

# Thermal physics involving waves in a box

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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.

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.

## 1 Modes and density of states

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

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

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

$$N = \frac{k}{\Delta k} = \frac{L}{\pi} k. \tag{2}$$

The number per unit change in  $k$  is therefore

**one dimension**

$$\frac{dN}{dk} = \frac{L}{\pi}. \quad (3)$$

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

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

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

**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

$$\omega = kc, \tag{10}$$

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

$$\hbar\omega = \frac{\hbar^2 k^2}{2m}, \tag{11}$$

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:

$$\omega \simeq kv \tag{12}$$

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 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

	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.

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

$$k_B T \gg \hbar\Delta\omega$$

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

$$k_{\text{B}}T \gg \frac{hc}{L}$$

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

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

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

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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.

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 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 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

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

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

**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  $u$ .

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

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

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).

**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 ...).

**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.)