

# THERMAL PHYSICS INVOLVING WAVES IN A BOX

Andrew M. Steane

*Exeter College and Department of Atomic and Laser Physics, University of Oxford.*

June 5, 2024

## Abstract

We will discuss the physics of thermal radiation. Many of the ideas apply also to other systems, such as lattice vibrations in crystals, and motion of electrons in crystalline solids. Our aim is both to understand the basic ideas, and also to avoid a common confusion which arises from looking at the same physical system in two different ways, and then muddling the two pictures. We will look at the system in two different ways, but take care not to muddle the two pictures.

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## 1 Modes and density of states

First we need some general information about *modes*. A *mode* is a state of oscillation of some physical system, such that the whole system oscillates at a single frequency. For example, consider the oscillation of a guitar string, or an electromagnetic wave, or the oscillations of atoms in a lattice.

We are interested in wave-like modes that can exist in a fixed, finite region of space.

Consider first of all a **one-dimensional system** of length  $L$ . We have in mind the infinite square well or ‘box’. If the box extends from  $x = 0$  to  $x = L$  then the energy eigenstates for a particle confined in such a box take the form

$$\phi(x) = \sqrt{\frac{2}{L}} \sin(k_n x)$$

where in order to satisfy the boundary condition  $\psi(L) = 0$  we must have

$$k_n = \frac{n\pi}{L}.$$

The gap between successive values of  $k_n$  is therefore

$$\Delta k = k_{n+1} - k_n = \frac{\pi}{L}. \quad (1)$$

Hence the total number of such states with values of  $k_n$  between zero and some given maximum value  $k$  is

$$N = \frac{k}{\Delta k} = \frac{L}{\pi} k. \quad (2)$$

The number per unit change in  $k$  is therefore

<p><b>one dimension</b></p> $\frac{dN}{dk} = \frac{L}{\pi}. \quad (3)$
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This quantity is called the *density of states* in  $k$ -space (for our 1-dimensional problem). It should not surprise you that it is equal to  $1/\Delta k$ . We often use the symbol  $g(k)$  for the density of states, so we have  $g(k) = L/\pi$ .

## 1.1 Periodic boundary conditions

Before proceeding to two, three or more dimensions, we shall now introduce another way of setting up the calculation, which often proves to be more convenient in higher dimensions.

Let us put out of our mind, for a moment, the calculation described above, and instead consider just plane-wave solutions of Schrödinger’s equation in free space. In one dimension these have the form

$$\psi(x, y) = e^{i(kx - \omega t)}.$$

where, note,  $k$  here can be either positive or negative and we have omitted the normalization.

Next let us restrict attention to plane waves which are periodic with the period  $L$ . This is called imposing *periodic boundary conditions*. The periodic boundary condition here is

$$e^{ik(x+L)} = e^{ikx} \implies e^{ikL} = 1 \implies kL = 2\pi n$$

where  $n = 0, \pm 1, \pm 2, \dots$  is an integer. It follows that the values of  $k$  are equally spaced along a line in  $k$ -space, with separation

$$\Delta k = \frac{2\pi}{L}. \quad (4)$$

Note that this separation is twice the one we found in (1).

The total number of such modes between  $-k$  and  $k$  is therefore

$$N = \frac{2k}{\Delta k} = \frac{L}{\pi}k. \quad (5)$$

This agrees with (2) because although these travelling-wave modes are more spread out in  $k$ -space than the standing-wave modes we considered before, the values of  $k$  are no longer restricted to positive numbers only,<sup>1</sup> and in  $N$  we are counting all those whose  $|k|$  is between zero and a given maximum. When using periodic boundary conditions in 1 dimension it is easy to forget that the range goes from  $-|k|$  to  $|k|$ , but in higher dimensions this aspect comes out naturally, because then we can use the familiar formula  $\pi k^2$  for the area of a circle, or  $(4/3)\pi k^3$  for the volume of a sphere.

Using (5) we get the same density of states as before, see (3). The interpretation of this is: *the number of plane-wave modes under periodic boundary conditions matches the number of standing-wave modes under  $\psi = 0$  boundary conditions, for any given range of  $|k|$ .*

For the case of a gas in a box, or radiation in a cavity, the fixed boundary condition is a natural choice. The plane waves with periodic boundary conditions offer a convenient way to treat a gas or radiation in free space. One then takes the limit  $L \rightarrow \infty$  at the end of any given calculation, and one extracts properties which remain finite in that limit. But since these plane wave solutions work equally well for finite  $L$ , one might as well use them to treat a finite cavity too. We shall do that in the following.

## 1.2 Two or more dimensions

When we proceed to two- or three-dimensional systems, we shall use  $k$  to indicate the size of the wavevector, which is always positive, but we shall include waves travelling in all directions at any given  $k$ .

In **two dimensions** a general plane wave is  $\exp(i(k_x x + k_y y - \omega t))$ . We apply periodic boundary conditions to a rectangular region with sides  $L_x, L_y$ . This leads to the restrictions

$$k_x L_x = 2\pi n_x, \quad k_y L_y = 2\pi n_y$$

where  $n_x$  and  $n_y$  are integers. Hence the allowed modes are arranged on a rectangular lattice in  $k$ -space, separated by

$$\Delta k_x = \frac{2\pi}{L_x}, \quad \Delta k_y = \frac{2\pi}{L_y}.$$

The collection of modes with wavevector between zero and  $k$  are those lying inside a circle of area  $\pi k^2$ . The number of such modes is the number of rectangles of size  $\Delta k_x \Delta k_y$  that can fit inside such a circle, which is

$$N = \frac{\pi k^2}{\Delta k_x \Delta k_y} = \frac{L_x L_y}{4\pi} k^2 = \frac{A}{4\pi} k^2 \quad (6)$$

where  $A = L_x L_y$  is the area of the region. The number of modes per unit change in  $k$  is therefore

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<sup>1</sup>This is because  $\exp(-ikx)$  is a different function to  $\exp(ikx)$ , not a scalar multiple of it, whereas  $\sin(-kx) = -\sin(kx)$ .

**Two dimensions**

$$\frac{dN}{dk} = \frac{A}{2\pi}k. \quad (7)$$

In **three dimensions**, we apply similar reasoning to a cuboid, and find the modes lying inside a sphere of volume  $(4/3)\pi k^3$  in  $k$ -space. Thus we obtain

$$N = \frac{(4/3)\pi k^3}{\Delta k_x \Delta k_y \Delta k_z} = \frac{V}{8\pi^3} \frac{4}{3} \pi k^3 = \frac{V}{6\pi^2} k^3 \quad (8)$$

and

**Three dimensions**

$$\frac{dN}{dk} = \frac{V}{2\pi^2} k^2. \quad (9)$$

Note the simple relationship between  $N(k)$  and the dimensionality of the space: in all cases,  $N(k) \propto k^D$  where  $D$  is the number of dimensions. Also note that since  $N$  is dimensionless, it should not surprise us to find that the proportionality constant is  $L, A, V$ , respectively, up to a numerical factor.

### 1.3 Density of states

The density of states is the number of states per unit change in some variable, such as wavevector, frequency or energy. In the above,  $dN/dk$  is, in each case, a density of states as a function of  $k$ . We often want to know the density of states per unit change in frequency or energy. This can be obtained from  $N(k)$  once we know the relationship between frequency and  $k$  or energy and  $k$ . This relationship varies from one physical system to another. It is given by the **dispersion relation**. For example, for electromagnetic waves in vacuum the dispersion relation is

$$\omega = kc, \quad (10)$$

whereas for de-Broglie waves of massive particles, the energy is given by  $\epsilon = \hbar\omega$  and the dispersion relation is

$$\hbar\omega = \frac{\hbar^2 k^2}{2m}, \quad (11)$$

for non-relativistic particles of mass  $m$ . For vibrations of a crystal lattice, the dispersion relation is in general more complicated, but can be approximated by a linear function of  $k$  at low frequencies:

$$\omega \simeq kv \quad (12)$$

where  $v$  is the speed of sound.

To obtain the density of states as a function of  $\omega$ , we first express  $N$  in terms of  $\omega$  and then differentiate. The reader is invited to check the answers displayed in table 1.

Note that the density of states  $g_\omega$  is flat (independent of  $\omega$ ) in one dimension for photons, and in two dimensions for massive particles. This leads to many important phenomena in

	1 dimension	2 dimensions	3 dimensions
<b>Any waves</b>			
$N(k)$	$\frac{L}{\pi}k$	$\frac{A}{4\pi}k^2$	$\frac{V}{6\pi^2}k^3$
$g(k) \equiv \frac{dN}{dk}$	$\frac{L}{\pi}$	$\frac{A}{2\pi}k$	$\frac{V}{2\pi^2}k^2$
<b>Electromagnetic waves</b>			
$N(\omega)$	$\frac{L}{\pi c}\omega$	$\frac{A}{4\pi c^2}\omega^2$	$\frac{V}{6\pi^2 c^3}\omega^3$
$g_\omega \equiv \frac{dN}{d\omega}$	$\frac{L}{\pi c}$	$\frac{A}{2\pi c^2}\omega$	$\frac{V}{2\pi^2 c^3}\omega^2$
<b>de Broglie waves</b>			
$N(\omega)$	$\frac{L}{\pi} \left( \frac{2m\omega}{\hbar} \right)^{1/2}$	$\frac{Am}{2\pi\hbar}\omega$	$\frac{V}{6\pi^2} \left( \frac{2m\omega}{\hbar} \right)^{3/2}$
$g_\omega \equiv \frac{dN}{d\omega}$	$\frac{L}{\pi} \left( \frac{m}{2\hbar\omega} \right)^{1/2}$	$\frac{Am}{2\pi\hbar}$	$\frac{V}{4\pi^2} \left( \frac{2m}{\hbar} \right)^{3/2} \omega^{1/2}$

Table 1: Number of modes and density of states for different types of waves, in 1, 2 and 3 dimensions. The table lists the number of modes of each polarization. Since for electromagnetic waves there are two orthogonal polarizations, the total number of modes is twice the number given in the table. Similar, if the de Broglie waves are associated with spin-half particles, then one should multiply by 2 to account for the two possible spin states for each plane wave.

the case of electrons restricted to move in a two-dimensional region. Note also that the results in table 1 do not allow for polarization or spin. This means they give the number of modes of each polarization, or of each spin state. Finally, note that throughout this section we have discussed *modes*, which are wave-like oscillations. There is no need to mention particles such as photons, or phonons, or electrons. For the case of electromagnetic waves, and also lattice vibrations, we do not at this stage need to invoke quantum mechanics. The term ‘density of states’ here means the *number of modes per unit frequency range*.

## 2 Thermal (black body) radiation

### 2.1 Method 1: a collection of oscillators

We will now treat thermal radiation, using the standard tools of statistical mechanics, applied to electromagnetic waves in a box. Note, there will be **no need to mention photons, or indistinguishable particles, or Bose-Einstein statistics**. The method is to treat

the *electromagnetic field* as the system under consideration, using *quantum field theory* to describe the field.

The quantum field theory we need is called *quantum electrodynamics* or QED, and in its complete form it involves some subtle and complex ideas. However, fortunately, we do not need here the complete theory, which describes electrons and their interactions with the electromagnetic field, because there are no electrons in the system under consideration. We only need to treat the electromagnetic field in free space. This is reasonably easy to do. According to QED, the electromagnetic field in free space is modelled mathematically as a collection of quantum harmonic oscillators, one for each mode of oscillation of the field. The modes are precisely the ones we discussed in the previous section, but we should remember that there can be two polarizations for each plane wave, so the total number of modes is twice the number of possible  $\mathbf{k}$  values.

This statement—that a field mode behaves like a harmonic oscillator—is a foundational assumption of QED, and therefore it cannot be derived, but only presented as a reasonable claim. Its reasonableness is demonstrated by the success of the theory, but it can be motivated a little by noting that the energy density in the electromagnetic field is given by  $(\epsilon_0/2)(E^2 + c^2B^2)$ , i.e. a quadratic function of the field variables, which is reminiscent of the quadratic potential energy function for simple harmonic motion. Also, of course, in the classical case the field does oscillate with a simple harmonic motion.

Our system, then, is a collection of harmonic oscillators of given frequencies  $\omega$ . The number of oscillators at each frequency is given by  $2g_\omega d\omega$  where  $g_\omega$  is given in table 1. These oscillators are all **distinguishable** physical systems: they can be distinguished by the values of the wave-vector  $\mathbf{k}$  and polarization of the associated field mode.

First let us treat a single mode using statistical mechanics. Since it behaves as a quantum harmonic oscillator, the energy levels are

$$\epsilon_n = (n + 1/2)\hbar\omega \quad (13)$$

and the partition function is

$$Z_1 = \sum e^{-\beta\epsilon_i} = \sum_{n=0}^{\infty} e^{-(n+1/2)\beta\hbar\omega} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$$

where  $\beta \equiv 1/k_B T$  and the final step was accomplished by summing the geometric series. The mean energy in thermal equilibrium is

$$\bar{E} = -\frac{1}{Z_1} \frac{\partial Z_1}{\partial \beta} = \hbar\omega \left( \frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right), \quad (14)$$

as the reader should verify.

We can now write down a formula for the *spectral energy density*,  $\rho_\omega$ —that is, the amount of energy per unit volume, per unit frequency range. We simply need to multiply the number of modes per unit frequency range by the mean energy of any given mode, and divide by the volume of the box:

$$\rho_\omega = \frac{2g_\omega \bar{E}}{V} = \frac{\hbar\omega^3}{\pi^2 c^3} \left( \frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right). \quad (15)$$

This is the famous **Planck distribution law** first obtained by Max Planck, except that we have an extra term in the bracket, equal to  $1/2$ . This term comes from the  $1/2$  in eqn (13). It is the energy associated with ‘zero point motion’. This is just another way of saying that it is an energy that is present even when the field is in its ground state. Since the zero point energy is fixed for any given system, it does not affect the thermal behaviour and for many purposes it can be dropped by arguing that it amounts to a shift in the position of the zero potential energy, and therefore has no physical significance. We shall do that here, and thus obtain

$$\rho_\omega = \frac{2g_\omega \bar{E}}{V} = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\beta\hbar\omega} - 1} \quad (16)$$

which is the standard form of the Planck law, and which has been verified experimentally to high accuracy.

This is a good moment to mention that the Planck law only applies at high temperature for any given cavity of fixed size. This is because in order to obtain it we have treated the modes by using a continuous density of states function. But in fact the modes are discrete (in a cavity of finite size). The condition for the continuous approximation to be valid is

$$k_{\text{B}}T \gg \hbar\Delta\omega$$

where  $\Delta\omega = c\Delta k$  is the typical gap between the mode frequencies. So for a cavity of diameter  $L$  we require

$$k_{\text{B}}T \gg \frac{\hbar c}{L}$$

in order for the Planck distribution to be valid. (This limit is about 1 kelvin for a cavity of size 1 centimetre.)

(Note also that when summed over all frequencies, the zero point energy in (15) is large: it diverges if we extend the sum to arbitrarily high frequencies. It is an open question whether or not this energy has any observable physical consequences. In some versions of quantum gravity theory it contributes to gravitation of the vacuum, but it is not yet clear whether this is correct. Its presence is also suggested by an effect called the Casimir effect, but in that case the effect can be calculated in more than one way, and does not necessarily require an interpretation in terms of zero point energy of the vacuum.)

## 2.2 Thermal radiation, method 2: a gas of photons

I reiterate: the above, fully correct, treatment of thermal radiation has no need to mention photons or indistinguishability. It models the electromagnetic field in precisely the correct way, according to our best knowledge of electromagnetism, namely quantum electrodynamics. However, it is interesting to note that many of the properties of the electromagnetic field can be captured by thinking of it as a collection of particles called photons. The basic idea is that when a given field mode is in its  $n$ 'th state, we say there are ‘ $n$  photons present’ at that frequency, polarization and direction of travel. This photon idea has persisted because it elucidates many issues surrounding the interaction of the field with other things such as electrons. However, it also introduces some awkwardness when it comes to counting states.

To apply the photon idea to thermal radiation, we model the radiation as a gas of massless Bosons (namely, photons). These photons are indistinguishable particles, and therefore in

thermal equilibrium they do not follow Boltzmann statistics. Instead, if there is a quantum state of energy  $\epsilon$  available to the photons, then the mean number of photons in that state, in conditions of thermal equilibrium, is

$$\bar{n} = \frac{1}{e^{\beta(\epsilon-\mu)} - 1} \quad (17)$$

where  $\mu$  is the chemical potential. This is the **Bose-Einstein distribution function** and by quoting it we have accomplished in one step—or, depending on your point of view, swept under the carpet—a large part of the calculation of the Planck distribution law.<sup>2</sup>

Next we argue that when the particle number is not conserved we have the case  $\mu = 0$ , and this is what happens for photons. This is a non-trivial statement which needs to be justified. It can be justified either by a thermodynamic or a statistical argument. The thermodynamic argument first obtains the equation of state (using  $p = u/3$ ) and from this the Gibbs function, and one finds  $G = 0$ . But  $G = \mu N$  so we must have  $\mu = 0$ . The statistical argument involves rehearsing the sequence of steps leading to the Bose-Einstein distribution function, but now omitting any constraint on the particle number. In this case  $\mu$  never arises and one obtains

$$\bar{n} = \frac{1}{e^{\beta\epsilon} - 1}. \quad (18)$$

On reflection, it should not surprise us that  $\mu = 0$  corresponds to an unconstrained particle number because if we regard  $\mu$  as a Lagrange multiplier then the condition  $\mu f = 0$ , where  $f = 0$  expresses a constraint, will imply  $\mu = 0$  if the constraint does not hold.

Next, to get the spectral energy density, we need to combine this statement about mean photon number with a statement about the energy, and a statement about the number of states at each frequency. The energy associated with any given photon of frequency  $\omega$  is  $\epsilon = \hbar\omega$ .

Calculating the number of quantum states available to the photons requires some careful thought. It is very tempting (and it is a widespread practice) simply to state, without further comment, that the number of states per unit frequency range is given by the mode density  $2g_\omega$ . This turns out to be right, but it is not obvious and needs justification. The problem is that we are trying to apply the concepts of single-particle quantum theory to particles (photons) that are not conserved.

To understand the issue, consider the conceptually simpler case of a single conserved particle such as an electron. In that case one can apply Schrödinger's equation, and one finds that, for a particle confined in a box, the available quantum states are indeed the plane waves that we calculated in section 1. At any given time, a given electron will be in one of these states, or a superposition of them, and it will move among states as it interacts occasionally with other systems, such as by collisions with other electrons in a gas at low density. Here the counting of states is straightforward.

When we come to a single photon, however, the counting is much less clear. In a scattering process, one or more photons may be annihilated from one state, and one or

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<sup>2</sup>The Bose-Einstein distribution can be derived either by a Lagrange multiplier method or by applying the methods of statistical mechanics using the grand partition function, allowing that there can be any number of photons in any given quantum state.



more photons may be created in another state, but one cannot meaningfully say that a given photon moves from one state to another. However, if we focus attention on a photon of given energy, and suppose that it is neither created nor destroyed, then we can agree that the number of mutually orthogonal quantum states that such a photon might possibly be in is given by  $2g_\omega$ . To be precise, if we allow a range of energies  $d\epsilon = \hbar d\omega$ , then the number of states available, per photon in that energy range, is  $2g_\omega d\omega$ . Each of those states has a mean occupation given by the Bose-Einstein distribution, eqn (17), so the total spectral energy density in the gas of photons is

$$\rho_\omega = \frac{2g_\omega \hbar \omega \bar{n}}{V} = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{\beta \hbar \omega} - 1} \quad (19)$$

as we found before.

### 2.2.1 Comparing the two approaches

Now let's compare the two methods of calculation: collection of oscillators (field modes) on the one hand, gas of photons on the other.

In the first approach the individual oscillators (field modes) are clearly separate quantum systems, all mutually distinguishable, and it is straightforward to calculate the mean energy of any given oscillator at a given temperature, and we have counted the oscillators correctly. Everything is clear. We do not need the grand canonical ensemble. The canonical ensemble is sufficient and we can calculate everything, including the partition function and all the other properties.

In the second approach we had to quote (or derive) the Bose-Einstein distribution function and then argue in a somewhat hand-waving way about 'states occupied by photons' in order to bring in the density of states  $g_\omega$ . In such language one is adopting the concepts of non-relativistic quantum theory (Schrödinger's equation applied to particle wave-functions) and trying to apply them to particles which are neither conserved nor slow-moving. Really to treat photons you have to adopt relativistic quantum theory, and that means quantum electrodynamics, and that means you are driven back to the first type of calculation after all. So what happens in practice is that people often *say* they regard the thermal radiation as 'a gas of photons' but what they actually do when they calculate the properties is to model it as a collection of distinguishable field modes, i.e. harmonic oscillators.

This is not say that the phrase 'a gas of photons' is wrong. It is just to warn us that the phrase is sometimes misused.

The terminology of 'photon' comes into its own when one considers how the field interacts with other things. It gives up its energy in chunks called quanta, and it is convenient to say that 'a photon was absorbed' or 'a photon was emitted'. The photon idea is therefore useful in many calculations. However, in the present case, in my opinion, the treatment of thermal radiation as a collection of oscillators is clearer. It is very clear what quantum system is under discussion at any one time, such as a single harmonic oscillator, and what its quantum states are. In the photon picture one finds oneself adopting very loose language such as 'different states of a photon' when referring to different modes of the field—when in fact those different modes are *different physical systems*, according to quantum field theory, not different states available to a single physical system. In short, the photon language is in danger of becoming either muddled or convoluted—the second alternative being what happens if one is careful

only to say what is strictly accurate. Note also that when discussing the counting of states in this section, we ignored the fact that the photons are indistinguishable particles. This was acceptable because the exchange symmetry requirements have been taken into account via the Bose-Einstein distribution function. However, the only way to convince oneself of this is to think carefully about the whole method of calculation.

### 3 Complete thermodynamic information

The thermal radiation inside a cavity can be regarded as a simple compressible system: its thermodynamic state can be uniquely specified by supplying the values of two parameters such as pressure and volume. The standard route to obtaining thermodynamic information such as an equation of state or a heat capacity is to find first the partition function, and hence the Helmholtz function (free energy) and other information. However in the case of cavity radiation there is another approach which is also convenient. We argue from internal energy and pressure, as follows.

We can find the energy density, and hence the total internal energy, by integrating the Planck distribution over all frequencies:

$$u = \frac{U}{V} = \frac{\hbar}{\pi^2 c^3} \int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega} - 1} d\omega \quad (20)$$

To perform the integral, use a change of variable to  $x = \beta\hbar\omega$ , which gives

$$u = \frac{k_B^4 T^4}{\pi^2 \hbar^3 c^3} \int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{\pi^2 k_B^4 T^4}{15 \hbar^3 c^3}. \quad (21)$$

It is useful to gather the various fundamental constants together in order to reduce clutter in this expression. This can be done conveniently by introducing the **Stefan-Boltzmann constant**, which is given by

$$\sigma = \frac{\pi^2 k_B^4}{60 \hbar^3 c^2}. \quad (22)$$

Then we have that the total internal energy of a volume  $V$  of cavity radiation at temperature  $T$  is

$$U = \frac{4\sigma}{c} VT^4. \quad (23)$$

Therefore the heat capacity at constant volume is

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{16\sigma}{c} VT^3. \quad (24)$$

To find the equation of state (that is, the equation relating  $T$  to a pair of other state parameters such as  $p$  and  $V$ ), we must return to the statistical analysis of the radiation field. The basic idea is that we can relate pressure to energy density. Any electromagnetic radiation field carries momentum in proportion to its energy, and pressure is force per unit

**Relationship between pressure and energy density.**

Consider first of all a single plane wave incident on the wall of a cavity at angle  $\theta$  to the normal. In time  $\delta t$  a volume  $Ac\delta t \cos\theta$  of such a plane wave is brought up to an area  $A$  on the wall. Therefore the energy brought up is

$$E_1 = Ac\delta t \cos(\theta)u_1$$

where  $u_1$  is the energy density of this particular wave. The momentum brought up is  $E_1/c$ , and the component of this momentum in the direction normal to the wall is

$$p_{1,\perp} = (E_1/c) \cos\theta = A\delta tu_1 \cos^2\theta.$$

In thermal equilibrium, the wall both absorbs this momentum and, in the same time  $\delta t$ , also emits the same amount of radiation in the opposite direction, so that the wall receives a net impulse per unit time of  $2p_{1,\perp}/\delta t$  from this contribution to the radiation field. The pressure is obtained by integrating this force over all the plane-wave components, and dividing by the area  $A$ . To do this, replace  $u_1$  by  $\rho_\omega d\omega$  and integrate over  $\omega$  and over the solid angle of the hemisphere on one side of the wall (i.e. over all of  $\phi$ , and over  $\theta$  values up to  $\pi/2$ ):

$$p = \int_0^{2\pi} \int_0^{\pi/2} 2 \cos^2(\theta) \frac{\sin(\theta)d\theta d\phi}{4\pi} \int_0^\infty \rho_\omega d\omega = \frac{1}{3}u. \quad (26)$$

The function  $\sin(\theta)d\theta d\phi/4\pi$  here gives the proportion of the radiation propagating in each direction since we know the radiation is isotropic. The integral over solid angle gives  $1/3$  and the integral of the spectral energy density gives  $u$ .

area, which is momentum change per unit time per unit area. It is shown in the box that for thermal radiation the pressure and the energy density are directly related to one another:

$$p = \frac{1}{3}u. \quad (25)$$

By combining eqns (25) and (23) we find the equation of state

$$p = \frac{4\sigma}{3c}T^4. \quad (27)$$

Since we now know one heat capacity and the equation of state, we have complete thermodynamic information. For example, the entropy can be obtained from

$$dS = \frac{C_V}{T}dT + \left(\frac{\partial p}{\partial T}\right)_V dV = \frac{16\sigma}{c} \left( VT^2 dT + \frac{1}{3}T^3 dV \right). \quad (28)$$

Upon integrating<sup>3</sup>, this gives

$$S = \frac{16\sigma}{3c}VT^3 + \text{const} \quad (29)$$

<sup>3</sup>To integrate (28), find a function  $f(T, V)$  which has partial derivatives  $(\partial f/\partial T)_V = VT^2$  and  $(\partial f/\partial V)_T = T^3/3$ .

and the constant of integration must be zero so that  $S = 0$  at  $T = 0$ . Notice that all the intensive variables,  $u$ ,  $p$  and  $s = S/V$  can be expressed in terms of temperature alone.

The Helmholtz function is

$$F = U - TS = -\frac{4\sigma}{3c}VT^4 \quad (30)$$

and the Gibbs function is

$$G = F + pV = 0. \quad (31)$$

### 3.0.1 Calculation via partition function

The other way to obtain this thermodynamic information is to go via the partition function, as we already mentioned, but obtaining the partition function in the first place is a little tricky. Here is one way.

First note that the partition function for a simple harmonic oscillator is

$$Z_1 = \frac{1}{1 - e^{-\beta\hbar\omega}},$$

where we have taken the energy levels as  $\epsilon_n = n\hbar\omega$ . That is, we have taken the ground state energy as the zero of energy for this oscillator.

For a system of many such oscillators, each acting independently, the total partition function is

$$Z = \prod_i \frac{1}{1 - e^{-\beta\hbar\omega_i}}. \quad (32)$$

Hence

$$\ln Z = -\sum_i \ln [1 - e^{-\beta\hbar\omega_i}]. \quad (33)$$

The set of values of  $\omega_i$  is here discrete, but we can approximate this sum by an integral as long as the discreteness is small compared to the thermal energy  $k_B T$ , which will be true in the high temperature limit. (We made this same approximation previously when using the density of states functions listed in table 1.) In the high-temperature limit, then, we have

$$\ln Z = -\int_0^\infty g(\omega) \ln [1 - e^{-\beta\hbar\omega}] d\omega \quad (34)$$

$$= -\frac{V}{\pi^2 c^3} \int_0^\infty \omega^2 \ln [1 - e^{-\beta\hbar\omega}] d\omega \quad (35)$$

where we have treated the three-dimensional case, and included the factor 2 for two independent polarization states of each plane-wave mode.

Now let  $x = \beta\hbar\omega$ . Then  $\omega^2 d\omega = (\beta\hbar)^{-3} x^2 dx$  so

$$\ln Z = -\frac{V(k_B T)^3}{(\hbar c)^3} \int_0^\infty x^2 \ln [1 - e^{-x}] dx. \quad (36)$$

**Integration of  $x^2 \ln(1 - \exp(-x))$ .**

Integrate by parts:

$$\int_0^\infty x^2 \ln(1 - \exp(-x)) dx = \left[ \frac{1}{2} x^3 \frac{1}{e^x - 1} \right]_0^\infty - \frac{1}{2} \int_0^\infty \frac{x^3 dx}{e^x - 1}.$$

The square bracket evaluates to zero at both limits. The integral can be evaluated by contour integration, but it is difficult and it is common to simply quote the answer. We shall present a few further remarks.

Introduce  $r = e^{-x}$  and note that

$$\frac{1}{e^x - 1} = \frac{e^{-x}}{1 - e^{-x}} = \frac{r}{1 - r} = r \sum_{n=0}^{\infty} r^n,$$

where we used the expression for the sum of a geometric series (or the Taylor expansion of  $(1 - r)^{-1}$ , which amounts to the same thing). Hence we have

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \int_0^\infty x^3 \sum_{n=0}^{\infty} e^{-(n+1)x} dx = \sum_{n=0}^{\infty} \int_0^\infty x^3 e^{-(n+1)x} dx. \quad (39)$$

(continued in next box ...).

The integral is treated in the box. One finds

$$\ln Z = \frac{\pi^2 V (k_B T)^3}{45 (\hbar c)^3} \quad (37)$$

and therefore

$$F = -k_B T \ln Z = -\frac{\pi^2 V (k_B T)^4}{45 (\hbar c)^3} = -\frac{4\sigma}{3c} V T^4 \quad (38)$$

which agrees with (30).

## 4 The heat capacity of a solid

When heat is supplied to a solid body, at ordinary temperatures most of the energy is stored internally in the form of vibrations of the atomic nuclei in the solid about their equilibrium positions. In any case, the vibrating nuclei form a physical system which can store energy, and we can take an interest in the heat capacity of such a system.

### 4.1 Einstein model

Einstein suggested that the motion of each nucleus might be treated, to first approximation, as independent of the others. As it oscillates about its equilibrium position, each

**Evaluation of integral, continued:**

Eqn. (39) is a sum of easy integrals (e.g. by parts 3 times, or by developing a recurrence relation). The answer is

$$\sum_{n=0}^{\infty} \Gamma(4) \frac{1}{(n+1)^4}.$$

where  $\Gamma$  is the Gamma function. A sum of a given inverse power of integers is known to evaluate to the Riemann zeta function, in the present case at  $z = 4$  (indeed it may be regarded as the definition of that function when evaluated on an integer). So we have

$$\int_0^{\infty} \frac{x^3}{e^x - 1} dx = \Gamma(4)\zeta(4).$$

Finally, we use the fact that both these functions have known values for integer arguments. In the present case  $\Gamma(4) = 3! = 6$  and  $\zeta(4) = \pi^4/90$ . Hence

$$\int \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}.$$

(Here we have avoided the full calculation by quoting  $\zeta(4)$ , which could itself be found by performing the contour integration which we chose to avoid.)

nucleus could be regarded as a three-dimensional harmonic oscillator with natural frequencies  $\omega_x, \omega_y, \omega_z$ . It is reasonable to assume the same frequencies for all the nuclei if the solid is crystalline. We will also assume  $\omega_x = \omega_y = \omega_z \equiv \omega$ , which is reasonable if the solid has equal compressibility in all directions; in any case this simple assumption is a suitable starting point. In this model, if there are  $N$  atoms in the solid then there are a total of  $3N$  1-dimensional harmonic oscillators, all acting independently and all having the same vibrational frequency (since each 3-dimensional oscillator can be thought of as three 1-dimensional oscillators). In thermal equilibrium the mean energy of each oscillator is given by eqn (14), so the total internal energy of the solid is

$$U = 3N\hbar\omega \left( \frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right) \quad (40)$$

and the heat capacity is

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \left( \frac{\partial U}{\partial T} \right)_\omega = 3Nk_B \frac{x^2 e^x}{(e^x - 1)^2} \quad (41)$$

where  $x = \hbar\omega/k_B T$  and we used that at constant volume the lattice has a fixed layout so the vibrational frequency  $\omega$  remains constant.

This model gives a sensible result, with  $C_V \rightarrow 0$  as  $T \rightarrow 0$ , and  $C_V \simeq 3Nk_B$  when  $k_B T \gg \hbar\omega$ . However, it is a rather crude model and cannot be expected to match experimental observations very accurately. In particular, at low but non-zero temperatures, the Einstein model greatly underestimates the heat capacity.

## 4.2 Debye model

*In university physics courses the Einstein model is often treated in year 2 (with appropriate cautions about its degree of validity), and then the Debye model may be treated in year 3.*

Debye improved the treatment substantially, by a nice idea which, with hindsight, seems very natural. Instead of treating the nuclei independently, regard the lattice as a system of coupled masses with a set of normal modes of oscillation. These normal modes are none other than the modes we already discussed in section 1, but now instead of electromagnetic waves, or de Broglie waves, they are modes of oscillation of a collection of coupled masses, with forces between them satisfying Hooke's law. So we model the solid not as a collection of harmonic oscillators all at the same frequency, but as a collection of harmonic oscillators at different frequencies—the frequencies of the normal modes. These frequencies lie on a spectrum from zero to some maximum. There is a cut-off or maximum frequency because there is a finite number of different normal modes of oscillation for a lattice of point-like masses, as we now show.

For electromagnetic waves in a cavity, all frequencies are in principle possible and represent different physical conditions, so different states of the system. For the modes of vibration of a lattice of point-like masses, this is not true. The reason is that when the waves are sampled at a discrete set of points (namely, the equilibrium positions of the atomic nuclei), a mode of short enough wavelength is not a new solution, but is completely equivalent to a mode of longer wavelength.

To make this idea precise, consider modes of a one-dimensional chain of atoms first of all. Let  $z_n$  be the displacement from its equilibrium position of the  $n$ 'th nucleus. In a mode of wavevector  $k = 2\pi/\lambda$  the displacements are given by

$$z_n(k) = Ae^{i(kx_n - \omega t)} = Ae^{i(kna - \omega t)} \quad (42)$$

where  $a$  is the lattice spacing and  $A$  is the amplitude of the oscillation. Now consider the mode of wavevector  $k' = k + 2\pi/a$ :

$$z_n(k + 2\pi/a) = Ae^{i((k+2\pi/a)na - \omega t)} = Ae^{i(kna - \omega t)} e^{i2\pi n} = z_n(k) \quad (43)$$

since  $e^{i2\pi n} = 1$ . It follows that when we count the modes, starting from  $k = 0$ , then  $k = \Delta k$ , then  $k = 2\Delta k$ , etc. (with  $\Delta k$  given by eqn (4)), then we shall find a total of  $L/a$  modes until we start repeating at  $k = 2\pi/a$ . But  $L = Na$  so the number of different modes is equal to the number of atoms  $N$  in the chain. You can think of these modes as having wavevectors in the range 0 to  $2\pi/a$ , or, equivalently (and slightly more intuitively), in the range  $-\pi/a$  to  $\pi/a$ . The maximum frequency in this case is the frequency of the mode at  $k = \pi/a$  (since the dispersion relation is typically monotonic for  $0 < k < \pi/a$ ).

Note that the normal mode of shortest wavelength is the one at  $k = \pi/a$ , hence a wavelength  $\lambda = 2a$ , when neighbouring atoms oscillate in antiphase.

In two and three dimensions, similar considerations apply. One finds that if there are  $N$  atoms in a crystalline lattice, then there are  $3N$  different normal modes of vibration in total. The maximum frequency is typically obtained for the highest values of  $|k_x|, |k_y|, |k_z|$  that are not equivalent to some lower value. These are the modes for which neighbouring atoms oscillate in antiphase.

Having counted the normal modes, the rest of Debye's model consists in making the simplest possible reasonable assumptions about the mode frequencies and the density of

states. In a real crystal these frequencies are a complicated function of all three wavevector components, but a reasonable approximation at low frequencies is the linear relationship

$$\omega = v_\sigma k. \quad (44)$$

where  $v_\sigma$  is a constant and  $\sigma$  indicates the polarization (i.e. the direction of oscillation of the wave, relative to its direction of propagation). In other words, we assume the dispersion relation is linear, and isotropic with respect to direction of propagation. The constant  $v_\sigma$  is obviously the phase velocity of the waves, and it is called the speed of sound. Typically  $v_\sigma$  has a higher value for longitudinal oscillation (waves of compression) than for transverse oscillation, but the two directions of transverse oscillation have very similar velocities. We will refer to the longitudinal phase velocity as  $v_\parallel$  and the transverse phase velocity as  $v_\perp$ .

In the first instance we will make the further simplification  $v_\parallel = v_\perp \equiv v$ , but it will turn out that retaining the two different velocities does not greatly complicate the calculation and we will present that refinement as we go along.

With a linear dispersion relation, and a known set of normal mode wave vectors, we can calculate the density of states. It will be the same as the one for electromagnetic waves in 3 dimensions given in table 1, except with  $c$  replaced by  $v_\perp$  or  $v_\parallel$ , and we must add the various possibilities:

$$g(\omega) = \frac{V}{2\pi^2} \left( \frac{1}{v_\perp^3} + \frac{2}{v_\parallel^3} \right) \omega^2 \simeq \frac{3V}{2\pi^2 v^3} \omega^2. \quad (45)$$

Owing to the fact that the modes at high enough ( $|k_x|, |k_y|, |k_z|$ ) are in fact equivalent to modes at lower ( $|k_x|, |k_y|, |k_z|$ ), this dispersion relation cannot in fact be reliable for the higher frequency modes. However, since we will in any case only be using it up to some maximum frequency, this does not introduce too much inaccuracy. What we need to do next is decide what the appropriate choice of the frequency cut-off should be. Debye's idea is to set the cut-off *not* at the highest frequency mode that the lattice can in fact support, but rather at such a frequency that the total number of modes, in the simplified model under consideration, matches the correct total number,  $3N$ . This will guarantee that the model produces the correct behaviour at high temperatures, when the heat capacity should be  $3Nk_B$  (from the Equipartition Theorem). In other words, we define the cutoff  $\omega_D$  by

$$\int_0^{\omega_D} g(\omega) d\omega = 3N \quad (46)$$

which gives

$$\omega_D = \left( \frac{6\pi^2 N v^3}{V} \right)^{1/3}. \quad (47)$$

Notice that, in terms of  $\omega$  and  $\omega_D$ , the density of states can be written

$$g(\omega) = \frac{9N}{\omega_D^3} \omega^2. \quad (48)$$

In fact, merely by assuming that  $g \propto \omega^2$  and that its integral up to  $\omega_D$  is  $3N$ , one could write down this form without needing to go via the expression in terms of volume and speed



of sound. If we now allow that the speed of sound is different for different polarizations, then eqn (48) does not change, but eqn (47) is refined to the slightly more accurate expression

$$\omega_D = \left( \frac{18\pi^2 N}{V(v_{\parallel}^{-3} + v_{\perp}^{-3})} \right)^{1/3} \quad (49)$$

(this is obtained by substituting  $3/v^3 = 1/v_{\parallel}^3 + 2/v_{\perp}^3$  in eqn (47)).

We can now calculate the total energy of the vibrations, by combining eqn (48) with eqn (14) for the mean energy of a harmonic oscillator in thermal equilibrium:

$$\begin{aligned} U &= \int_0^{\omega_D} \bar{E}g(\omega) d\omega = \frac{9N\hbar}{\omega_D^3} \int_0^{\omega_D} \omega^3 \left( \frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right) d\omega \\ &= \frac{9N}{8} \hbar\omega_D + \frac{9N\hbar}{\omega_D^3} \int_0^{\omega_D} \frac{\omega^3}{e^{\beta\hbar\omega} - 1} d\omega. \end{aligned} \quad (50)$$

The first term is independent of temperature (it is zero point energy), so the heat capacity is given by the derivative of the second term. Differentiating under the integral sign with respect to  $T$ , we have

$$C_V = \frac{9Nk_B\hbar^2\beta^2}{\omega_D^3} \int_0^{\omega_D} \frac{\omega^4 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} d\omega. \quad (51)$$

The integral cannot be evaluated analytically for arbitrary  $\omega_D$ , but it is useful to convert it into a standard form by the change of variable  $x = \beta\hbar\omega$ , giving

$$C_V = \frac{9Nk_B}{x_D^3} \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx. \quad (52)$$

Thus the Debye heat capacity is  $Nk_B$  multiplied by a function of  $x_D$  alone. It is a universal function, in which one lattice is distinguished from another only by the value of its Debye frequency. Writing  $x_D = \theta_D/T$ , where  $\theta_D \equiv \hbar\omega_D/k_B$  is called the Debye temperature, we see that the molar heat capacity is a function of  $T/\theta_D$  alone. This function can be tabulated, and it is plotted in figure ???. The Debye theory matches experimental observations very well at low temperatures, and does a reasonable job at all temperatures.

The integrand in eqn (52) can be written

$$\frac{x^4 e^x}{(e^x - 1)(e^x - 1)} = \frac{x^4}{(e^x - 1)(1 - e^{-x})} = \frac{x^4}{2(\cosh x - 1)}.$$

At high temperature, ( $T \gg \theta_D$ ,  $x_D \ll 1$ ) we have  $e^x - 1 \simeq x + x^2/2$  and  $1 - e^{-x} \simeq x - x^2/2$  so

$$C_V \simeq \frac{9Nk_B}{x_D^2} \int_0^{x_D} \frac{x^4}{x^2} dx = 3Nk_B, \quad (53)$$

as expected for a set of  $3N$  harmonic oscillators.

When  $x$  is large the integrand tends to  $x^4 e^{-x}$  and this tends rapidly to zero for large  $x$ . Therefore, at low temperature ( $T \ll \theta_D$ ,  $x_D \gg 1$ ) the integrand is very small at  $x \geq x_D$  and

the range of integration can be extended to infinity without affecting the result substantially. Hence the prediction at low temperatures is

$$C_V \simeq \frac{9Nk_B}{x_D^3} \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} dx = \frac{12\pi^4}{5} Nk_B \left( \frac{T}{\theta_D} \right)^3 \quad (54)$$

(since the integral evaluates to  $4\pi^4/15$ ).

The  $T^3$  prediction of eqn (54) is well obeyed in practice. This is because Debye's model becomes more and more accurate at low temperatures, where the linear approximation to the dispersion relation is more and more accurate. Of course eventually, at some temperature, it is no longer appropriate to use a continuous function for the density of states, as we have been doing, but one must take into account the discrete nature of the allowed values of  $\omega$ . However for a crystal of length 1 cm, the longest wavelength modes have  $\lambda \simeq 1$  cm and therefore an angular frequency  $\omega \simeq 10^6$  s<sup>-1</sup> (taking the speed of sound in the solid to be around a few thousand metres per second). Therefore the discreteness of the mode frequencies only affects  $g(\omega)$  significantly at temperatures around  $\hbar\omega/k_B \simeq 10$   $\mu$ K.

The cubic dependence of  $C_V$  on temperature, at low temperatures, can be understood as follows. Recall that figure ?? shows the heat capacity as a function of temperature in the Einstein theory, and this is essentially the heat capacity of a single harmonic oscillator, simply multiplied by  $3N$ . Notice that this capacity has an overall form which tends to zero very rapidly once the temperature is less than about one tenth of  $\hbar\omega/k_B$ , whereas it approaches one unit of  $k_B$  (for each oscillator) quite closely once the temperature rises above  $\hbar\omega/k_B$ . This means that, in the Debye model, all the normal modes whose frequency is below  $k_B T/\hbar$  contribute about one unit of  $k_B$  to the heat capacity, while all those with frequencies above  $10k_B T/\hbar$  do not contribute significantly. The higher frequency modes are 'frozen out' because they have little thermal excitation. Therefore to estimate the heat capacity we need to count the number of modes with  $\omega \lesssim 3k_B T/\hbar$  and assign one unit of  $k_B$  to each such mode:

$$C_V \simeq k_B \int_0^{3k_B T/\hbar} g(\omega) d\omega = \frac{9Nk_B}{\omega_D^3} \int_0^{3k_B T/\hbar} \omega^2 d\omega = 81Nk_B \left( \frac{T}{\theta_D} \right)^3. \quad (55)$$

This answer is roughly right, but the most important feature is that it suggests the  $T^3$  dependence is largely owing to the fact that the number of modes up to a given frequency increases as  $\omega^3$  in a three-dimensional lattice with linear dispersion.