogen at 273 K, of course.



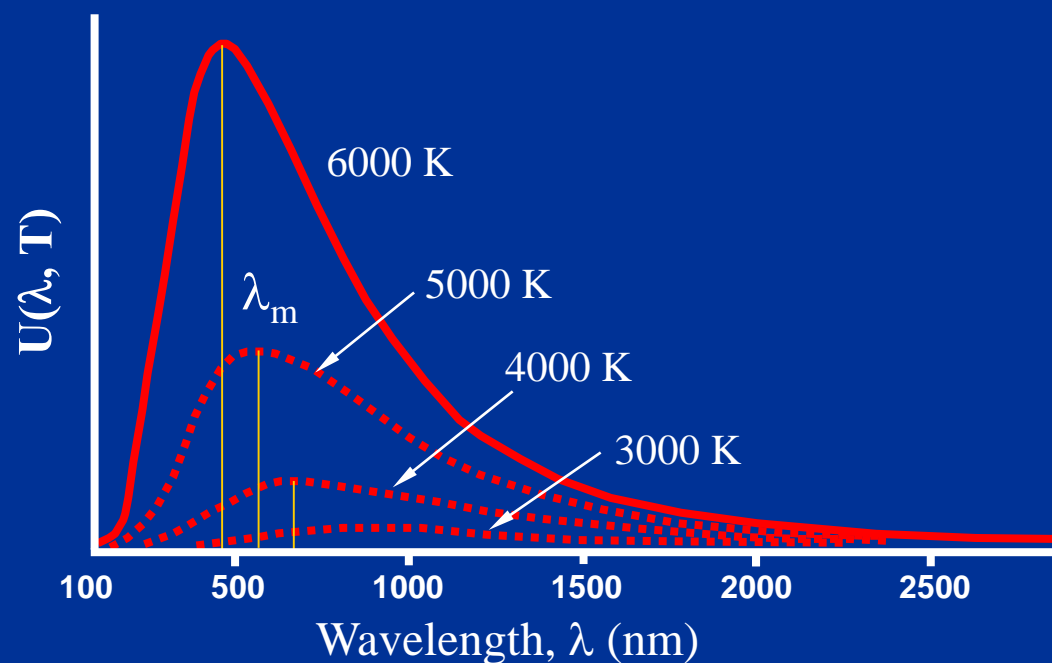


**Figure 9.4** The distributions of molecular speeds in oxygen at 73 K, in oxygen at 273 K, and in hydrogen at 273 K.



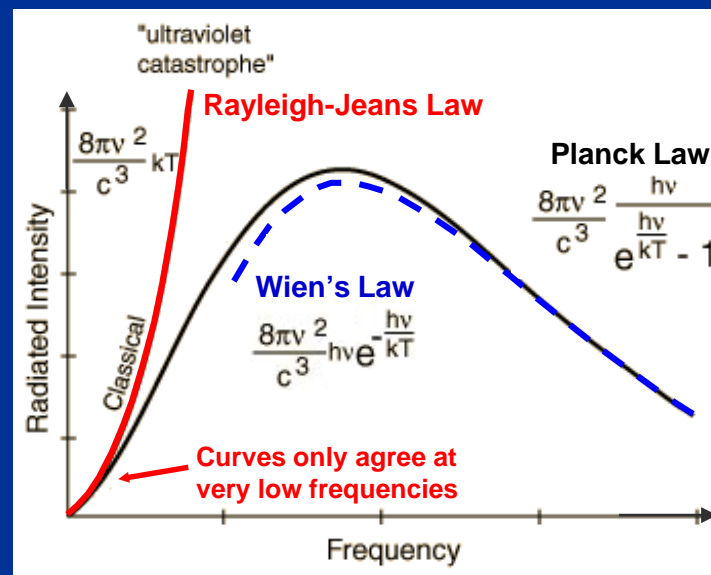
# 9.5 RAYLEIGH-JEANS FORMULA

*The classical approach to blackbody radiation*



In classic physics, the blackbody emission was described by two contradictory theorems:

- Rayleigh-Jeans radiation law, valid in the low frequency region
- Wien's law, valid in the high frequency region



$$U(\nu, T) = \frac{g(\nu) \times \bar{u}}{V}$$

$$\bar{u} = \int_0^{\infty} u n(u) du$$

Think a cavity made of metal

**E=0 at x=0, L**; otherwise there is a current flowing on the wall !

Wave equation for one-dimensional electromagnetic waves:

$$\frac{\partial^2 E}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2}$$

The solutions have the plane-wave form:

$$E = E_0 \sin(kx) \cdot \sin(\omega t) \quad \text{with } c = \omega/k$$

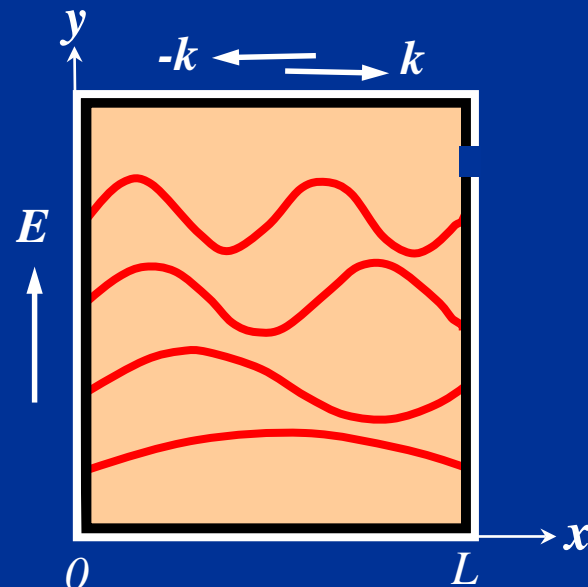
(here  $\omega = 2\pi\nu$  is the angular frequency,  $k = 2\pi/\lambda$  the wave vector)

When  $x=L$ ,  $E = E_0 \sin(kL) \cdot \sin(\omega t) = 0$  for any  $t$ , hence  $kL = n\pi$  ( $n=1, 2, 3, \dots$ ),

i.e.

$$\mathbf{k = n\pi/L}$$

So, for the standing waves:  $\mathbf{E = E_0 \sin(n\pi x/L) \cdot \sin(\omega t)}$



Similarly, for electromagnetic waves in a 3-dimensional cubic cavity:

$$\frac{\partial^2 E}{\partial x^2} + \frac{\partial^2 E}{\partial y^2} + \frac{\partial^2 E}{\partial z^2} = \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2}$$

and the solutions for the standing waves are:

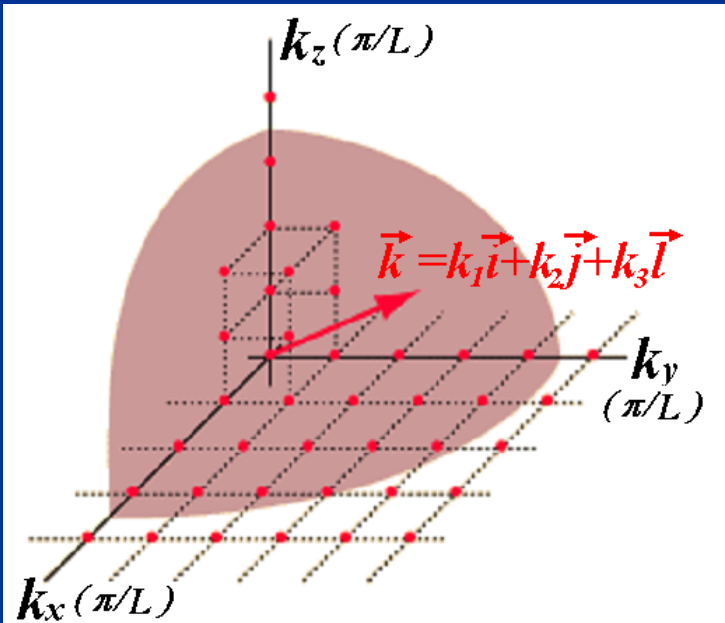
$$E = E_0 \sin(k_x x) \cdot \sin(k_y y) \cdot \sin(k_z z) \cdot \sin(\omega t)$$

where,  $k_x = n_x \pi / L$ ,  $k_y = n_y \pi / L$ ,  $k_z = n_z \pi / L$   
( $n_x, n_y, n_z$  are integers: 1, 2, 3, ...)

and  $c = \omega / k$  with ( $k^2 = k_x^2 + k_y^2 + k_z^2$ )

Let  $\vec{k} = k_x \vec{i} + k_y \vec{j} + k_z \vec{l}$ , which is the 3-dimensional wave-vector.

For each of  $k$ , there are many combinations (modes) of  $k_x, k_y, k_z$  to meet  $k^2 = k_x^2 + k_y^2 + k_z^2$  and all of them are on the first octant of a sphere with radius of  $k$ .

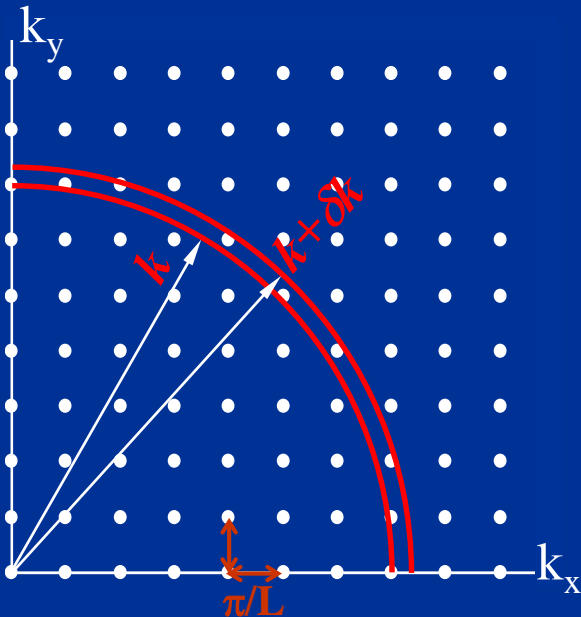


All the modes with  $k$  between  $k$  and  $k+\delta k$  fall inside the shell, whose internal radius is  $k$  and external radius  $k+\delta k$ .

Every mode (i.e. a spot in the picture) take a space of  $(\pi/L)\times(\pi/L)\times(\pi/L)$  on average

Hence the number of modes inside the shell is:

$$\delta N = \frac{1}{8} \times \frac{\frac{4}{3} \pi (k + \delta k)^3 - \frac{4}{3} \pi k^3}{(\pi / L) \cdot (\pi / L) \cdot (\pi / L)} = \frac{L^3}{6 \pi^2} [(k + \delta k)^3 - k^3]$$



ignore  $(\delta k)^2$  and higher orders,  $(k+\delta k)^3 \approx k^3 + 3k^2 \delta k$

So  $\delta N = \frac{L^3}{2 \pi^2} k^2 \delta k$ , replace  $k$  with  $v = \omega / 2 \pi = c \cdot k / 2 \pi$ , then  $\delta N(v) = \frac{4 \pi L^3}{c^3} v^2 \delta v$

When  $\delta v \rightarrow 0$ , we have the density of modes:  $g(v) = \frac{dN(v)}{dv} = \frac{4 \pi L^3}{c^3} v^2$  (i.e. the number of standing waves at a given frequency  $v$ )

If the averaged energy for the standing waves is  $\bar{u}$ , then the energy density of blackbody radiation, i.e. energy per unit volume per frequency, is:

$$U(v, T) = 2 \times g(v) \times \bar{u} \times \frac{1}{L^3} = \frac{8 \pi v^2}{c^3} \bar{u}$$

(the factor of 2 is because each electromagnetic wave has two polarisations)



Now we need to work out average energy of the radiation system —  $\bar{u}$

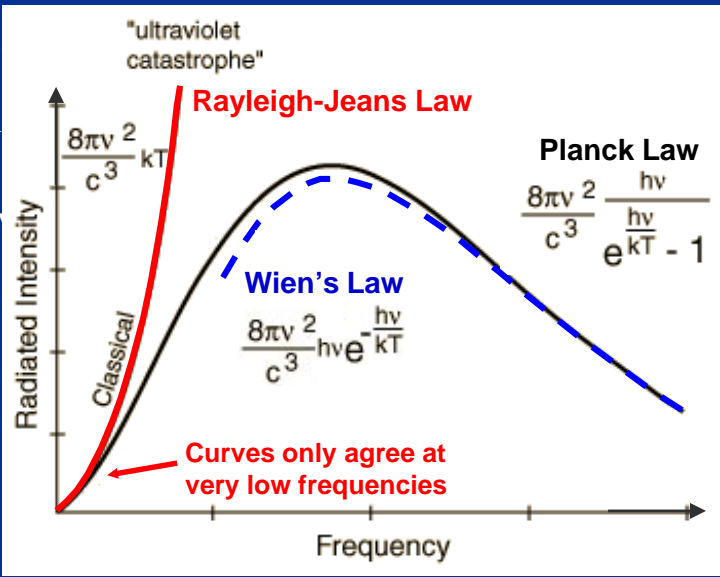
According to classic theory, the energy of each elec  $u$ , is the square of its amplitude and can be any val

The large numbers of the standing electromagnetic cavity are the entities of a same kind, which follow

distribution:  $Ae^{-\frac{u}{kT}}$

Hence the average energy is:

$$\bar{u} = \frac{\int_0^\infty ue^{-\frac{u}{kT}} du}{\int_0^\infty e^{-\frac{u}{kT}} du}$$



Let  $x=-u/kT$  the denominator:  $\int_0^\infty e^{-\frac{u}{kT}} du = kT \int_0^\infty e^{-x} dx = -kT e^{-x} \Big|_0^\infty = kT$

the numerator:  $\int_0^\infty ue^{-\frac{u}{kT}} du = (kT)^2 \int_0^\infty xe^{-x} dx = (kT)^2 (xe^{-x} \Big|_0^\infty + \int_0^\infty e^{-x} dx) = (kT)^2$

So,  $\bar{u} = \frac{(kT)^2}{kT} = kT$ ,  $U(\nu,T) = \frac{8\pi\nu^2}{c^3} \bar{u} = \frac{8\pi\nu^2}{c^3} kT$  Rayleigh-Jeans radiation law

# Planck's Assumption (1901):

- The energy exchange between the electrons in the cavity wall and electromagnetic waves only occur in discrete amounts.
- The minimum unit of energy exchange, which is called as “quantum of energy”, is  $h\nu$ . Here,  $h=6.626\times10^{-34}$  (J.s) is the Plank's constant,  $\nu$  the frequency of electromagnetic waves.

i.e.  $u=n h \nu, n=0, 1, 2, 3, \dots$

So, the average energy is now:

$$\bar{u} = \frac{\sum_{n=0}^{\infty} n h \nu e^{-\frac{n h \nu}{k T}}}{\sum_{n=0}^{\infty} e^{-\frac{n h \nu}{k T}}}$$

Let  $Y=\sum_{n=0}^{\infty} e^{-n h \nu x}, x=1 / k T$ , then

$$\bar{u} = -\frac{d}{d x} \ln Y$$

$$Y=\sum_{n=0}^{\infty} e^{(-h \nu x) n}=\lim _{n \rightarrow \infty} \frac{1-e^{(-h \nu x)(n+1)}}{1-e^{(-h \nu x)}}=\frac{1}{1-e^{(-h \nu x)}}$$

$$\bar{u}=-\frac{d}{d x} \ln \left[\frac{1}{1-e^{-h \nu x}}\right]=\frac{d}{d x} \ln \left(1-e^{-h \nu x}\right)=\frac{h \nu e^{-h \nu x}}{1-e^{-h \nu x}}=\frac{h \nu}{e^{h \nu x}-1}$$

$x=1 / k T, \bar{u}=\frac{h \nu}{e^{\frac{h \nu}{k T}}-1},$

$$U(\nu, T)=\frac{8 \pi \nu^2}{c^3} \bar{u}=\frac{8 \pi \nu^2}{c^3} \frac{h \nu}{e^{\frac{h \nu}{k T}}-1}$$

Planck Law !

$$\bar{u}=\frac{\int_0^{\infty} u e^{-\frac{u}{k T}} d u}{\int_0^{\infty} e^{-\frac{u}{k T}} d u}$$

compare to classic

Plank's law 
$$U(\nu,T)=\frac{8\pi\nu^2}{c^3}\frac{h\nu}{e^{\frac{h\nu}{kT}}-1}$$

Rayleigh-Jeans and Wien's laws are special cases of Plank's law

We know: 
$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$$

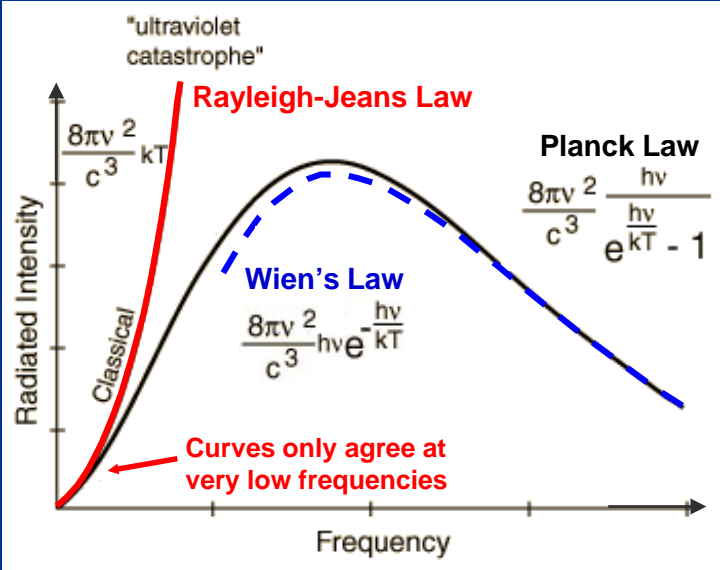
If  $x$  is small,  $e^x \approx 1 + x$ , and so for  $h\nu/kT \ll 1$  we have

$$\frac{h\nu}{e^{h\nu/kT} - 1} \approx \frac{h\nu}{1 + \frac{h\nu}{kT} - 1} \approx kT \quad h\nu \ll kT$$

Thus at low frequencies Plank's formula becomes

$$U(\nu,T) \approx \frac{8\pi h}{c^3} \nu^3 \left(\frac{kT}{h\nu}\right) d\nu \approx \frac{8\pi kT}{c^3} \nu^2$$

which is the Rayleigh-Jeans formula.



When  $h\nu/kT \gg 1$ , then

$$e^{h\nu/kT} \gg 1 \quad e^{h\nu/kT} - 1 \approx e^{h\nu/kT}$$
$$\frac{h\nu}{e^{h\nu/kT} - 1} \approx h\nu e^{-h\nu/kT} \quad U(\nu,T) \approx \frac{8\pi\nu^2}{c^3} h\nu e^{-\frac{h\nu}{kT}}$$

which is Wien's law.

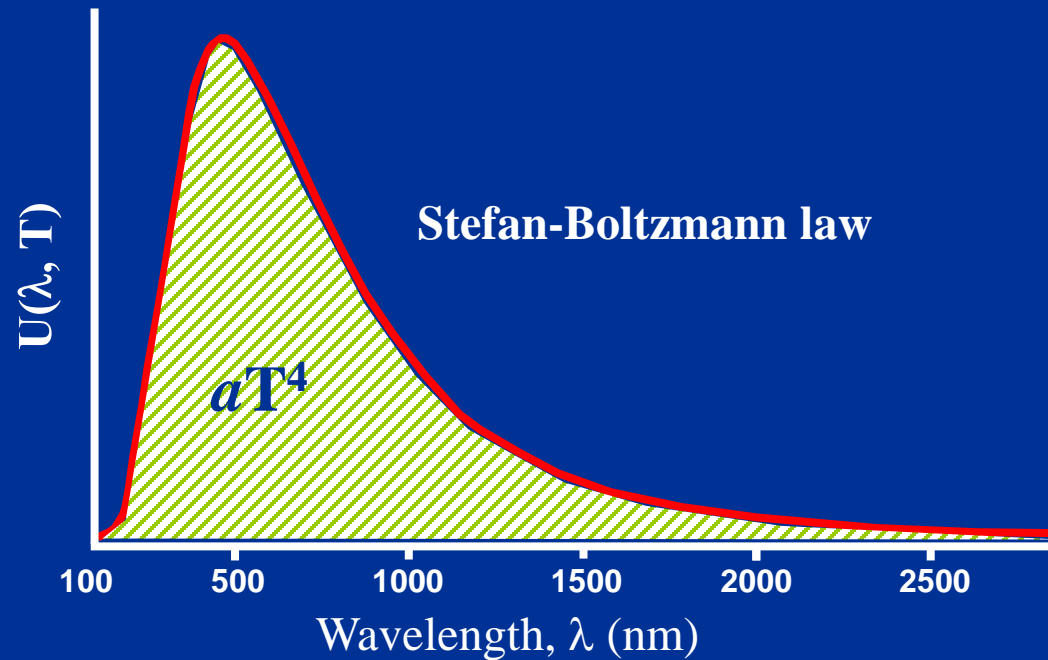
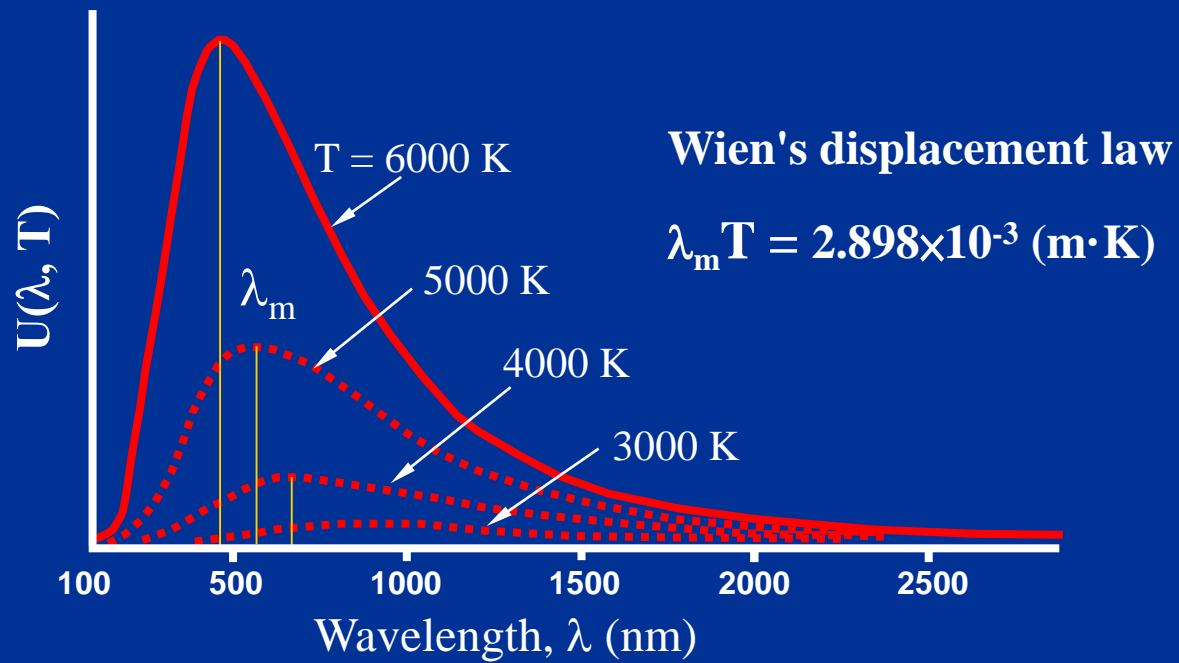
## Wien's Displacement Law

An interesting feature of the blackbody spectrum at a given temperature is the wavelength  $\lambda_{\max}$  for which the energy density is the greatest. To find  $\lambda_{\max}$  we first express Eq. (9.38) in terms of wavelength and solve  $du(\lambda)/d\lambda = 0$  for  $\lambda = \lambda_{\max}$ . We obtain in this way

$$\frac{hc}{kT\lambda_{\max}} = 4.965$$

which is more conveniently expressed as

**Wien's displacement law**  $\lambda_{\max} T = \frac{hc}{4.965k} = 2.898 \times 10^{-3} \text{ m} \cdot \text{K} \quad (9.40)$





## Stefan-Boltzmann Law

Another result we can obtain from Eq. (9.38) is the total energy density  $u$  of the radiation in a cavity. This is the integral of the energy density over all frequencies,

$$u = \int_0^{\infty} u(\nu) d\nu = \frac{8\pi^5 k^4}{15c^3 h^3} T^4 = aT^4$$

where  $a$  is a universal constant. The total energy density is proportional to the fourth power of the absolute temperature of the cavity walls. We therefore expect that the energy  $R$  radiated by an object per second per unit area is also proportional to  $T^4$ , a conclusion embodied in the **Stefan-Boltzmann** law:

$$\text{Stefan-Boltzmann law} \quad R = e\sigma T^4 \quad (9.41)$$

The value of **Stefan's constant**  $\sigma$  is

$$\text{Stefan's constant} \quad \sigma = \frac{ac}{4} = 5.670 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$$

The emissivity  $e$  depends on the nature of the radiating surface and ranges from 0, for a perfect reflector which does not radiate at all, to 1, for a blackbody. Some typical values of  $e$  are 0.07 for polished steel, 0.6 for oxidized copper and brass, and 0.97 for matte black paint.

## 9.4 QUANTUM STATISTICS

*Bosons and fermions have different distribution functions*

### Bose-Einstein and Fermi-Dirac Distribution Functions

The probability  $f(\epsilon)$  that a boson occupies a state of energy  $\epsilon$  turns out to be

**Bose-Einstein  
distribution  
function**

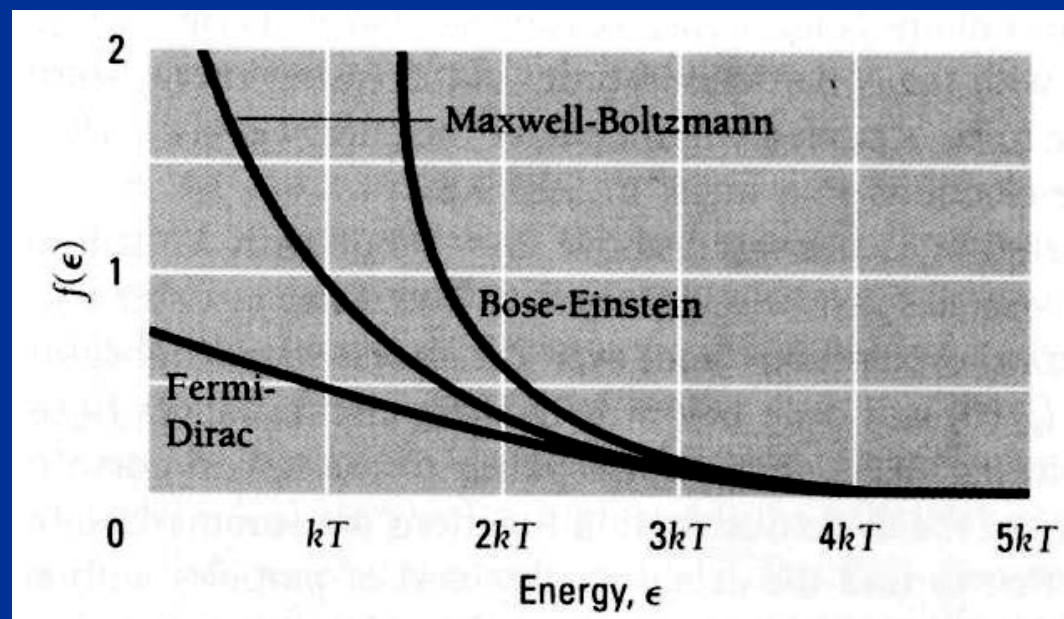
$$f_{BE}(\epsilon) = \frac{1}{e^{\alpha} e^{\epsilon/kT} - 1} \quad (9.26)$$

and the probability for a fermion turns out to be

**Fermi-Dirac  
distribution  
function**

$$f_{FD}(\epsilon) = \frac{1}{e^{\alpha} e^{\epsilon/kT} + 1} \quad (9.27)$$

The quantity  $\alpha$  depends on the properties of the particular system and may be a function of  $T$ .



**Figure 9.5** A comparison of the three distribution functions for  $\alpha = -1$ . The Bose-Einstein function is always higher than the Maxwell-Boltzmann one, which is a pure exponential, and the Fermi-Dirac function is always lower. The functions give the probability of occupancy of a state of energy  $\epsilon$  at the absolute temperature  $T$ .

$$f_{FD}(\epsilon) = \frac{1}{e^{\alpha} e^{\epsilon/kT} + 1} \quad (9.27)$$

Denote the energy for  $f_{FD}=1/2$  as  $\epsilon_F$ , then we have:

$$f_{FD}(\epsilon_F) = \frac{1}{e^{\alpha} e^{\epsilon_F/kT} + 1} = \frac{1}{2}, \quad 2 = e^{\alpha} e^{\epsilon_F/kT} + 1, \quad e^{-\alpha} = e^{\epsilon_F/kT}$$

$$\epsilon_F = -\alpha kT, \quad \alpha = -\epsilon_F/kT$$

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

**Fermi energy**

$$\epsilon_F = -\alpha kT \quad (9.28)$$

This energy, called the **Fermi energy**, is a very important quantity in a system of fermions, such as the electron gas in a metal. In terms of  $\epsilon_F$  the Fermi-Dirac distribution function becomes

**Fermi-Dirac**

$$f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon - \epsilon_F)/kT} + 1} \quad (9.29)$$

To appreciate the significance of the Fermi energy, let us consider a system of fermions at  $T = 0$  and investigate the occupancy of states whose energies are less than  $\epsilon_F$  and greater than  $\epsilon_F$ . What we find is this:

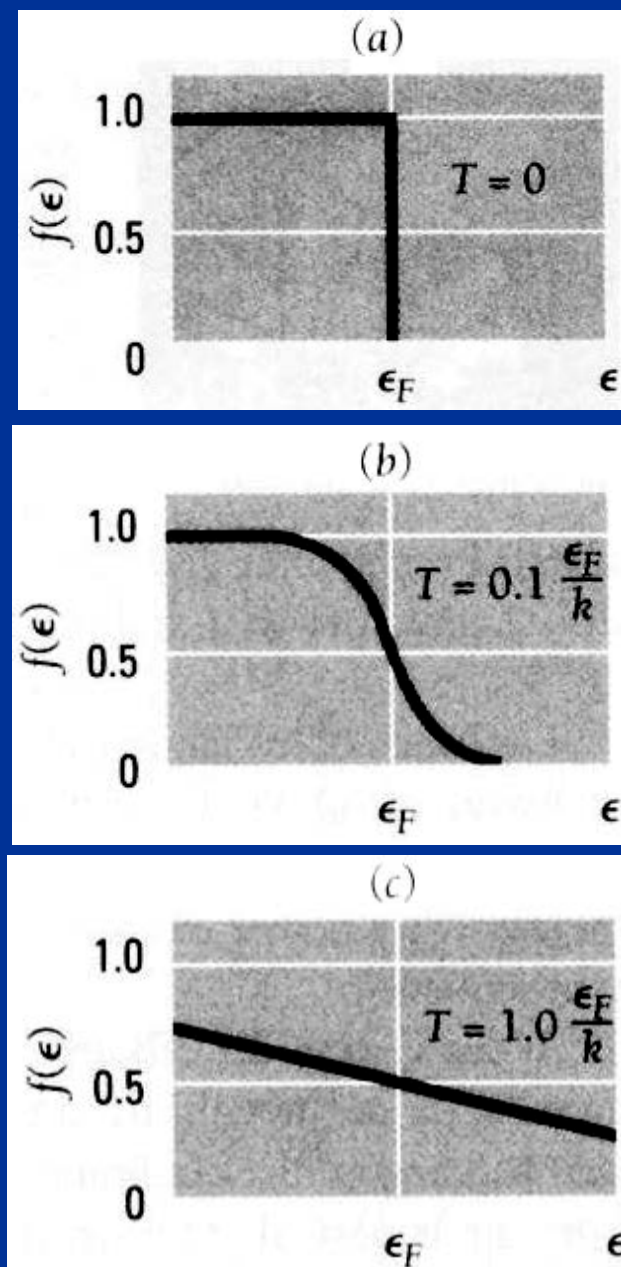
$$T = 0, \epsilon < \epsilon_F: \quad f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon - \epsilon_F)/kT} + 1} = \frac{1}{e^{-\infty} + 1} = \frac{1}{0 + 1} = 1$$

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

Thus at absolute zero all energy states up to  $\epsilon_F$  are occupied, and none above  $\epsilon_F$  (Fig. 9.6a). If a system contains  $N$  fermions, we can calculate its Fermi energy  $\epsilon_F$  by filling up its energy states with the  $N$  particles in order of increasing energy starting from  $\epsilon = 0$ . The highest state to be occupied will then have the energy  $\epsilon = \epsilon_F$ . This calculation will be made for the electrons in a metal in Sec. 9.8.

As the temperature is increased above  $T = 0$  but with  $kT$  still smaller than  $\epsilon_F$ , fermions will leave states just below  $\epsilon_F$  to move into states just above it, as in Fig. 9.6b. At higher temperatures, fermions from even the lowest state will begin to be excited to higher ones, so  $f_{FD}(0)$  will drop below 1. In these circumstances  $f_{FD}(\epsilon)$  will assume a shape like that in Fig. 9.6c, which corresponds to the lowest curve in Fig. 9.5.





**Figure 9.6** Distribution function for fermions at three different temperatures. (a) At  $T = 0$ , all the energy states up to the Fermi energy  $\epsilon_F$  are occupied. (b) At a low temperature, some fermions will leave states just below  $\epsilon_F$  and move into states just above  $\epsilon_F$ . (c) At a higher temperature, fermions from any state below  $\epsilon_F$  may move into states above  $\epsilon_F$ .



## 9.7 SPECIFIC HEATS OF SOLIDS

*Classical physics fails again*

A 1-dimensional classic harmonic oscillator at temperature  $T$  has an average energy  $= kT$

A 3-dimensional classic harmonic oscillator  $= 3kT$

A mole of solid has  $N_0$  (Avogadro's number) of atoms, and has energy

$$E = 3N_0kT$$

## Classical internal energy of solid

$$E = 3N_0kT = 3RT \quad (9.42)$$

where  $R = N_0k = 8.31 \times 10^3 \text{ J/kmol} \cdot \text{K}$  is the universal gas constant.

The specific heat at constant volume is given in terms of  $E$  by

## Specific heat at constant volume

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

and so here

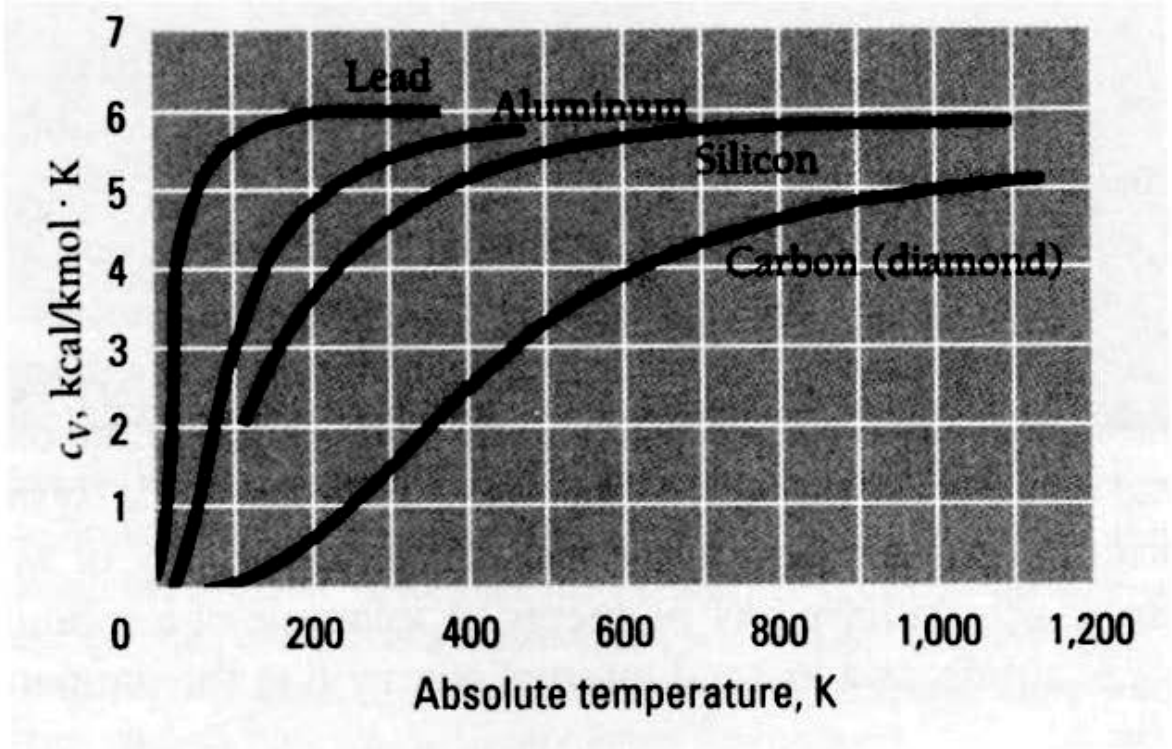
## Dulong-Petit law

$$c_V = 3R = 5.97 \text{ kcal/kmol} \cdot \text{K} \quad (9.43)$$

Over a century ago Dulong and Petit found that, indeed,  $c_V \approx 3R$  for most solids at room temperature and above, and Eq. (9.43) is known as the **Dulong-Petit law** in their honor.

However, the Dulong-Petit law fails for such light elements as boron, beryllium, and carbon (as diamond), for which  $c_V = 3.34$ ,  $3.85$ , and  $1.46 \text{ kcal/kmol} \cdot \text{K}$  respectively at  $20^\circ\text{C}$ . Even worse, the specific heats of *all* solids drop sharply at low temperatures and approach 0 as  $T$  approaches 0 K. Figure 9.9 shows how  $c_V$  varies with  $T$  for several elements.

**Figure 9.9** The variation with temperature of the molar specific heat at constant volume  $c_V$  for several elements.



## Einstein's Formula

In 1907 Einstein discerned that the basic flaw in the derivation of Eq. (9.43) lies in the figure of  $kT$  for the average energy per oscillator in a solid. This flaw is the same as that responsible for the incorrect Rayleigh-Jeans formula for blackbody radiation.

**Average energy per  
quantum oscillator**

$$\bar{\epsilon} = \frac{h\nu}{e^{h\nu/kT} - 1} \quad (9.44)$$

and not  $\bar{\epsilon} = kT$ . The total internal energy of a kilomole of a solid therefore becomes

**Internal energy of  
solid**

$$E = 3N_0\bar{\epsilon} = \frac{3N_0h\nu}{e^{h\nu/kT} - 1} \quad (9.45)$$

and its molar specific heat is

**Einstein specific  
heat formula**

$$c_V = \left( \frac{\partial E}{\partial T} \right)_V = 3R \left( \frac{h\nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} \quad (9.46)$$

# 9.8 FREE ELECTRONS IN A METAL

Average occupancy  
per state

$$f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon - \epsilon_F)/kT} + 1} \quad (9.29)$$

What we also need is an expression for  $g(\epsilon) d\epsilon$ , the number of quantum states available to electrons with energies between  $\epsilon$  and  $\epsilon + d\epsilon$ .

Free electrons in metal can be treated as “particle in a box”, because they have the same potential, i.e. inside the metal  $U=0$ , outside the metal  $U=\infty$ .

So, their wave functions are standing waves, which are the same as those inside the blackbody cavity, and they have the same  $g(\epsilon)d\epsilon$

$$g(v) = \frac{dN(v)}{dv} = \frac{4\pi L^3}{c^3} v^2$$

$$g(\epsilon) = \frac{dN(\epsilon)}{d\epsilon} = \frac{dN(v)}{dv} \cdot \frac{dv}{d\epsilon} = g(v) \frac{dv}{d\epsilon} = \frac{4\pi L^3}{V^3} v^2 \frac{dv}{d\epsilon}$$

replace with  $V$   
(phase velocity of electron wave)

$$g(\epsilon) = \frac{4\pi L^3}{V^3} v^2 \frac{dv}{d\epsilon} = \frac{4\pi L^3}{V^3 h^3} (h\nu)^2 \frac{d(h\nu)}{d\epsilon} = \frac{4\pi L^3}{V^3 h^3} \epsilon^2$$

$$V = \lambda v = \frac{h}{p} \cdot \frac{\epsilon}{h} = \frac{\epsilon}{p} = \frac{\epsilon}{\sqrt{2m\epsilon}} = (2m)^{-1/2} \epsilon^{1/2}$$

We have

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

As in the case of standing waves in a cavity the exact shape of the metal sample does not matter, so we can substitute its volume  $V$  for  $L^3$  to give

Number of  
electron states

$$g(\epsilon) d\epsilon = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \sqrt{\epsilon} d\epsilon \tag{9.47}$$



# Fermi Energy

As shown previously, at  $T = 0$  K,

$$f_{FD}(\epsilon) = 0 \quad \text{if } \epsilon > \epsilon_F; \quad f_{FD}(\epsilon) = 1 \quad \text{if } \epsilon < \epsilon_F$$

So, total number of electrons  $N$  is:

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

and so

$$\text{Fermi energy} \quad \epsilon_F = \frac{h^2}{2m} \left( \frac{3N}{8\pi V} \right)^{2/3} \quad (9.48)$$

The quantity  $N/V = n_e$  is the density of free electrons,  $\epsilon_F \propto n_e^{2/3}$

## 9.9 ELECTRON-ENERGY DISTRIBUTION

*Why the electrons in a metal do not contribute to its specific heat except at very high and very low temperatures*

With the help of Eqs. (9.29) and (9.47) we have for the number of electrons in an electron gas that have energies between  $\epsilon$  and  $\epsilon + d\epsilon$

$$n(\epsilon) d\epsilon = g(\epsilon)f(\epsilon) d\epsilon = \frac{(8\sqrt{2}\pi V m^{3/2}/h^3) \sqrt{\epsilon} d\epsilon}{e^{(\epsilon-\epsilon_F)/kT} + 1} \quad (9.49)$$

If we express the numerator of Eq. (9.49) in terms of the Fermi energy  $\epsilon_F$  we get

Electron energy distribution

$$n(\epsilon) d\epsilon = \frac{(3N/2) \epsilon_F^{-3/2} \sqrt{\epsilon} d\epsilon}{e^{(\epsilon-\epsilon_F)/kT} + 1} \quad (9.50)$$

This formula is plotted in Fig. 9.10 for  $T = 0, 300$ , and  $1200$  K.

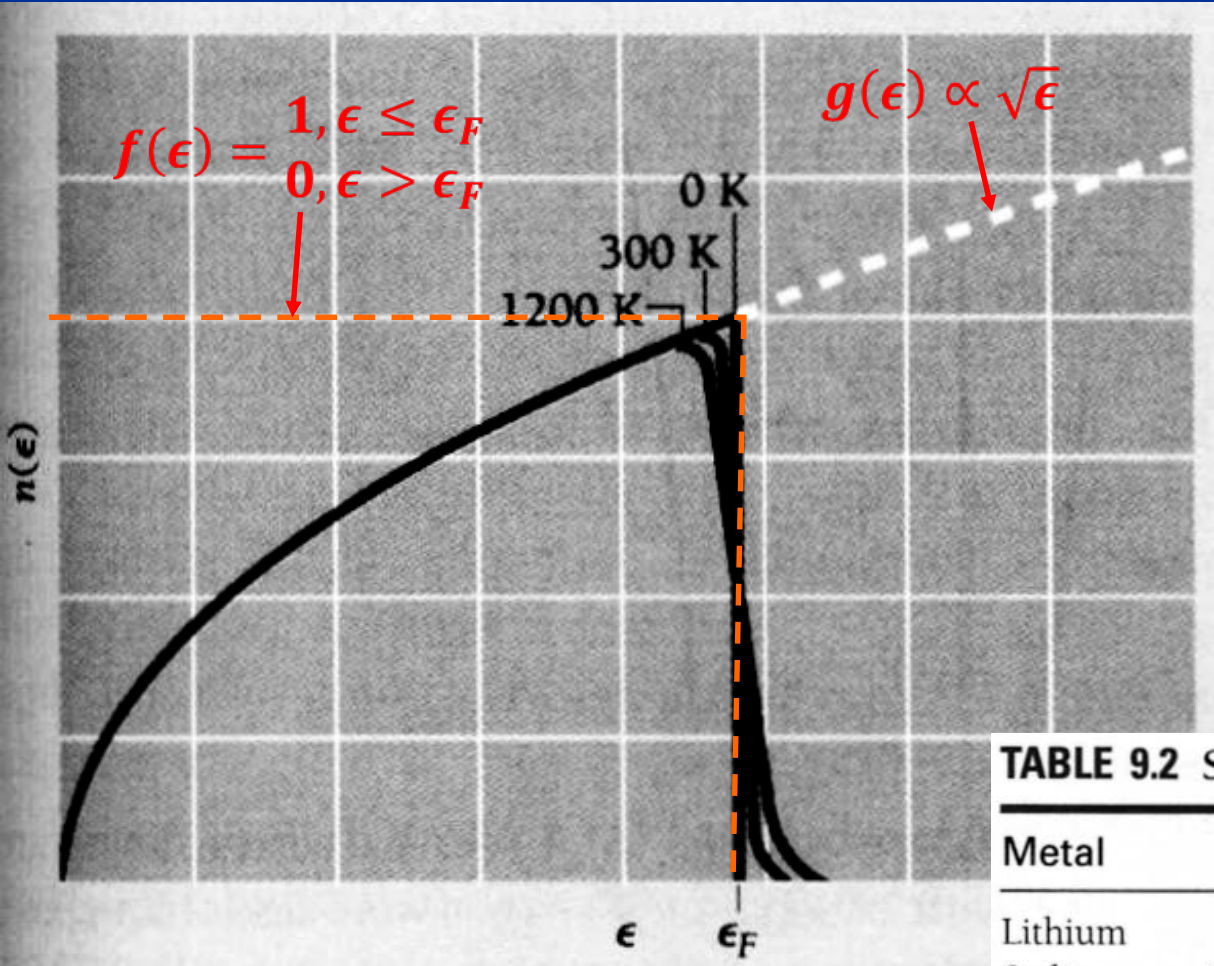


Figure 9.10 Distribution of electron energies in a metal at various temperatures.

TABLE 9.2 Some Fermi Energies

Metal		Fermi energy, eV
Lithium	Li	4.72
Sodium	Na	3.12
Aluminum	Al	11.8
Potassium	K	2.14
Cesium	Cs	1.53
Copper	Cu	7.04
Zinc	Zn	11.0
Silver	Ag	5.51
Gold	Au	5.54

$$n(\epsilon) d\epsilon = \frac{(3N/2) \epsilon_F^{-3/2} \sqrt{\epsilon} d\epsilon}{e^{(\epsilon - \epsilon_F)/kT} + 1} \quad (9.50)$$

It is interesting to determine the average electron energy at 0 K. To do this, we first find the total energy  $E_0$  at 0 K, which is

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

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

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

and

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

The average electron energy  $\bar{\epsilon}_0$  is this total energy divided by the number  $N$  of electrons present, which gives

Average electron  
energy at  $T = 0$


$$\bar{\epsilon}_0 = \frac{3}{5} \epsilon_F \quad (9.51)$$

A detailed calculation shows that the specific heat of the electron gas in a metal is given by

Electron specific heat

$$c_{Ve} = \frac{\pi^2}{2} \left( \frac{kT}{\epsilon_F} \right) R \tag{9.52}$$

At room temperature,  $kT/\epsilon_F$  ranges from 0.016 for cesium to 0.0021 for aluminum for the metals listed in Table 9.2, so the coefficient of  $R$  is very much smaller than the classical figure of  $\frac{3}{2}$ .


$$E = \frac{3}{5} N \epsilon_F \left[ 1 + \frac{5\pi^2}{12} \left( \frac{T}{T_f} \right)^2 \dots \right]$$

$(\epsilon_F = kT_f)$

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{1}{2} \pi^2 Nk \left( \frac{T}{T_f} \right) \dots$$

**TABLE 9.2** Some Fermi Energies

Metal		Fermi energy, eV
Lithium	Li	4.72
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Aluminum	Al	11.8
Potassium	K	2.14
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Zinc	Zn	11.0
Silver	Ag	5.51
Gold	Au	5.54