

Chapter 7 - Quantum Statistics

7.1 The Gibbs Factor

The Boltzmann factor only allows for systems to exchange energy, yet not particles. However it can often be useful to consider a system that also has the ability to exchange particles with its environment. We start with the first modifications for the rate of probabilities

$$\frac{P(s_2)}{P(s_1)} = \frac{\Omega_R(s_2)}{\Omega_R(s_1)} = \frac{e^{S_R(s_2)/k}}{e^{S_R(s_1)/k}} = e^{(S_R(s_2) - S_R(s_1))/k}$$

where S_R is the change of entropy of the reservoir as the system goes from state 1 to state 2. We use the thermodynamical identity

$$dS_R = \frac{1}{T}(dU_R + PdV_R - \mu dN_R)$$

Since we consider a system of only system and reservoir anything lost by the system must be gained by the reservoir so we simply change the changes from reservoir to the system with a negative coefficient. Moreover the change here is between two states so the terms can be written as for example $dU = U(s_2) - U(s_1)$. The term PdV is often 0 or approximately close so we neglect it and get

$$S_R(s_2) - S_R(s_1) = -\frac{1}{T}[E(s_2) - E(s_1) - \mu N(s_2) + \mu N(s_1)]$$

Taking these terms into the rate of probabilities we get

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{-[E(s_2) - \mu N(s_2)]/kT}}{e^{-[E(s_1) - \mu N(s_1)]/kT}}$$

So we then see that the ratio of probability is a ratio of simple exponential factors, each a function of the temperature of the reservoir and the corresponding microstate. However in contrast to the Boltzmann factor these also depend on the chemical potential and the number of particles in the system for state s . The new exponential is called a **Gibbs factor**.

$$\text{Gibbs factor} = e^{-[E(s) - \mu N(s)]/kT}$$

And as we did with the Boltzmann factor, if we want the absolute probability for one state we need to normalise the function by dividing it with the sum of all states.

$$P(s) = \frac{1}{\mathcal{Z}} e^{-[E(s) - \mu N(s)]/kT}$$

Where the quantity \mathcal{Z} is called the **Grand Partition Function**, or the Gibbs sum.

$$\mathcal{Z} = \sum_s e^{-[E(s) - \mu N(s)]/kT}$$

where the sum runs over all possible states (including all possible values of N). If more particles are present the term $\mu N(s)$ becomes a sum of the form $\mu N(s) = \mu_A N_A(s) + \mu_B N_B(s) + \dots$.

An example for carbon monoxide poisoning can be found in the book at page 259.

7.2 Bosons and Fermions

The most important application of Gibbs factors is to **quantum statistics**, the study of dense systems in which two or more identical particles have a reasonable chance of wanting to occupy the same single-particle state. The equation for a system of N indistinguishable, non-interacting particles

$$Z = \frac{1}{N!} Z_1^N$$

breaks down, where the problem is the term $N!$, the number of ways of interchanging the particles among their various states is only correct if the particles are always in different states. (here the word state means a single-particle state.)

Particles that can share the same state are called **bosons** and you can as many as you want of them in the same state. Particles that can not share a state are called **fermions**, and this follows from the Pauli's exclusion principle. This directly affects the distribution of particles over a set of states. Particles with integer spin are bosons and particles with half integer spin are fermions. In many situations it does not matter whether the particles in a fluid are bosons or fermions. When the number of available single-particle states is much greater than the number of particles $Z_1 \gg N$ the chance that two particles will occupy the same state is negligible. Only a tiny fraction of all system states have a significant number of states double occupied.

For an ideal gas, the single-particle partition function is $Z_1 = V Z_{int} / v_Q$, where Z_{int} is a reasonably small number and v_Q is the quantum volume

$$v_Q = \left(\frac{h}{\sqrt{2\pi m k T}} \right)^3$$

The condition for this formula to apply was that $\frac{V}{N} \gg v_Q$ which says that the average distance between the particles must be greater than the average de Broglie wavelength. For a gas like air this condition holds, however when it starts to break down what actually happens to the gas is not so trivial. We can try to imagine it as if a gas is sufficiently dense or v_Q is large enough, then the wavefunctions of the gas particles will try to overlap and this is where it makes a difference whether they are fermions or bosons, and the gas will behave very different from a "normal" gas. There are many systems which break this condition where the three most common reasons is that the gas is very dense (so the term $V/N \ll 1$), composed of light particles($v_Q \propto 1/m^{3/2}$) or extremely cold ($v_Q \propto 1/T^{3/2}$).

The Distribution Function

When a system violates the condition $Z_1 \gg N$, so that it can not be treated using the previous method of chapter 6, we can use the Gibbs factor instead. The main idea is to first consider a system consisting of one single particle state rather than a particle itself. This makes the system consist of a particular spatial wavefunction and a spin-function if spin is also included. The system and the reservoir then "occupy" the same physical space. However the Gibbs factor and the mathematics behind it does not concern itself with this fact, so we can apply it to a single-particle-state system.

Imagine a single-particle state of a system where the energy when occupied by a single particle is ϵ . This means that when unoccupied the energy will be zero. When occupied by n particles it will then have energy $n\epsilon$. The probability for the state being occupied by n particles is then

$$P(n) = \frac{1}{Z} e^{-(n\epsilon - \mu n)/kT} = \frac{1}{Z} e^{-n(\epsilon - \mu)/kT}$$

where Z is the grand partition function. If the particles are fermions then $n = 0, 1$ because of the exclusion principle. So the grand partition function becomes

$$\mathcal{Z} = 1 + e^{-(\epsilon-\mu)/kT} \quad (\text{fermions}).$$

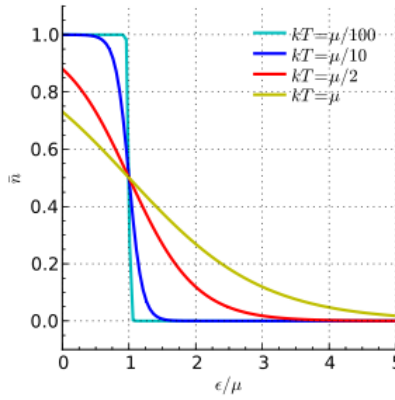
And this shows us that the probability of the state being occupied or unoccupied is a function of ϵ , μ and T . With this we can also compute the average number of particles in the state, called the **occupancy** of the state:

$$\langle n \rangle = \sum_n nP(n) = \frac{e^{-(\epsilon-\mu)/kT}}{1 + e^{-(\epsilon-\mu)/kT}} = \frac{1}{e^{(\epsilon-\mu)/kT} + 1} \quad (\text{fermions}).$$

This formula is rather important and it is called the **Fermi-Dirac distribution**. ($\langle n \rangle_{FD}$)

$$\langle n \rangle_{FD} = \frac{1}{e^{(\epsilon-\mu)/kT} + 1} \quad (\text{fermions}).$$

Important things about this equation is that it goes to zero when $\epsilon \gg \mu$, and it goes to 1 when $\epsilon \ll \mu$. From this we can conclude that states with energy much less than μ tend to be occupied, while states with energy much greater than μ tends to be unoccupied. Further a state with energy equal to μ has a 50% chance of being occupied.



If the particles are bosons however the number of particles in the single state can be infinite $n = 0, 1, 2, 3, \dots$. So the grand partition function becomes

$$\mathcal{Z} = 1 + e^{-(\epsilon-\mu)/kT} + e^{-2(\epsilon-\mu)/kT} + \dots$$

We see that it is a geometric sum so it can be rewritten to

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

However finding the average number of particles with the equation $\langle n \rangle = \sum_n nP(n)$ can not be done as the sum goes to infinity, to evaluate it we first set $x = (\epsilon - \mu)/kT$. We get

$$\langle n \rangle = \sum_n n \frac{e^{-nx}}{\mathcal{Z}} = -\frac{1}{\mathcal{Z}} \sum_n \frac{\partial}{\partial x} e^{-nx} = -\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial x}$$

Evaluating this we get an equation called the **Bose-Einstein distribution**;

$$\langle n \rangle_{BE} = \frac{1}{e^{(\epsilon-\mu)/kT} - 1}$$

Much like the Fermi-Dirac distribution, the Bose-Einstein distribution goes to zero when $\epsilon \gg \mu$. Unlike the Fermi-Dirac distribution, however, it goes to infinity as ϵ approaches μ from above. It would be negative if ϵ could be less than μ yet this is

not allowed. A comparison between Fermi-Dirac and Bose-Einstein against Boltzmann statistics can be seen on page 268.

7.3 Degenerate Fermi Gases

To demonstrate the Fermi-Dirac distribution we consider a gas of fermions at low temperatures, like electrons in a chunk of metal. And by low temperature we mean a temperature where it is sufficiently low enough so that the condition $V/N \gg v_Q$ is badly violated, so Boltzmann statistics can not be applied to an ideal gas. In fact the opposite is true $V/N \ll v_Q$. For an electron at room temperature, the quantum volume is

$$v_Q = \left(\frac{h}{\sqrt{2\pi mkT}} \right)^3 = (4.3 \text{ nm})^3$$

However in a metal there is about one conductive electron per atom, so the volume per conduction electron is roughly the volume of an atom $(0.2 \text{ nm})^3$. So the temperature is too small for Boltzmann statistics to apply, however the temperature is so close to zero that we can assume $T = 0$. And we will begin by considering this.

Zero Temperature

At $T = 0$ the Fermi-Dirac function becomes a square step function. All single-particle states with energy less than μ are occupied while all states with $\epsilon > \mu$ are unoccupied. And in this context μ is called the **Fermi Energy**, denoted by ϵ_F .

$$\epsilon_F = \mu(T = 0)$$

When a gas of fermions is so cold that nearly all states below ϵ_F are occupied while nearly all states above ϵ_F are unoccupied, the gas is said to be degenerate. (This use of the word is unrelated to the quantum mechanical term degeneracy). The actual value of ϵ_F is determined by the total numbers of electrons present. We can imagine an empty box where we add one electron after another, the electrons will try to fit into the state with lowest energy, electrons will begin to pile up as only two can fill for a specific energy, this pattern will continue until the last electron fills up a shell with energy just below the fermi energy. To add one more electron you would have to give it the energy equal to the fermi energy.

In order to calculate ϵ_F , among other quantities we make the assumption that the electrons are free particles, subject to no force except that they are confined to a box of volume $V = L^3$. For a metal this is not an accurate approximation, yet it will work for now. The definite energy wavefuntions of a free electron in a box are sine waves. For a 1D box the allowed wavelengths and momentas are as before

$$\lambda_n = \frac{2L}{n}, \quad p_n = \frac{h}{\lambda_n} = \frac{hn}{2L}$$

where n is a positive integer. In 3D we can evaluate it as

$$p_i = \frac{hn_i}{2L}$$

where $i \in \{x, y, z\}$. The allowed energies are therefore

$$\epsilon = \frac{|\vec{p}|^2}{2m} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2)$$

We can approximate this to n-space, and we can see that it will form a sphere which exists in one eight of a sphere where all the n values are positive where the radius of the sphere shell where we find the configuration of n_x, n_y, n_z that correspond to the fermi energy, we call it n_{max} . From this we find that the fermi energy is calculated by

$$\epsilon_F = \frac{h^2 n_{max}^2}{8mL^2}.$$

Another way of calculating the fermi energy is to say that the total volume of the eight-sphere in n-space equals the number of lattice points enclosed, since the lattices are separated by 1 in all three directions. Hence the total number of occupied states is twice this volume (because of the two spin orientation).

$$N = 2 \times (\text{volume of an eight-sphere}) = 2 \cdot \frac{1}{8} \cdot \frac{4}{3} \pi n_{max}^3 = \frac{\pi n_{max}^3}{3}$$

and from this we get that the fermi energy can be calculated as a function of N and $V = L^3$ of the box

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

Further we notice that this quantity actually is intensive! Since you divide one extensive quantity on another. The Fermi energy is the highest energy of all the electrons, on average however they will have little more than half ϵ_F . To find the total energy we need to do an integral of the form

$$U = 2 \sum_{n_x} \sum_{n_y} \sum_{n_z} \epsilon(\vec{n}) = 2 \iiint \epsilon(\vec{n}) dn_x dn_y dn_z$$

Where the factor two comes from the fact that each state can be occupied by two electrons. What allows us to change from a sum to an integral is that the number of terms is very very large, so we approximate it to a continuous function. Once evaluated by switching to spherical coordinates we get that

$$U = \frac{3}{5} N \epsilon_F$$

So the **average energy** is $3/5$ the Fermi energy.

When the condition $kT \ll \epsilon_F$ is met the approximation $T \approx 0$ is fairly accurate for many purposes, and the gas is referred to as degenerate. The temperature you would have to have for kT to be equal ϵ_F is called the Fermi temperature, but it is a theoretical temperature as it has no real use, metals liquefy and evaporate long before it is reached.

Using the relation $P = - \left(\frac{\partial U}{\partial V} \right)_{S,N}$ we can calculate the pressure of a degenerate electron gas.

$$P = \frac{2N\epsilon_F}{5V} = \frac{2U}{3V} \quad (\text{degeneracy pressure})$$

and this quantity is called the **degeneracy pressure**. It is positive because when you compress a degenerate electron gas, the wavelengths of all the wavefunctions are reduced, hence their energies increases. Degeneracy pressure is what keeps matter from collapsing under the huge electrostatic forces that try to pull electrons and protons together, and it rises purely from the exclusion principle (and not from electrostatic repulsion which we have ignored). The degeneracy pressure can be calculated numerically to be around a few billion N/m^2 for a typical metal. But the number is not really measurable, what is a more fitting thing to measure is the **Bulk modulus**, which is the change in pressure when the material is compressed, divided by the fractional change in volume.

$$B = -V \left(\frac{\partial P}{\partial V} \right)_T = \frac{10U}{9V}$$

And this formula agrees with experiments with a factor of around 3 for most metals.

Small Nonzero Temperatures

One thing which can not be calculated for Fermi gases using the approximation $T = 0$ is the heat capacity. Since this is a measure of how the energy of the system depends on T . We observe what happens when the temperature is very small, yet nonzero.

At temperature T all particles typically acquire a thermal energy of approximately kT . However for a degenerate electron gas, most of the electrons cannot acquire such a small amount of energy since there are no free energyboxes to jump to. Most if not all are occupied. However the electrons that are within about kT of the Fermi energy can acquire this energy, because they can jump into the states above ϵ_F . The number of electrons that can be affected by the increase in T is proportional to T . The number is also proportional to N . Thus we arrive at

$$\text{additional energy} \propto (\text{number of affected electrons}) \times (\text{energy acquired by each})$$

$$\Rightarrow \text{additional energy} \propto N(kT)^2$$

We use dimensional analysis to guess the constant of proportionality and we find it to be the inverse of the Fermi energy. This gives

$$U = \frac{3}{5}N\epsilon_F + \frac{\pi^2}{4}N\frac{(kT)^2}{\epsilon_F}$$

And from this the heat capacity becomes

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{\pi^2 N k^2 T}{2\epsilon_F}$$

And we observe that the heat capacity goes to zero when T goes to zero, as required by the third law of thermodynamics.

The Density of States

For $T = 0$ you can show that the energy integral for a Fermi gas is

$$U = \int_0^{\epsilon_F} \epsilon \left[\frac{\pi}{2} \left(\frac{8mL^2}{h^2} \right)^{3/2} \sqrt{\epsilon} \right] d\epsilon \quad (T = 0)$$

The number of single-particle states per unit energy is called the **density of states**. The symbol for it is $g(\epsilon)$, and it can be written in various ways:

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

The second expression is compact and handy, however somewhat misleading as it implies that $g(\epsilon)$ is proportional on N , which it is not, this is because the dependence is cancelled out by ϵ_F . However from the first term we can see that the density of states is actually dependent on V . Moreover if we want to know how many states are in between two energies ϵ_1 and ϵ_2 you just integrate $g(\epsilon)$ over the desired range, so again we have a function who's entire existence revolves around being integrated. How sad.

The nice thing about $g(\epsilon)$ is that determining it for more complex systems is purely a problem of quantum mechanics, so it has nothing to do with for example thermal effects or temperature, so if you know g for some system you can forget about the quantum mechanical aspects and focus on the thermal parts. Here in our equation of $g(\epsilon)$ we assumed that the electrons are

"free", however for a more correct version of metals we would have to take into account the attraction of the electrons towards the positive ions in the crystal lattice.

We can also get the total number of electrons by integrating g from 0 to ϵ_F at zero temperature.

$$N = \int_0^{\epsilon_F} g(\epsilon) d\epsilon \quad (T = 0)$$

However when T is nonzero to calculate N and U we use

$$N = \int_0^{\infty} g(\epsilon) \langle n_{FD} \rangle(\epsilon) d\epsilon = \int_0^{\infty} g(\epsilon) \frac{1}{e^{-(\epsilon-\mu)/kT} + 1} \quad (\text{any } T)$$

$$U = \int_0^{\infty} \epsilon g(\epsilon) \langle n_{FD} \rangle(\epsilon) d\epsilon = \int_0^{\infty} \epsilon g(\epsilon) \frac{1}{e^{-(\epsilon-\mu)/kT} + 1} \quad (\text{any } T)$$

The Sommerfeld Expansion

The way we evaluate these integral can be tricky and we use an expansion called the **Sommerfeld expansion** which is limited to $kT \ll \epsilon_F$. The actual expansion can be found on page 282 and should be read the main results are

$$U = \frac{3}{5} N \epsilon_F + \frac{\pi^2}{4} N \frac{(kT)^2}{\epsilon_F} + \dots$$

$$\frac{\mu}{\epsilon_F} = \left[1 - \frac{\pi^2}{8} \left(\frac{kT}{\epsilon_F} \right)^2 + \dots \right]^{2/3}$$

And as we can see the chemical potential gradually decreases as T is raised.

7.4 Blackbody Radiation

We begin this by considering the electromagnetic radiation inside some "box" at a given temperature. We begin by examining the system in a classical way. In classical physics we consider electromagnetic radiation as a continuous field in all directions, inside a box all of this field is a combination of standing wave patterns, where each wave behaves as a harmonic oscillator with frequency $f = c/\lambda$. Like any harmonic oscillator these have two degrees of freedom, so it should have an average thermal energy of $2 \frac{1}{2} kT$, and since the total numbers of oscillators in the field is infinite, the thermal energy should also be infinite. However this is simply not true, this is called the **ultraviolet catastrophe**. (because the infinite energy would come mostly from small wavelengths.)

The Plank Distribution

The solution to the catastrophe comes from quantum mechanics, by quantifying the energies that the harmonic oscillator can have to

$$E_n = 0, hf, 2hf, \dots$$

The partition function becomes a geometric sum much like the Bose-Einstein distribution so it becomes

$$Z = \frac{1}{1 - e^{-\beta hf}}$$

with the average energy being

$$\langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{hf}{e^{hf/kT} - 1}.$$

and if we think that the energy comes in units of hf then the average number of units of energy in the oscillator is

$$\langle n_{Pl} \rangle = \frac{1}{e^{hf/kT} - 1}$$

which is called the **Planck distribution**.

Photons

These units can be thought of as particles called photons, they are bosons so they can be expressed by the Bose-Einstein distribution

$$\langle n_{BE} \rangle = \frac{1}{e^{(\epsilon - \mu)/kT} - 1}$$

and here $\epsilon = hf$ and the chemical potential is $\mu = 0$. We consider the Helmholtz free energy, which must attain the minimum possible value at equilibrium with T and V held fixed. With photons the number of particles N is not constant, and it will actually take values that minimise F . So if there is a small change in the number of particles, the change in F should be zero. So

$$\left(\frac{\partial F}{\partial N} \right)_{T,V} = 0 \quad (\text{at equilibrium})$$

and this is also the formula for the chemical potential, which points to that it must be zero.

Summing Over Modes

The Planck distribution tells us how many photons are in any single-particle state of the electromagnetic field. If we want to calculate the total numbers of photons in the box or the total energy we need to sum over all states.

$$U = \int_0^\infty dn \int_0^{\pi/2} d\theta \int_0^{\pi/2} d\phi n^2 \sin(\theta) \frac{hcn}{L} \frac{1}{e^{hcn/2LkT} - 1}$$

And again the angular integrals give $\pi/2$, the surface area of an eighth of a unit sphere.

The Planck Spectrum

The integral over n looks nicer if we change variable $\epsilon = hcn/2L$. We then get a factor $L^3 = V$, so the total energy per unit volume is

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

And the integrand is the energy density per unit photon energy, also called the **spectrum** of the photons.

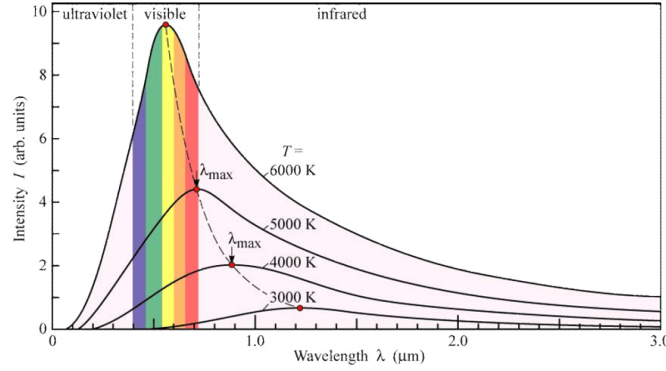
$$u(\epsilon) = \frac{8\pi}{(hc)^3} \frac{\epsilon^3}{e^{\epsilon/kT} - 1}$$

The function $u(\epsilon)$ gives a relative intensity of the radiation as a function of photon energy, if you integrate between ϵ_1 and ϵ_2 you get the energy per unit volume within the range of photons. However if you wish to evaluate it, a change of variables to

$x = \epsilon/kT$. The integral then becomes

$$\frac{U}{V} = \frac{8\pi(kT)^4}{(hc)^3} \int_0^\infty \frac{x^3}{e^x - 1} dx$$

And this gives rise to Wien's law, where you can measure the temperature of something by looking at the colour or wavelength of the light it emits.



Total Energy

It can be shown that

$$\frac{U}{V} = \frac{8\pi(kT)^4}{(hc)^3} \int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{8\pi^5(kT)^4}{15(hc)^3}$$

Which is then the total electromagnetic energy inside of a box, where the most important aspect of this is that it is dependant on the **fourth** power of the temperature.

Entropy of a Photon Gas

Besides the total energy of the photon gas we would also like to know the total numbers of photons present or the total entropy. These turn out to be the same, up to a constant factor. The entropy can be calculated by using the heat capacity at constant volume. We begin with

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 4aT^3$$

where $a = 8\pi^5 k^4 V / 15(hc)^3$. And this expression works for all temperatures even when approaching zero. We integrate to find the entropy T

$$S(T) = \int_0^T \frac{C_V(T')}{T'} dT' = 4a \int_0^T T'^2 dT' = \frac{4}{3} a T^3 = \frac{32\pi^5}{45} V \left(\frac{kT}{hc} \right)^3 k.$$

Where the total number of photons is given by the same formula, with different numerical coefficients and without the final k .

The Cosmic Background Radiation

The grandest example of a photon gas is the radiation that fills the entire observable universe, with an almost perfect thermal spectrum of $2.73K$. However the interpretation of this is somewhat odd, there is no longer any mechanism to keep the photons in thermal equilibrium with each other or anything else, the radiation is thought to be the leftovers from when the

universe was filled with ionised gas that interacted strongly with electromagnetic radiation. At this time the temperature was around $3000K$, and since the universe has expanded in all directions and the photon length has been stretched out, preserving this spectrum has shifted the effective temperature down to $2.73K$.

The photons making up this background radiation have low energies, the spectrum peaks at $\epsilon = 2.82kT = 6.6 \times 10^{-4} \text{ eV}$. These waves don't penetrate our atmosphere, however the parts of the spectrum at the microwave dimension does, and can be observed quite well. What more is that the total energy per volume of the background radiation is very small compared to ordinary matter, however its entropy is very large compared to the entropy of ordinary matter (which is not easy to calculate). The numbers for entropy and energy can be found on page 296.

Photons Escaping Through a Hole

Until now we have only discussed the insides of a hot box in thermal equilibrium, now we will talk about what if things are emitted by a hot object. If we poke a hole in a hot box filled with a photon gas, there will be an equal probability for all photons to escape the box regardless of energy, since all travel at the same speed.

The probability that energy will escape from a chunk of space inside the box is

$$\text{probability of escape} = \frac{A \cos(\theta)}{4\pi R^2}$$

where A is the width of the opening, R is the radius from the centre of the opening to the chunk and θ is the angle between the normal of the box surface and the vector R . (fig 23, page 301).

The amount of energy escaping from the chunk is then

$$\text{energy escaping from the chunk} = \frac{A \cos(\theta)}{4\pi} \frac{U}{V} c dt \sin(\theta) d\theta d\phi$$

The total energy escaping per dt can be found by evaluating the angle integrals and it becomes

$$\text{total energy escaping} = \frac{AU}{4V} c dt$$

further if we divide by A and dt we get the power per unit area

$$\text{power per unit area} = \frac{c}{4} \frac{U}{V}.$$

Using this result and the earlier result for energy per volume we get

$$\text{power per unit area} = \frac{2\pi^5}{15} \frac{(kT)^4}{h^3 c^2} = \sigma T^4$$

where $\sigma = \frac{2\pi^5 k^4}{15 h^3 c^2} = 5.67 \times 10^{-8} \frac{\text{W}}{\text{m}^2 \text{K}^4}$ and it is called the **Stefan-Boltzmann constant**.

Radiation from Other Objects

Although Stephan's law for photons emitted was derived from a hole in a box it also holds for photons emitted by any non-reflective, also referred to as black surfaces at temperature T . Such radiation is called **blackbody radiation**.

The power a blackbody radiates can be expressed as

$$P = \sigma e A T^4$$

where σ is the SB constant, e is the **emissivity** which can be a value between 1 and 0 where 1 is a perfect blackbody and 0 is a perfect reflector. A is the area of the blackbody and T is the temperature. Generally the emissivity depends upon the wavelength of the light, so the spectrum of radiation emitted will differ from a perfect blackbody spectrum.

7.5 Debye Theory of Solids

Takes into account the thermal vibrations of a crystal, and therefore the interactions between each atom in the grid. The mechanical oscillations are sound waves, and can be modelled as so-called **phonons**.

This is necessary because the Einstein model does not predict a very important property of crystals: $C_V \propto T^3$ when $T \rightarrow 0$.

Some important properties of sound waves

- travel at a speed c_s , which is dependant on the stiffness and density of the material the wave is moving through
- has three polarisation directions, because it can be longitudinally polarised in addition to the two transversal polarisations
- cannot have a wavelength shorter than twice the atomic spacing

The number of units of energy in a sound wave is given by the Planck distribution, where $\epsilon = hf = \frac{hc_s n}{2L}$ in analogy to light waves. L is the length of the crystal and $n = |\vec{n}|$ is the magnitude of the vector in n -space specifying the shape of the wave.

Phonons are **bosons**, and will therefore obey Bose-Einstein statistics. This means that the total thermal energy will be equal to $U = 3 \sum_{n_x} \sum_{n_y} \sum_{n_z} \epsilon \bar{n}_{Pl}(\epsilon)$.

After converting to integrals we find that the total energy of a crystal with n nodes is given by

$$U = 3 \cdot \frac{\pi}{2} \int_0^{n_{\max}} \frac{hc_s}{2L} \frac{n^3}{e^{hc_s n / 2LkT} - 1} dn$$

where $n_{\max} = (6N/\pi)^{1/3}$ is the number of atoms in a row when you approximate the crystal as 1/8th of a sphere.

By changing variables one finds that the upper limit on the energy is $hc_s/2kT \cdot (6N/\pi V)^{1/3} = T_D/T$, where T_D is the **Debye temperature**. After the variable change, the integral becomes

$$U = \frac{9NkT^4}{T_D^3} \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx$$

It can not be evaluated analytically, but we can still obtain some useful results when studying two particular cases:

- $T \gg T_D$: $U = 3NkT \Rightarrow C_V = 3Nk$
- $T \ll T_D$: $U = \frac{3\pi^4}{5} \frac{NkT^4}{T_D^3} \Rightarrow C_V = \frac{12\pi^4}{5} Nk \left(\frac{T}{T_D} \right)^3$ (A metal will also have an extra term γT added to C_V)

We can often predict the Debye temperature from the speed of sound in a material, but most of the time it is more useful to fit the heat capacity of the material to experimental data and find T_D from that.