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Modern physics

8. Statistical physics

Outline

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8.1. The description of a classical gas

One mole contains of about $6 \cdot 10^{23}$ particles, interacting with one another. Thus, it is practically impossible to solve the Schrödinger equation and find the wave functions of all individual particles.

The approach we use in this case is the domain of **statistical physics** (both classical and quantum mechanical). It will useful in the description of semiconductors.

We assume that a system at a temperature T in contact with a thermal reservoir will reach a **thermal equilibrium** after a long time.

We are interested in an ***average*** molecule speed, ***average*** velocity, ***average*** kinetic energy, etc.

The physically measurable quantities that characterize a system of many particles can all be obtained if one knows the probability that for a temperature T the system has particular energy E.

8.1. The description of a classical gas

The classical expression for the probability is due to Boltzmann and is a result that is central to much of physics, chemistry, biology, and technology.

Quantum effects dominate large systems of direct practical interest, including most solids at room temperature.

At low temperatures the effects of the Pauli principle – the consequences of the particles being fermions or bosons – are of great importance. **At higher temperature**, these effects cease to be important.

The classical statistical physics and quantum statistical physics merge into each other as the temperature of the system rises.

8.1. The description of a classical gas

A gas of pointlike, **noninteracting** atoms or molecules provides the most direct example of a classical gas. A dilute gas is a good example of such a system.

Kinetic theory of gases predicts that the gas molecules move about freely, except for the very brief moments during which they undergo impulsive collisions with other gas molecules or with the walls of the container.

The internal energy U of the system is the sum of the kinetic energies of all its atoms or molecules, which in turn can be expressed as the average kinetic energy per molecule <K> times the number of molecules N:

$$U = N\langle K\rangle$$

8.1. The description of a classical gas

For a classical gas, the **temperature** T is a measure of the average kinetic energy <K> of the molecules of the gas.

$$\langle K\rangle = \left(\frac{3}{2}\right) k_B T$$

Boltzmann constant $k_B = 1.38\cdot 10^{-23}$ J/K

Similarly, the origin of **pressure** is the transfer of momentum imparted to the walls when molecules bounce off of them.

$$p = \left(\frac{mv^2}{3}\right)\frac{N}{V} = \left(\frac{2}{3}\right) n\langle K\rangle$$

n=N/V is the total number of molecules per unit volume

8.1. The description of a classical gas

In the statistical approach we take into account that molecules may have a variety of velocities and energies – **velocity** or **energy distribution.**

In a box of unit volume full of molecules with a variety of velocities, there is no molecule with a particular chosen velocity. Instead, there is only a set of molecules with a velocity within the little window *about* the chosen velocity.

The number density $n(\vec{\mathbf{v}})$– the number per unit volume– of molecules with a velocity between $\vec{\mathbf{v}}$ and $\vec{\mathbf{v}}+d^3\vec{\mathbf{v}}$

$n(\vec{\mathbf{v}})$ **is the number density distribution**

The total molecular density n: $n=\int n(\vec{\mathbf{v}})d^3\vec{\mathbf{v}}$

The probability of finding a molecule with the velocity in this range: $f(\vec{\mathbf{v}})d^3\vec{\mathbf{v}}=n(\vec{\mathbf{v}})\frac{d^3\vec{\mathbf{v}}}{n}$

8.1. The description of a classical gas

$f(\vec{\mathbf{v}})$ **is the probability density function**

$$\boxed{f(\vec{\mathbf{v}})=\frac{n(\vec{\mathbf{v}})}{n}}$$

Averages can be simply written using the probability density function as

$$<\vec{\mathbf{v}}^2>=\int\vec{\mathbf{v}}^2 f(\vec{\mathbf{v}})d^3\vec{\mathbf{v}}$$

To calculate quantities such as $<\vec{\mathbf{v}}^2>$ we need to know the exact form of the probability density (distribution) function $f(\vec{\mathbf{v}})$

8.2. The Maxwell distribution

In 1860 **James Clerk Maxwell** found the distribution function *f*(*v*)

He assumed that f depends only on speed v:

$$f(v_x, v_y, v_z) = f(v_x^2 + v_y^2 + v_z^2)$$

Without a preferred direction, the motions in the three directions are independent meaning the probability of finding a molecule with x-component of velocity in the range from v_x to v_x+dv_x is independent of the probability of finding the molecule's y-component of velocity in the range from v_y to v_y+dv_y , and so on.

$$f(v_x, v_y, v_z) = h(v_x)h(v_y)h(v_z)$$

h is a distribution in the one-dimensional variable (its argument)

8.2. The Maxwell distribution

Thus $$h(v_x)h(v_y)h(v_z) = f(v_x^2 + v_y^2 + v_z^2)$$

Distribution function h is the *same* for each of the three Cartesian direction! It follows from symmetry: we could relabel the x-, y- and z-axes, and that should not have any effect on the physical distribution of molecules.

The above equation is a very restrictive one, not satisfied just by any function. If we take the natural logarithm of both sides we find

$$\ln\left[h(v_x)\right] + \ln\left[h(v_y)\right] + \ln\left[h(v_z)\right] = \ln\left[f(v_x^2 + v_y^2 + v_z^2)\right]$$

and

$$h(v_x) = cons \times \exp\left(-Bv_x^2\right)$$

8.2. The Maxwell distribution

In turn, $f(v) = C\exp[-B(v_x^2 + v_y^2 + v_z^2) = C\exp(-Bv^2)$

From the normalization condition (the sum of probabilities must add to unity) we find the constants B and C

The Maxwell distribution of molecular velocities takes a final form:

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

- The Maxwell distribution depends only on the magnitude of the velocity, not on its direction
- For a fixed temperature, the Maxwell distribution drops exponentially with the kinetic energy K=mv^2/2 of the molecule, falling by a factor of *e* every time K increases by a factor of k_BT

8.2. The Maxwell distribution

- As with any probability distribution, the Maxwell distribution can be used find averages; for example:

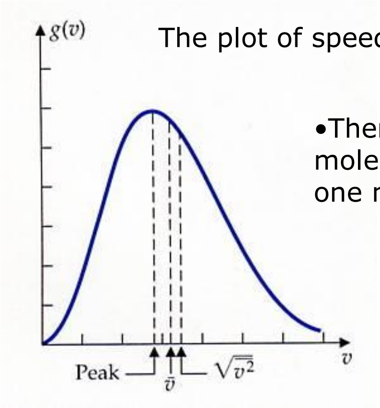
$$<v^n> = \int v^n f(v) d^3\vec{\mathbf{v}}$$

- The Maxwell distribution is, properly speaking, a velocity distribution, but it can be used to calculate a speed distribution g(v)

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

$g(v)dv$ describes the probability that a molecule will have a speed between v and v+dv

8.2. The Maxwell distribution



The plot of speed distribution for molecules in a gas

- There is no probability of finding a molecule nearly at rest, nor of finding one moving at an arbitrarily high speed.
- There is a speed for which the distribution is a maximum that is not far from the average.

8.2. The Boltzmann distribution

The Maxwell distribution is a special case of a more general result:

The probability that a single member of a large number of molecules in equilibrium at temperature T has an energy E is proportional to:

$$\exp(-\frac{E}{k_B T})$$

the Boltzmann factor

The energy E can be a function of the velocity of the molecules (kinetic energy for the pointlike case), but it can also contain rotational ($E=I\omega^2/2$) or vibrational energy ($E=kx^2/2$) for nonpointlike molecules.

8.2. The Boltzmann distribution

For a gas in equilibrium, we can consider a number density distribution n(E) in energy. The number of molecules with energies from E to E+dE is n(E)dE.

Collisions between molecules are relevant to finding n(E) because molecules exchange energy in these collisions.

$$n(E) = n(0)\exp(-\frac{E}{k_B T})$$

n(0) is a normalization constant

The total density of molecules is: $n = \sum n(E)$

where the sum is over all allowed energies

8.2. The Boltzmann distribution

In atomic and molecular systems we often have degeneracies.

For example, for a rotator whose energy is: $E = \frac{L^2}{2I}$

has $2\ell+1$ energy levels, each with energy: $E = \frac{\hbar^2 \ell(\ell+1)}{2I}$

and in the absence of an external magnetic field these are degenerate

Thus if the degeneracy for a given value of E is g(E), then the probability of measuring the energy E is

$$P(E) = \frac{n(E)}{n} = \frac{g(E)\exp(-\frac{E}{k_B T})}{\sum g(E)\exp(-\frac{E}{k_B T})}$$

g(E)=$2\ell+1$ in the example above

8.4. The Fermi-Dirac distribution

A **Fermi-Dirac** system is composed of identical fermions, particles that obey the Pauli exclusion principle.

A gas of electrons in a background of neutralizing positive charge is an example of the Fermi-Dirac system.

The average number N(E) of particles with spin ½ at a given energy E is given by:

$$N(E)=2n(E)=\frac{2}{\exp[\beta(E-\mu)]+1}$$

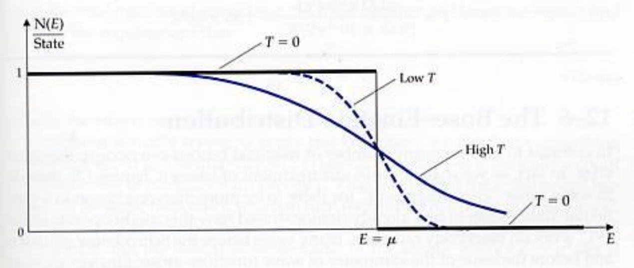
To identify the constants β and μ we can use some known limits.

In the limit of high energies, the energy distribution must reduce to the classical Boltzmann distribution. That is because at very high E, the N(E) will be so small that the exclusion principle is no longer important. Thus,

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

8.4. The Fermi-Dirac distribution

A plot of the Fermi-Dirac distribution for various values of the temperature T.

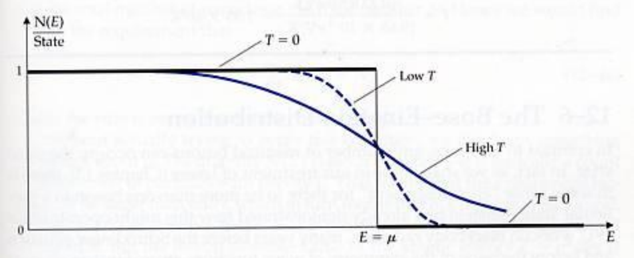


At low temperatures, or equivalently $\beta \to \infty$, there are only two states (N(E) can take only two values). If E>μ then N(E)=0, while if E<μ then N(E)=2.

This is just the form we expect for a collection of fermions in their ground state; there will be two electrons for each possible energy value up to the Fermi energy E_F and none above E_F. Thus we identify μ with E_F

8.4. The Fermi-Dirac distribution

A plot of the Fermi-Dirac distribution for various values of the temperature T.



For low T, the deviation from the case where T=0 is concentrated near Fermi energy. At high temperatures there is no dramatic change near E=μ.

$$N(E)=\frac{2}{\exp\dfrac{E-E_F}{k_BT}+1}$$

8.5. The Bose-Einstein distribution

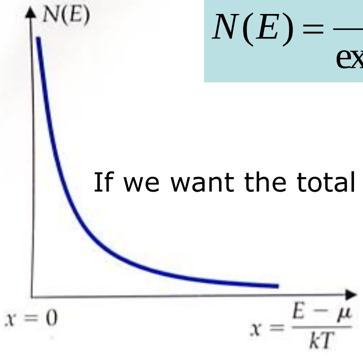
In contrast to fermions, any number of bosons can occupy the same state. There is in some sense „encouragement" for there to be more than one boson in a particular state.

Einstein had already demonstrated how this might operate in his work on blackbody radiation (1917), many years before the Schrödinger equation and before the issue of the symmetry of the wave function arose. Einstein showed that the transition rate to a state containing n photons is **enhanced** by a factor n+1.

$$n(E)=\frac{1}{\exp\beta(E-\mu)-1}$$

Recall that for the Fermi-Dirac distribution there was a factor 2 in the numerator that reflected the possibility that a particle with ½ spin has two spin states („up" and ‵down"), each with the same energy. Likewise, since bosons have (an integer-valued) spin label s, there are 2s+1 spin states that all have the same energy

8.5. The Bose-Einstein distribution



$$N(E) = \frac{2s+1}{\exp\left[\beta(E-\mu)\right]-1}$$

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

$$N = \sum N(E)$$

If we want the total number N of bosons to be fixed then

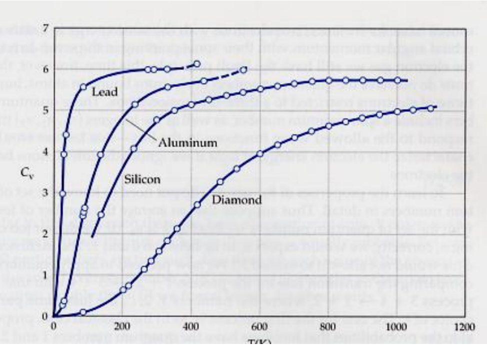
$$\mu \leq 0$$

For photons, because their total number is not always fixed μ=0

8.6. Some applications

8.6.1. The specific heat of electrons in metals

The law of Dulong and Petit predicts for 3D solids, the specific heat C=3R where R is the universal gas constant.



In metals, electrons contribute to the specific heat at low temperatures because only some fraction of them (close to the Fermi energy) participate in the conduction mechanism. This is totally quantum effect

$$C_{el} = \frac{\pi^2}{2} R \frac{T}{T_F}$$

T_F-Fermi temperature is of the order of 60 000 K.

At ordinary temperatures, electrons contribute little to the total specific heat

8.6. Some applications

8.6.2. Bose-Einstein condensation

The parameter μ is determined for massive bosons by the requirement that the sum of the numbers of bosons with all energies add to the total number N of bosons. This number is independent of energy, so μ must vary with energy in just such a way as to keep N fixed. We note that μ depends on temperature, it must increase towards μ=0 as T decreases. At $T=T_c$, μ=0.

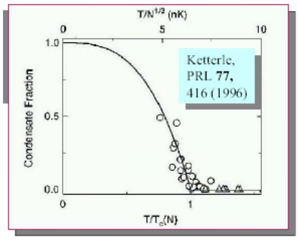
In 1924 Einstein proposed that theoretically one should separate the ground state with E=0 from the rest of the sum. There would be two distributions of particles with relative numbers N_0 and N_e for the ground state and the excited states, respectively.

As the temperature drops below T_c a larger and larger fraction „condenses" into the ground state. As the temperature approaches absolute zero, all the particles condense into the ground state. This phenomenon, which occurs even in the absence of direct interactions between the bosons, is called **Bose-Einstein condensation.**

8.6. Some applications

8.6.2. Bose-Einstein condensation

The fraction of particles that are condensing into the ground state are all in the same quantum state.



The **condensate** is a **macroscopic quantum system** – a quantum system that makes its quantum properties known through large-scale observable effects**.**

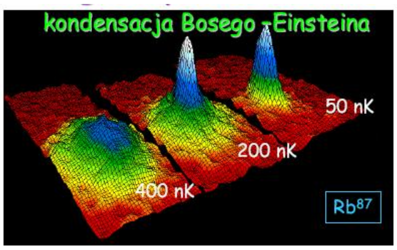
It is interesting that it took until 1995 to observe the condensation phenomenon experimentally. The reasons is that the condensation temperature is very low and at these temperatures most materials solidify. When atoms (if they are bosons) solidify to form a crystal lattice, the fact that they are identical bosons is irrelevant. In that case, the atoms are distinguished by their positions.

8.6. Some applications

8.6.2. Bose-Einstein condensation

In 1995 a group of physicists headed by E.Cornel and C.Weiman in a joint program of the University of Colorado and National Institute of Standards and Technology performed experiments on a gas of ^{87}Rb atoms (which are bosons). The gas was cooled down and at a critical temperature T_c=190 nK a Bose-Einstein condensation occurred.

A study of speed distribution showed a transition from the Maxwell-Boltzmann distribution above T_c to one in which there was pronounced peak around v=0 as the temperature was lowered beyond T_c



8.6. Some applications

8.6.2. Bose-Einstein condensation

Finally, in 2001, there was a Nobel prize for Bose-Einstein condensation.

Cornell, Ketterle, Weiman

8.6. Some applications

8.6.3. Liquid helium and superfluidity

Liquid helium is another system in which the Bose-Einstein condensate occurs. The fact that the helium atoms interact with one another – because the atoms are closely spaced- modifies the properties of the condensate substantially. The effects associated with the condensate in liquid helium were observed long before the noninteracting condensate was.

In 1908, the Dutch physicist Heike Kamerlingh Onnes working in Leiden, in the Netherlands, first succeeded in liquefying helium. The transition from gas to liquid occurs at 4.2 K. In 1928 the Dutch physicist Willem Hendrik Keesom, working in Kamerlingh Onnes Laboratory in Leiden, discovered that at the temperature T_c=2.17 K liquid helium makes a transition to a **new phase**.

8.6. Some applications

8.6.3. Liquid helium and superfluidity

Some extraordinary properties of this new phase:

- When liquid helium at above T_c is cooled by letting it evaporate and pumping the liquid away, the liquid beneath the vapor boils. As the temperature drops below T_c, the boiling stops suddenly
- Above T_c liquid helium behaves like any other viscous fluid; it cannot flow through channels that are too narrow. Below T_c the flow through a narrow channel is completely unobstructed, to the point that the helium appears to have no viscosity whatever
- When liquid helium below T_c is put in a bottle with a stopper containing a channel too narrow for normal fluids to pass through, and the bottle is heated (e.g. by infrared radiation), the liquid helium in the bottle produces a jet-like fountain as it passes through the stopper channel

8.6. Some applications

8.6.3. Liquid helium and superfluidity

At T_c the helium atoms begin to form a condensate. Just at T_c the fraction of the atoms in the condensate is small. As T decreases to 0, the fraction increases to unity. The condensate becomes a **superfluid.**

Below T_c it is useful to describe helium as a mixture of two fluids:

- the normal fluid
- the superfluid

The relative density of normal fluid to supefluid changes with temperature between T=0 and $T=T_c$.

8.6. Some applications

8.6.3. Liquid helium and superfluidity

Because the helium atoms interact, even weakly, with each other, the phenomena observed are different from Bose-Einstein condensation. It is not possible for a small subset of atoms of the superfluid to leave the ground state and get to the excited state. As a consequence it takes a macroscopic amount of energy to create excites states of the superfluid.

The lack of viscosity is explained by the inability of the condensate to lose arbitrarily small amounts of energy. Viscosity – a kind of internal friction-is just a manifestation of energy dissipation in the fluid as a result of its flow.

Conclusions

- A statistical treatment of matter is an absolute necessity given the large number of particles involved; for that same reason the predictions of such a treatment are absolutely reliable
- For a classical gas, a connection is made between the temperature and other thermodynamic variables such as pressure and kinetic energy, through the kinetic theory
- The distribution of energies in a large system is described by the Boltzmann distribution. When the energies are purely kinetic, as in the classical gas of pointlike atoms, the Boltzmann distribution becomes a distribution in velocity – the Maxwell distribution
- For identical particles, at low temperatures, quantum mechanics should be used for statistical systems. The energy distribution for identical fermions is the Fermi-Dirac distribution while that for identical bosons – the Bose-Einstein distribution