1

We introduced the periodic table and the elements of major interest in semi-conductor electronics (the group IV elements, especially silicon and germanium, and the group III and group V elements, which are used as dopants). We discussed the lattice structure of silicon (see Chapter 3 of the supplementary notes) and the fact that electrons in a crystal sample are better thought of as belonging to the entire sample rather than to individual atoms

The following sections 2 -6 flesh out the discussion of the Fermi-Dirac distribution in the lecture.

2

In Chapter 17 of the book of Giancoli, for instance, you will find a discussion of how experimental scientists studying gases in various regimes of pressure, volume and temperature arrived at the *ideal gas law*

$$PV = nRT$$

where P is the pressure, which is a force per unit area, V the volume, T is the absolute temperature, measured in degrees Kelvin, n is the number of *moles* of the gas, and R is a constant of nature, called the *universal gas constant*, which is roughly 8.315 Joules/mole-K. This law applies pretty well to *every* gas, if the temperature is not too close to the liquefaction temperature of the gas and the pressure is not too high (i.e the gas is sufficiently dilute). As a matter of fact, these experiments are what led to the notion of absolute temperature, because extrapolating from the data suggested the physical impossibility of temperatures below -273.15 degrees Centigrade. The ideal gas law is an *equation of state*, since it ties together certain variables relating to the state of the gas in a (more or less) inexorable way.

In this equation, a mole is the amount of the gas that has N_0 molecules, where N_0, which is roughly 6.02×10^{23}, is the *Avogadro number*. $\frac{R}{N_A}$, i.e. the ratio of the universal gas constant to the Avogadro number, is called the *Boltzmann constant*. It is denoted k and equals roughly $1.38 \times 10^{-23} Joules/K$. We may rewrite the ideal gas law as

$$PV = NkT \tag{1}$$

where now N is the number of molecules of the gas.

3

A triumph of the kinetic theory of gases, developed by Maxwell, was to "explain" the ideal gas law. This is discussed in Chapter 18 of the book of Giancoli. If one considers a collection of N molecules of a gas, each with mass m, confined to a cubical box and assumes that they never interact with each other (we think of the molecules as being "point particles", i.e. they are so small that they never influence one another: this corresponds to the diluteness required of real-world gases for them to obey the ideal gas law) and undergo perfect elastic reflections at the surfaces of the box, one can prove the relation (as done in Chapter 18 of Giancoli)

$$PV = \frac{2}{3}N(\frac{1}{2}m\bar{v^2})$$

Here P denotes the average pressure exerted by the particles on the surfaces of the box, V the volume of the box, and $\bar{v^2}$ the mean-square velocity of the particles (the average over the particles of the square of its speed, where the speed of a molecule is the square root of the sum over all three coordinates of the square of its individual velocity coordinates). This appears to explain the ideal gas law and leads to the observation that the average kinetic energy, i.e. $\frac{1}{2}m\bar{v^2}$, equals $\frac{3}{2}kT$. Since there are three degrees of freedom for each of the N point particles to move in three-dimensional space, one can think about each degree of freedom of each particle as contributing an energy of $\frac{1}{2}kT$ to the total kinetic energy of the system. Note that this is proportional to T.

4

The kinetic theoretic "explanation" of the ideal gas law in the preceding section was possible without needing to worry about what the actual distribution of velocities of the molecules of the gas is. Based on some natural physical assumptions, Maxwell came up with a formula for this distribution,

called the *Maxwell distribution*, whose validity can also be experimentally tested on real-world gases. The Maxwell distribution has been found to be in remarkable agreement with experimental observations.

Think of a very large number N of molecules of a gas confined to a cubical box, as in the preceding section. Each molecule has a velocity with three coordinates, which we may denote as v_x, v_y and v_z respectively. We require that the mean-square speed of the collection of molecules is some given value $\bar{v^2}$ and ask what is the most likely distribution of the individual velocities. Maxwell made two postulates. First, he assumed that the likelihood of an individual molecule having some velocity should be a function only of its energy, or equivalently of its speed, i.e the direction of motion of the molecule should be irrelevant. Next, he assumed that the distribution of velocities in each coordinate should be independent of each other, in the sense that whatever one might know about the actual velocities of the molecule in some pair of coordinates (say the x-coordinate and the y-coordinate) one learns nothing about the distribution of the velocity of the molecule in the remaining coordinate. Remarkably, these two conditions are sufficient to pin down what the distribution of velocities of molecules is. This is demonstrated in the next section, which you can skip if you want. The Maxwell distribution of speeds is

$$f(v) = 4\pi N \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{-\frac{1}{2}\frac{mv^2}{kT}} \ .$$

(Here $f(v)$ is defined for $v \geq 0$ and $\int_0^\infty f(v)dv = 1$. $f(v)dv$ denotes the rough fraction of molecules that have speed in $(v, v + dv)$, assuming that dv is small and that N is very large. Also $\int_0^\infty v^2 f(v)dv$ equals the target mean square speed $\bar{v^2}$ corresponding to the formula $\frac{1}{2}m\bar{v^2} = \frac{3}{2}kT$, which relates the average kinetic energy to the absolute temperature.) Note that, since we assumed that the direction of motion of molecules is irrelevant, this also gives the distribution of their velocities.

5 Optional: you may skip this section if you prefer.

In this section we present Maxwell's calculation that resulted in the Maxwell distribution. You may skip this section if you wish.

Let $g(v_x)$ denote the distribution of the x-coordinate of the velocity of the molecules. By the hypothesis that the direction of motion of the molecules is irrelevant, the distribution of the y-coordinate of the velocity of the molecules will have to be $g(v_y)$ and that of the z-coordinate of the molecules will have to be $g(v_z)$. By the hypothesis that the distribution of velocities in the individual coordinates are independent, the distribution of velocities must be given by the product $g(v_x)g(v_y)g(v_z)$.

We now imagine another velocity $(v_x + dv_x, v_y + dv_y, v_z + dv_z)$, where dv_x, dv_y and dv_z are very small. By differentiating the product $g(v_x)g(v_y)g(v_z)$ we may write $g(v_x + dv_x)g(v_y + dv_y)g(v_z + dv_z)$ up to first order in the terms dv_x, dv_y and dv_z as $g(v_x)g(v_y)g(v_z) + g'(v_x)g(v_y)g(v_z)dv_x + g(v_x)g'(v_y)g(v_z)dv_y + g(v_x)g(v_y)g'(v_z)dv_z$, where $g'(v)$ denotes $\frac{dg}{dv}(v)$.

Suppose now that the speed (or equivalently the kinetic energy) is the same at $(v_x + dv_x, v_y + dv_y, v_z + dv_z)$ as it is at (v_x, v_y, v_z). Then, by the hypothesis that the direction of the molecule does not matter, we must have

$$g(v_x + dv_x, v_y + dv_y, v_z + dv_z) = g(v_x, v_y, v_z).$$

Using the formula we just derived for $g(v_x + dv_x, v_y + dv_y, v_z + dv_z)$ and dividing it through by $g(v_x, v_y, v_z)$, this gives the equation

$$\frac{g'(v_x)}{g(v_x)}dv_x + \frac{g'(v_y)}{g(v_y)}dv_y + \frac{g'(v_z)}{g(v_z)}dv_z = 0.$$

This equation should hold up to first order whenever the kinetic energy at $(v_x + dv_x, v_y + dv_y, v_z + dv_z)$ is the same as that at (v_x, v_y, v_z), i.e. whenever $(v_x + dv_x)^2 + (v_y + dv_y)^2 + (v_z + dv_z)^2$ equals $v_x^2 + v_y^2 + v_z^2$. However, by differentiating $v_x^2 + v_y^2 + v_z^2$ we see that (recall that dv_x, dv_y and dv_z are very small) $(v_x + dv_x)^2 + (v_y + dv_y)^2 + (v_z + dv_z)^2$ equals

$$v_x^2 + v_y^2 + v_z^2 + 2v_x dv_x + 2v_y dv_y + 2v_z dv_z$$

up to first order in the terms dv_x, dv_y and dv_z. This tells us that the equation

$$v_x dv_x + v_y dv_y + v_z dv_z = 0$$

must also hold up to first order whenever the kinetic energy at $(v_x + dv_x, v_y + dv_y, v_z + dv_z)$ is the same as that at (v_x, v_y, v_z).

The only way both these equations can hold for *all* (v_x, v_y, v_z) and all such choices of dv_x, dv_y and dv_z is if we have $\frac{g'(v)}{g(v)} = cv$, for some constant c. This means we must have $\ln g(v) = a + bv^2$ for some constants a and b. From this, the Maxwell distribution can be arrived at, since the constants a and b can be determined from the normalization conditions that $\int_{-\infty}^{\infty} g(v)dv = 1$ and $\int_{-\infty}^{\infty} v^2 g(v) = \frac{1}{3}\bar{v^2}$.

6

The Maxwell distribution was discussed in the preceding section as a distribution on speeds. It can be equivalently discussed as a distribution on energies. The key principle underlying Maxwell's approach (the key physical insight, if you will) is that *all states of nature that have the same energy are equally likely.* If instead of a gas of classical molecules we deal, as we will do below, with a gas of subatomic particles, such as electrons, quantum mechanical issues come into play. Quantum mechanics does not change this physical insight of Maxwell. Rather, what it changes is the way in which one counts the number of states available to nature at any energy level. For the specific case of electrons, of interest to us below, the *Pauli exclusion principle* comes into play and prevents more than one electron from occupying any given quantum state. As a result of this different way of counting the number of available states, one arrives at the *Fermi-Dirac distribution* for the distribution of energies in an ideal electron gas of N electrons. Writing ϵ for the energy of a quantum mechanically allowed energy level, the function

$$f(\epsilon) = \frac{1}{e^{\frac{\epsilon - \mu}{kT}} + 1} \tag{2}$$

gives the probability that a state at this energy level is occupied, where μ is a normalization constant which is to be chosen such that the overall number of particles in the system comes out correctly to N. Note that μ is a function of the temperature.

As we let T approach 0, i.e. as we approach absolute zero, we will find that there is an energy level, denoted ϵ_F, such that $f(\epsilon) \to 1$ for all $\epsilon < \epsilon_F$ and $f(\epsilon) \to 0$ for all $\epsilon > \epsilon_F$. This level ϵ_F is called the *Fermi level*.

Finally, notice that if for any positive T, if the energy ϵ is large enough (how large it needs to be depends on T) then in the denominator of equation (2) we can neglect 1 relative to $e^{\frac{\epsilon-\mu}{kT}}$, so the Fermi-Dirac distribution begins to look increasingly like the Maxwell distribution.

7

We next discussed the basics of the band theory of crystalline solids. This is a consequence of the electron wavefunctions interacting with the ions left behind in the lattice if the wavenumber (wavelength) is just right. View the webcast video if you did not fully grasp this discussion. You can also read about band theory in the initial parts of Chapter 3 of the supplementary notes.