Chapter 11. Boltzmann Statistics

The Boltzmann probability distribution that was introduced in Chapter 10 has many applications that describe everyday physical phenomena. These include some of the thermodynamic principles such as the Equipartition Theorem, and why vibrations don't account towards degrees of freedom in the same. Here, we will use the Boltzmann distribution to describe the lightbulb, specifically the white light spectrum and how energy efficient they are (hint: they are not energy efficient). Also we will study the heat capacity of solids, insights into which led to the development of quantum theory.

11.1 The Black body Radiator. We will begin with exploring the marvelous complexity of the wonder of nature known as the lightbulb. There are some technicalities that must be employed, which is why this derivation is generally referred to as the "black body radiator" problem. This means that we are describing an object that is hot, and self-contained like an empty box. The interior is perfectly black, causes any photons that come into existence to be re-absorbed. The fact that light photons, which have an energy $hv = \frac{hc}{\lambda}$ (where h is Planck's constant 6.626×10^{-34} J·s, v is the frequency of light, c is the speed of light and λ is the wavelength), do not escape results in the system maintaining thermal equilibrium. This is sensible because, if the photons got out, the box would cool. Nonetheless, we do have to drill a small hole into the side to see what is going on, which means that we measure the number and wavelengths of all the photons inside of it as shown in Figure 11.1A. The best way to measure emission is to record the spectrum, which would vary with the equilibrium temperature as shown in Figure 11.1.B. What is interesting is how the intensity at first rises with decreasing wavelength (increasing energy), maximizes and then rapidly falls off. Also, the spectrum of a ~5000K black body is nearly identical to the sun. This gives us a hint about the first step of our approach, which is that we must think about what kinds of wavelengths of photons fit inside the black body box to begin with.



Figure 11.1. A. An incandescent light bulb can be described by the emission of a hot, completely self-absorptive black box. **B.** Emission specra of a black box radiator as a function of temperature. At ~5000K the emission is "white light" and bears many similarities with the solar spectrum.



Figure 11.2. A. Light waves can fit in the black box over multiple wavelengths as a function of λ =2L/n (n=0,1,2,...), where n is the net mode number. **B.** There is a "mode" for every dimension.

11.1.1 Wavelength. Shown in Figure 11.2A are some representations about how light might fit inside the box of length L, which serves to dictate the wavelength of the box. These are the first four "allowed" wavelengths in the x-direction, and note how Figure 11.2.B shows that there are three directions since the Universe is three dimensional. Looking back to Figure 11.2.A we see that the first allowed photon has an infinite wavelength. While this seems odd, it is ok due to a sort of technicality because it has no energy and thus doesn't actually exist. It "counts" because there can be non-zero wavelengths components in the y- or z- directions; this will be more clear later on. Next, we see that the next allowed wavelength has λ =2L, then L, followed by 2L/3, which clearly reveals the empirical relationship:

$$\lambda = \frac{2L}{n_x}$$
, $n_x = 1, 2, 3 ...$

where n_x is called the "mode number", which represents the #nodes-1 of the confined radiation. As you can see, increasing the mode number shortens the wavelength and raises the energy of the photon. There are mode numbers in the y- and z- directions, which can form a set { n_x , n_y , n_z } sort of like a vector. For example, we can describe the highest energy photon in Figure 11.2A as {3,0,0} since there are no components of the wavelength in the y- and z- directions. There can be, as you can have mode number sets such as {3,1,1} etc.

Now that we have a relationship that defines the wavelengths, we can determine a mathematical function to represent them, which is proposed to be:

$$E(x, y, z) = \sin\left(\frac{n_x \pi}{L} \cdot x\right) \cdot \sin\left(\frac{n_y \pi}{L} \cdot y\right) \cdot \sin\left(\frac{n_z \pi}{L} \cdot z\right)$$

where E is the electric field of the photons. You can verify that these are the proper representation for the waves that have corresponding mode numbers such as those shown in Figure 112.

At this point in your academic career you should be aware that a photon is an oscillating electric and magnetic fields. The ability of light's electric component to perturb objects and impart force is significantly greater than the magnetic field, so we usually don't need to describe the magnetic properties of light. Regardless, the fact that electromagnetism has entered the discussion means that we now need to examine whether our relationship conforms to Maxwell's Equations, which are laws that govern all electromagnetism phenomena including light itself. As it applies here, what happens is that when we apply Gauss's Law to the equation, we can derive , which is known as the wave equation.

$$\left\{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z}\right\} E(x, y, z, t) = \frac{-1}{c^2} \frac{\partial^2}{\partial t^2} E(x, y, z, t)$$

When we insert our relationship we find:

$$E(y, z, t)\frac{\partial^2}{\partial x^2}\sin\left(\frac{n_x\pi}{L} \cdot x\right) + E(x, z, t)\frac{\partial^2}{\partial y^2}\sin\left(\frac{n_y\pi}{L} \cdot y\right) + E(x, y, t)\frac{\partial^2}{\partial z}\sin\left(\frac{n_z\pi}{L} \cdot z\right) = E(x, y, z)\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\sin\left(\frac{2\pi c}{\lambda} \cdot t\right)$$

We can evaluate terms such as:

$$E(y, z, t) \frac{\partial^2}{\partial x^2} \sin\left(\frac{n_x \pi}{L} \cdot x\right) = -\frac{n_x^2 \pi^2}{L^2} E(x, y, z, t)$$

Which makes:

$$E(x, y, z, t) \left\{ \frac{n_x^2 \pi^2}{L^2} + \frac{n_y^2 \pi^2}{L^2} + \frac{n_z^2 \pi^2}{L^2} \right\} = E(x, y, z, t) \frac{4\pi^2}{\lambda^2}$$

The equation for the electric field can be divided out on the left and right sides leaving:

$$\frac{\pi^2}{L^2} \left(n_x^2 + n_y^2 + n_z^2 \right) = \frac{4\pi^2}{\lambda^2}$$

If we simply treat the mode set like a vector, which has a net value:

$$n^2 = n_x^2 + n_y^2 + n_z^2$$

then the above simplifies to:

$$\lambda^2 = \frac{4L^2}{n^2} \text{ or } \lambda = \frac{2L}{n}$$

One important aspect of this result is that it demonstrates that mathematical models can tell us more than what the model is.

11.1.2 Mode Degeneracy. We now can relate the wavelengths that fit inside the box to the net mode number n. These values are discrete, since n is composed of a combination of whole numbers as shown in Table 11.1. To visualize, we can think of the spectrum of emission as being composed of posts that can accommodate a stack disks; each post is positioned to represent an allowed wavelength, and the disks are photons that reside at those wavelengths. Technically, each post can hold one disk, and each disk represents two photons since light comes right and left circularly polarized form. This idea is

n ² =	$\{n_x, n_y, n_z\}$	Number of sets
$n_x^2 + n_y^2 + n_z^2$		(degeneracy)
1	{1,0,0},{0,1,0},{0,0,1}	3
2	{1,1,0},{0,1,1},{1,0,1}	3
3	{1,1,1}	1
4	{2,0,0},{0,2,0},{0,0,2}	3
5	$\{0,1,2\},\{0,2,1\},\{1,0,2\},$	6
	$\{2,0,1\},\{1,2,0\},\{2,1,0\}$	
6	{1,1,2},{1,2,1},{2,1,1}	3
7	No examples	-
8	{2,2,0},{0,2,2},{2,0,2}	3
9	{1,2,2},{2,1,2},{2,2,1},	6
	{0,0,3},{0,3,0},{3,0,0}	
10	{0,1,3},{0,3,1},{1,0,3},	6
	{3,0,1},{1,3,0},{3,1,0}	
:		• • •
10,800	{60,60,60},{20,76,68},	28
:		
24,300	{90,90,90},	91

Table 11.1. How net mode numbers n^2 can be composed of multiple whole number $\{n_x, n_y, n_z\}$ sets. $n_z\}$ that given = 1; they are $\{1,0,0\}, \{0,1,0\}$ and $\{0,0,1\}$. Likewise a mode number of $n = \sqrt{2}$ can also come about from three sets, $\{1,0,1\}, \{1,1,0\}$ and $\{0,1,1\}$. However, $n = \sqrt{3}$ can only come about from $\{1,1,1\}$, and there is no combination of whole mode numbers that provide $n = \sqrt{7}$.

The reason that the emission spectrum initially rises with decreasing wavelength as seen in Figure 11.1B is because of how the number of sets that yield the same net mode number is generally increasing as seen in Table 11.1 and Figure 11.3. Since the net mode number corresponds to a specific wavelength and thus energy of light, the number of sets is the degeneracy of the energy state. Now our purpose here is to generate a



Figure 11.3. The box wavelengths can be viewed as posts that photons are stacked upon. The trend is upward as the net mode number "n" increases. The solid line is the analytical result for a 1 cm³ box, and is proportional to λ -4.



Figure 11.4 A. There is no simple relationship between the number of modes {nx, ny} and the corresponding net mode number n. **B.** Each unique set of mode numbers {nx,ny} can be associated with an area of 1, due to the fact that the point resides on a 1×1 area. **C.** Since the number of modes is the same as the area, the degeneracy can be calculated from the area of a quarder disk of radius n.

relationship between the net mode number and the degeneracy.

Unfortunately, as can be seen in Table 11.1 there isn't a simple formula that can take n or n² as an input and generate the degeneracy as the output. This can be visualized in 2D as shown in Figure 11.4, where we represent n as the radius of a circle on a graph of n_y vs. n_x . Each red cross represents distinct mode set, but we can see that a semi-circle of radius n doesn't cross many of them. In fact, it doesn't seem clear that there is a simple formula that relates the net mode number n to the number of nearby modes. However, as shown in Figure 11.4B, any particular point $\{n_x, n_y\}$ is offset from every other point by $\Delta n_x = \pm 1$ and/or $\Delta n_y = \pm 1$. As a result, we can say that each mode number occupies an area on the graph of $1^2 = 1$. Since one point occupies an area of 1, we now have a way to count up mode sets as a function of the net mode number n. This is easy because n looks just like a radius when plotted against n_x and n_y as in Figure 11.4C, and we can define an area associated with n using a quarter disk with a thickness of ∂n . Hence the degeneracy for the 2D system can be calculated via the area of a quarter disk, which is the circumference times the thickness:

2D degeneracy(n) =
$$\left(\frac{1}{4}\right) 2\pi n \cdot \partial n$$

Of course, we live in three dimensions. Since $1^3 = 1$, we can imagine that the 3D degeneracy can be calculated by volume. In fact, if the number of degeneracies in 2D is $1/4^{\text{th}}$ the area of a disk, then for 3D the degeneracy is $1/8^{\text{th}}$ the volume of a shell:

3D degeneracy(n) =
$$\left(\frac{1}{8}\right) 4\pi n^2 \cdot \partial n$$

where the shell volume is the surface area of a sphere $(4\pi n^2)$ times the shell's thickness ∂n . To make further progress we have to remove the mode number n and insert λ , since spectrometers report on

wavelength. Earlier, when we applied Maxwell's equations to the equation for the electric field of light we found that: $\lambda^2 = \frac{4L^2}{n^2}$ and therefore $n^2 = \frac{4L^2}{\lambda^2}$. Making this substitution into the above reveals:

3D degeneracy(n) =
$$\left(\frac{1}{8}\right) 4\pi \frac{4L^2}{\lambda^2} \cdot \partial n = \frac{2\pi L^2}{\lambda^2} \cdot \partial n$$

Two more problems; we have to multiply the above by 2 to represent the fact that light has both left and right circularly polarized forms. Also, we have to convert ∂n to $\partial \lambda$ using a Jacobian: $\partial n \rightarrow \left| \frac{\partial n}{\partial \lambda} \right| \partial \lambda$:

3D degeneracy(
$$\lambda$$
) = 2 × $\frac{2\pi L^2}{\lambda^2} \cdot \left| \frac{\partial n}{\partial \lambda} \right| \partial \lambda = \frac{4\pi L^2}{\lambda^2} \left| \frac{\partial \frac{2L}{\lambda}}{\partial \lambda} \right| \partial \lambda = \frac{8\pi L^3}{\lambda^4} \partial \lambda$

This is the analytical result plotted in Figure 11.3. Ultimately, we see that shorter wavelength photons "fit" into the black box better and thus have more degeneracies, which increases the light output from a bulb as seen in Figure 11.1.B. However, if the wavelength becomes too short then the intensity of light drops off, which is to say that there appears to be some sort of high energy cutoff. This suggests that the Boltzmann equation plays a role, since nature doesn't partition out energy into things if that energy is greater than k_BT .

11.1.3 Total Energy. Now that we have an expression for the degeneracy of light modes in the black body radiator, we can now calculate the total energy from a lightbulb using:

Total Energy =
$$\sum_{\lambda}$$
 degeneracy(λ) · (energy(λ))

Here we see that we need to calculate the average energy of the lightbulb's mode as a function of the mode's wavelength, $\langle \text{energy}(\lambda) \rangle$. We are already well aware that the energy of a photon is $\frac{\mathbf{h}\cdot\mathbf{c}}{\lambda}$, and with this we can apply the Boltzmann equation to calculate the average. A subtlety is revealed at this pointhow is the energy of the photon dialed up or down to conform to the Boltzmann equation? Afterall, to calculate the energy at a defined wavelength using $\frac{\mathbf{h}\cdot\mathbf{c}}{\lambda}$, everything is a constant (h is the Plank constant, 6.626×10^{-34} J·s, and c is the speed of light)! It turns out that the Boltzmann formula is satisfied by varying the *number* of photons, to which we now use in the equation:

$$P\left(\frac{j \cdot h \cdot c}{\lambda}\right) = \frac{e^{-Energy}/_{k \cdot T}}{\sum e^{-Energy}/_{k \cdot T}} = \frac{e^{-j \cdot h \cdot c}/_{\lambda \cdot k_B T}}{\sum_{i=0}^{\infty} e^{-i \cdot h \cdot c}/_{\lambda \cdot k_B T}}$$

where $P\left(\frac{j\cdot h\cdot c}{\lambda}\right)$ is the probability density for having j photons of wavelength λ given temperature T. First thing we do is to solve the normalizer (i.e. the denominator), $\sum_{i=0}^{\infty} e^{-i\cdot h\cdot c} \lambda k_B T$. The summation reflects

the fact that Nature can dictate that there are as little as 0 photons and as many as ∞ . To solve this part, we can use the following identity:

$$\sum_{i=0}^{\infty} a^{i} = \frac{1}{(1-a)}; i = 0,1,2,3 ...$$

This works because the number of photons is discrete, i.e. there can only be whole numbers (0, 1, 2, 3, ...) of them. Applying the identity means: $a = e^{-h \cdot c} / \lambda \cdot k_B T$, which makes:

$$\sum_{i=0}^{\infty} e^{-i \cdot h \cdot c /_{\lambda \cdot k_B T}} = \frac{1}{\left(1 - e^{-h \cdot c /_{\lambda \cdot k_B T}}\right)}$$

Now we can try to deal with the average energy via:

$$\langle energy \rangle = \sum energy \cdot Boltzmann \ distribution = \sum_{j=0}^{\infty} \left(\frac{j \cdot h \cdot c}{\lambda}\right) \cdot \left(1 - e^{-h \cdot c/\lambda \cdot k_B T}\right) e^{-j \cdot h \cdot c/\lambda \cdot k_B T}$$
where: $\left(\frac{j \cdot h \cdot c}{\lambda}\right)$ is the energy of a j number of λ -wavelength photons and: $\left(1 - e^{-h \cdot c/\lambda \cdot k_B T}\right) e^{-j \cdot h \cdot c/\lambda \cdot k_B T}$ is the normalized Boltzmann distribution. To solve the expression above we use the following identity:

$$\sum_{i=0}^{\infty} i \cdot a^{i} = \frac{a}{(1-a)^{2}}; \ i = 0, 1, 2, 3 \dots$$

Applying the identity above to $\sum_{j=0}^{\infty} \left(\frac{j \cdot h \cdot c}{\lambda}\right) \cdot e^{-j \cdot h \cdot c} / \lambda \cdot k_B T} \cdot \left(1 - e^{-h \cdot c} / \lambda \cdot k_B T}\right)$, we need to identify the constants: $\frac{h \cdot c}{\lambda} \cdot \left(1 - e^{-h \cdot c} / \lambda \cdot k_B T\right)$ and: $a = e^{-h \cdot c} / \lambda \cdot k_B T$. Thus, the average energy is:

$$\sum_{j=0}^{\infty} \left(\frac{j \cdot h \cdot c}{\lambda} \right) \cdot e^{-j \cdot h \cdot c} /_{\lambda \cdot k_{B}T} \cdot \left(1 - e^{-h \cdot c} /_{\lambda \cdot k_{B}T} \right) = \left(\frac{h \cdot c}{\lambda} \right) \cdot e^{-h \cdot c} /_{\lambda \cdot k_{B}T} \cdot \frac{\left(1 - e^{-h \cdot c} /_{\lambda \cdot k_{B}T} \right)}{\left(1 - e^{-h \cdot c} /_{\lambda \cdot k_{B}T} \right)^{2}}$$

This is:

$$\langle \text{energy} \rangle = \left(\frac{\mathbf{h} \cdot \mathbf{c}}{\lambda}\right) \cdot \frac{e^{-\mathbf{h} \cdot \mathbf{c}} /_{\lambda \cdot \mathbf{k}_{B} T}}{\left(1 - e^{-\mathbf{h} \cdot \mathbf{c}} /_{\lambda \cdot \mathbf{k}_{B} T}\right)}$$

Now we can simplify further by this neat trick of multiplying the top and bottom by $e^{h \cdot c_{\lambda \cdot k_B T}}$:

$$\left(\frac{\mathbf{h}\cdot\mathbf{c}}{\lambda}\right)\cdot\frac{\mathbf{e}^{-\mathbf{h}\cdot\mathbf{c}}_{\lambda\cdot\mathbf{k}_{B}T}}{\left(1-\mathbf{e}^{-\mathbf{h}\cdot\mathbf{c}}_{\lambda\cdot\mathbf{k}_{B}T}\right)}\cdot\frac{\mathbf{e}^{\mathbf{h}\cdot\mathbf{c}}_{\lambda\cdot\mathbf{k}_{B}T}}{\mathbf{e}^{\mathbf{h}\cdot\mathbf{c}}_{\lambda\cdot\mathbf{k}_{B}T}}=\left(\frac{\mathbf{h}\cdot\mathbf{c}}{\lambda}\right)\cdot\frac{\mathbf{e}^{0}}{\left(\mathbf{e}^{\mathbf{h}\cdot\mathbf{c}}_{\lambda\cdot\mathbf{k}_{B}T}-\mathbf{e}^{0}\right)}=\frac{\mathbf{h}\cdot\mathbf{c}}{\lambda\cdot\left(\mathbf{e}^{\mathbf{h}\cdot\mathbf{c}}_{\lambda\cdot\mathbf{k}_{B}T}-1\right)}$$

Done! The average energy of a λ -wavelength photon is:

$$\langle \text{energy}(\lambda) \rangle = \frac{\mathbf{h} \cdot \mathbf{c}}{\lambda \cdot \left(\mathbf{e}^{\mathbf{h} \cdot \mathbf{c}} / \lambda \cdot \mathbf{k}_{\mathrm{B}} \mathbf{T} - 1\right)}$$

This result is plotted in Figure 11.5, where we can see that the average energy rises with increasing wavelength. This is sensible, because if the energy of a photon is on the order of k_BT (or less), Nature allows you to have more of those photons.

We can now finally solve for the total energy output of a lightbulb and calculate the spectrum at the same time. Shown in Figure 11.5 is a representation of the average energy as a stack of discs that correlates to the number of photons. The modes and degeneracies of the blackbody were previously presented as a series of posts to stack the photon discs on. Now we see the reason that a lightbulb's spectrum rises and falls with increasing wavelength. Nature provides the energy to create more photons as the energy per photon drops with increasing wavelength. However, the photons must also reside in blackbody radiator modes, which decrease with increasing wavelength. The result is a rise and fall of intensity, which mimics the spectra shown in Figure 11.1.



Figure 11.5. Stacking photon "disks" onto the allowed wavelength "posts" recreates the spectrum of the blackbody radiator.

Now to create a mathematical representation of the same. First, we return to our original expression for the total energy:

$$\text{Fotal Energy} = \sum_{\lambda} \text{degeneracy}(\lambda) \cdot \langle \text{energy}(\lambda) \rangle$$

Technically, the above result is dependent on the volume of the lightbulb, as a bigger bulb produces more energy. We should instead present the result as the energy density, the total energy divided by the volume, which can be applied to any sized black box radiator:

Energy Density =
$$\frac{\text{Total Energy}}{\text{Volume}} = \frac{1}{L^3} \sum_{\lambda} \text{degeneracy}(\lambda) \cdot \langle \text{energy}(\lambda) \rangle$$

We insert the relationships derived above, and then we can approximate the wavelengths as varying continuously. This allows us to change the sum to an integral; we also do some algebraic cleaning:

Energy Density =
$$\left(\frac{1}{L^3}\right) \int_0^\infty \left(\frac{8\pi L^3}{\lambda^4}\right) \cdot \frac{\mathbf{h} \cdot \mathbf{c}}{\lambda \cdot \left(\mathbf{e}^{\mathbf{h} \cdot \mathbf{c}}/\lambda \cdot \mathbf{k}_B \mathbf{T} - 1\right)} \cdot \partial \lambda = \int_0^\infty \frac{8\pi \cdot \mathbf{h} \cdot \mathbf{c}}{\lambda^5 \cdot \left(\mathbf{e}^{\mathbf{h} \cdot \mathbf{c}}/\lambda \cdot \mathbf{k}_B \mathbf{T} - 1\right)} \cdot \partial \lambda$$

where the expression:

$$\frac{8\pi \cdot h \cdot c}{\lambda^5 \cdot \left(e^{h \cdot c} /_{\lambda \cdot k_B T} - 1\right)}$$

is known as the Planck distribution and is exactly what is plotted in Figure 11.1B. Last, we evaluate the integral above, which unfortunately is rather difficult and requires a bit of sophistication to derive. Regardless, the result is:

$$\frac{8\pi^5(k_BT)^4}{15(h\cdot c)^4}$$

and is known as the Stefan–Boltzmann law.

11.2 Heat Capacity of Solids. In the early 1800's French scientists Pierre Dulong and Alexis Petit noticed that many solid elements had near-identical per molar heat capacities as shown in Figure 11.6. This led to the Dulong–Petit law: $C_m = 3R$. Previously in Ch. 2 we encountered gases with such high heat capacities due to their three translational and three rotational motions, which imparts six degrees of freedom that rendered $C_m = 3R$ due to the equipartition theorem (Table 2.1). While



Figure 11.6. Per molar heat capacity of elements reveal clustering about the value 3R. Data from the CRC and wikipedia.

this is perfectly understandable for a gas, it's hard to reconcile why heavy metallic elements such as lead and a gas such as methane have the same heat capacities. The answer is simple- solids have three (vibrational) potential energy and three kinetic energy degrees of freedom due to their bonding. Thus, the equipartition theorem still appears valid for solids, unless, those solids are cold, in which case something goes terribly wrong as shown in Figure 11.7.

From the data in Figure 11.7 we can see that, at low temperatures, solids of copper and tungsten have almost no heat capacity! And while it rises with temperature to the Dulong-Petit limit, it was quite

the curiosity for many years why this behavior was observed in many materials. In fact, it was one of Albert Einstein's early contributions in 1907 to approximately describe the increase in heat capacity as vibrations in the solid state, called phonons, that behave just like Planck's photons. In this regard, instead of energy being related to the wavelength of light it was due to the frequency of an atomic vibration in the solid state. All one has to do is simply change the definition of average internal energy (U), as derived from the Boltzmann formula, from the Planck to the Einstein form: $\frac{h \cdot c/\lambda}{e^{h \cdot c/\lambda k_BT} - 1} \rightarrow 3N_A \cdot$



Figure 11.7. Temperature dependence of Cp,m of metals reveals a steep rise from 0 to ~3R near room temperature. Data from the CRC and wikipedia. Inset shows solid vibrations called phonons.

 $\frac{\hbar\omega}{e^{\hbar\omega/k_{\rm B}T}-1}$. The prefactor is due to solids existing in 3 dimensions and that a mole has N_A number of atoms, and note that Einstein assumed that all the vibrations inside the solid had the same frequency ω . Since heat capacity is just the derivative of the internal energy with temperature, the result is:

$$C = 3N_{A} \cdot \frac{\partial}{\partial T} \left(\frac{\hbar\omega}{e^{\hbar\omega/k_{B}T} - 1} \right) = 3N_{A} \cdot \frac{-\hbar\omega}{(e^{\hbar\omega/k_{B}T} - 1)^{2}} \frac{\partial e^{\hbar\omega/k_{B}T}}{\partial T} = 3N_{A} \cdot \frac{-\hbar\omega}{(e^{\hbar\omega/k_{B}T} - 1)^{2}} \frac{-\hbar\omega}{k_{B}T^{2}} e^{\hbar\omega/k_{B}T}$$
$$= 3N_{A}k_{B} \left(\frac{\hbar\omega}{k_{B}T} \right)^{2} \frac{e^{\hbar\omega/k_{B}T}}{(e^{\hbar\omega/k_{B}T} - 1)^{2}}$$

This result correctly predicts that, as T \rightarrow 0 K, the heat capacity also \rightarrow 0 J/K/mol. At higher temperatures where: $e^{\hbar\omega/k_BT} \sim 1 + \frac{\hbar\omega}{k_BT}$ we find that:

$$C \sim 3N_A k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{1 + \frac{\hbar\omega}{k_B T}}{\left(\frac{\hbar\omega}{k_B T}\right)^2} \sim 3N_A k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \left(\frac{k_B T}{\hbar\omega}\right)^2 = 3N_A k_B = 3R_A k_$$

All of these results make us believe that Einstein has the correct approach; however, this turns out not to be the case! The problem is that the heat capacity rises exponentially in the Einstein model whereas in reality most materials have a $C_{p,m}$ -T³ behavior. And as shown by Peter Debye in 1912 this was due to Einstein's use of a single frequency for the solid-state vibrations, whereas there are a range of frequencies as shown in the inset of Figure 11.7.



Figure 11.8. Phonons have an upper (Debye) phonon frequency limit as defined by the distance between neighboring atoms. This is because there is no practical difference between the Debye frequency and a shorter wavelength phonon as shown on the bottom.

The solution to address concerning the shortcoming of the Einstein model is to use a range of phonon frequencies to define the internal energy as so:

$$U = \int \text{degeneracy}(\omega) \cdot \langle \text{energy}(\omega) \rangle = \int \text{degeneracy}(\omega) \cdot \frac{\hbar \omega}{e^{\hbar \omega/k_BT} - 1} \partial \omega$$

So as not to labor the point one can show that the degeneracy of phonons as a function of frequency is $\frac{V\omega^2}{2\pi^2 v_s^3}$, where v_s is the speed of sound in the solid. As a result the Debye equation for the heat capacity of a solid is:

$$C = \frac{\partial U}{\partial T} = \frac{\partial}{\partial T} \frac{V\omega^2}{2\pi^2 v_s^3} \int_0^{\omega_D} \frac{V\omega^2}{2\pi^2 v_s^3} \frac{\hbar\omega}{e^{\hbar\omega/k_BT} - 1} \partial\omega \propto T^3$$

While we don't need to worry further about the mathematics of the result, suffice to say the result is proportional to T³ as experimentally observed. It is also interesting to note that the upper limit of the Debye equation isn't infinity as one might expect. This is because Debye realized that there was an upper limit to the range of phonon frequencies as shown in Figure 11.8, which we will call the Debye frequency ω_D . Clearly, there cannot be a frequency higher than allowed by the atomic spacing. In practice, this upper limit is an empirical parameter that can be used to create a fit to experimental data.

Conclusion. The purpose of this chapter was to demonstrate that the Boltzmann formula has uses far beyond that encountered with the Maxwell-Boltzmann description of the velocities of gases. In terms of the development of physical chemistry as a science, it wasn't long after the phenomena of Blackbody radiation and the Debye theory of heat capacity were described that scientists started to make the

connection between matter and waves. This ultimately resulted in quantum theory, which is the subject of the next chapter.

Problems: Numerical

1. a. Write Plank's constant ($h=6.626 \times 10^{-34} \text{ J} \cdot \text{s}$) in units of kg, m, and s.	(2 pts)
b. What are the unit(s) of $c \cdot h/\lambda$?	(2 pts)
c. What are the unit(s) of momentum squared over mass?	(2 pts)
d. What are the unit(s) of Plank's constant squared over mass over length squared?	(2 pts)
2. a. What is the de Broglie wavelength of Donald Trump, a 210 kg man who can	

run 1.0 m/s when chased by a mob at the Capitol? (3 pts)

b. What was the de Broglie wavelength of Secretariat, a 544 kg horse that could run 21.9 m/s? I'm using the past tense because the horse is dead. He's dead.

3. a. What is the de Broglie wavelength of Ted Cruz, a 100 kg man who can run 0.5 m/s when chased by a mob at the Capitol?

b. What was the de Broglie wavelength of Secretariat, a 544 kg horse that could run 21.9 m/s? I'm using the past tense because the horse is dead. He's dead. (3 pts)

4. Let's learn about a new unit- the electron Volt (eV). This is the energy an electron picks up by travelling across two metal plates, one at 0 V and the other at +1.0 V. The electron will accelerate towards the +1.0 V, picking up kinetic energy. Actually, it picks up 1.0 eV of kinetic energy to be exact! (rest mass of an electron is m_0 =9.109 $\times 10^{-31}$ kg and the speed of light is c=3 $\times 10^8$ m/s).

a. If the conversion of J to eV is $1.6 \times 10^{-19} \, \text{(J/}_{eV})$, how fast is an electron going once it passes through a +1.0 V plate? (3 pts)

b. What is interesting is that the mass of an electron is dependent on how fast it is

moving (thanks Einstein!) If the mass of the moving particle is: $m = \left(1 - \frac{v^2}{c^2}\right)^{-1/2}$.

 m_0 , where c is the speed of light and m_0 is the "rest mass" of the electron (9.109×10⁻³¹ kg), does the mass of the 1 eV electron change much? (3 pts)

c. What speed would an electron have to travel to have a mass that is 10% higher than its rest mass? How many eV is that? (7 pts)

Hint: for pt. c if you calculated 44.5 keV you forgot to account for the mass increase.

5. The length between chemical bonds is ~1 Å. To perform diffraction studies on bonds, you would practically need to use a particle with a wavelength that is about $1/100^{\text{th}}$ this value, i.e. 1×10^{-12} m.

a. What speed do you need to make electrons travel at to give them this wavelength such that they can be used in diffraction experiments for elucidating the structure of molecules? *Hint:* $\lambda = \frac{h}{m \cdot v}$. Also the electron rest mass is 9.109 ×10⁻³¹ kg.

(3 pts)



(3 pts)



b. Look really closely at your answer to pt. a, and you will find that there is a major problem with the speed you calculated.What it wrong with it? (2 pts)

c. Now if an electron is travelling 2.77×10^8 m/s (which is less than the speed of light) and the mass increases according to: $m = \left(1 - \frac{v^2}{c^2}\right)^{-1/2} \cdot m_0$, what is the de Broglie wavelength of the particle travelling at this speed? (5 pts)

Problems: Theoretical or Explain in Words

1. The correct equation that Einstein derived for the energy from the theory of relativity is not $E=mc^2$, rather $E^2=p^2 \cdot c^2 + m^2 \cdot c^4$ (m is mass, c is the speed of light).

a. What assumption allows you to say $E=m \cdot c^2$?

b. If energy of light is $E=c\cdot h/\lambda$, can you derive what the momentum of light is, i.e. p = ?

pt. b. hint: photons have no mass, so $E^2 = p^2 \cdot c^2$

2. A complex number is defined as having $\sqrt{-1}$ in it, where we abbreviate $i = \sqrt{-1}$. Hence "3i" is a complex number, and $(3i)^2 = 3^2 \cdot i^2 = -9$. A complex number can generally be expressed as: $z = a + i \cdot b$. Its absolute value |z| is: $|z| = \sqrt{a^2 + b^2}$; it works just like a vector!

Last thing, the complex conjugate of z, which we call z^* , is defined as: $z^* = a - i \cdot b$.

a. Can you prove that, for $z = a + i \cdot b$, then $z^* \cdot z = |z|^2$?

b. Let's make an equivalency between $z = a + i \cdot b$ and $z = |r| \cdot e^{i\phi}$ using the figure provided **axis** here. To answer this question, please define |r| and ϕ using a and b. FYI, the purpose of this question is to make you comfortable with Googling math identities. (3 pts)

c. Please use the FOIL method to evaluate: $z^2 = (a + i \cdot b)^2$.

d. If you had to evaluate z^{50} , which representation of z (i.e., $z = a + i \cdot b$ or $z = |r| \cdot e^{i\phi}$) would you use and why? (3 pts)

3. More math practice. A complex function ψ has "i" in it, and the complex conjugate of ψ is the same thing where every "i" is replaced with "-i". For example, if $\psi(x) = i \cdot \sin(-i \cdot kx)$, then $\psi^*(x) = -i \cdot \sin(i \cdot kx)$. Here is another: $-i^* = -(-i) = i$.

a. If
$$\psi(\phi) = \sin(\phi)$$
, what is $\psi(\phi) \cdot \psi^*(\phi)$? (3 pts)

b. If $\psi(\phi) = e^{i\phi}$, what is $\psi(\phi) \cdot \psi^*(\phi)$? Please simplify the product and provide one answer.

$$(fyi e^a e^b = e^{a+b}) (3 pts)$$

c. If
$$\psi(\phi) = e^{i\phi} \cdot \sin(\phi)$$
, what is $\psi(\phi) \cdot \psi^*(\phi)$? (3 pts)

4. More math practice. A complex function ψ has "i" in it, and the complex conjugate of ψ is the same thing where every "i" is replaced with "-i". For example, if $\psi(x) = i \cdot \sin(-i \cdot kx)$, then $\psi^*(x) = -i \cdot \sin(i \cdot kx)$. You see, everywhere the "i" appeared, we wrote "-i" instead. Here is another: $-i^* = -(-i) = i$.

a. If
$$\psi(\phi) = \cos(\phi)$$
, what is $\psi(\phi) \cdot \psi^*(\phi)$? (3 pts)

b. If $\psi(\phi) = e^{i\phi}$, what is $\psi(\phi) \cdot \psi^*(\phi)$? Please simplify the product and provide one answer.

$$(fyi e^a e^b = e^{a+b})$$
(3 pts)



(2 pts)

(3 pts)

(3 pts)

c. If
$$\psi(\phi) = e^{i\phi} \cdot \cos(\phi)$$
, what is $\psi(\phi) \cdot \psi^*(\phi)$? (3 pts)

5. Even more math practice! Perform the following operations. Oh, I'm sorry I didn't say that right. Perform the following operations please.

a.
$$\frac{\partial}{\partial x} \cdot \frac{\partial}{\partial x} \cdot x \cdot \cos(kx)$$

b. $\frac{\partial}{\partial x} \cdot x \cdot \frac{\partial}{\partial x} \cdot \cos(kx)$
c. $\frac{\partial}{\partial x} \cdot \frac{1}{x} \cdot \frac{\partial}{\partial x} \cdot e^{i \cdot k \cdot x}$ (9 pts)

Hint: Look at some of the identities at the top of the problem set!

6. Even more math practice! Perform the following operations. Oh, I'm sorry I didn't say that right. Perform the following operations please.

a.
$$\frac{\partial}{\partial x} \cdot \frac{\partial}{\partial x} \cdot x \cdot \sin(kx)$$
 b. $\frac{\partial}{\partial x} \cdot x \cdot \frac{\partial}{\partial x} \cdot \sin(kx)$ **c.** $\frac{\partial}{\partial x} \cdot \frac{1}{x} \cdot \frac{\partial}{\partial x} \cdot e^{-i \cdot k \cdot x}$ (9 pts)

7. Light has two "natural" forms- right and left circularly polarized. This comes about because light has angular momentum, specifically $\ell = 1$, where ℓ is the angular momentum quantum state (like how the hydrogen s-state has $\ell = 0$ and p states have $\ell = 1$, remember this?). This is why the selection rule $\Box \ell = \pm 1$ for absorption of light exists (i.e. why s-states absorb light and turn into p-states; this conserves angular momentum!). Here is another fact: if $\ell > 0$, then there are $2\ell + 1$ "sub" quantum states m_{ℓ} that range from: $m_{\ell} = \{-\ell, (-\ell + 1), ..., 0, ..., +\ell\}$ (you learned this in Freshman Chem). For a hydrogen p-state with quantum state $\ell = 1$, you have three $m_{\ell} = \{-1, 0, 1\}$ states, which is where the three p_x , p_y , and p_z orbitals come from!

If light has angular momentum and is in quantum state $\ell = 1$, then there must be three $m_{\ell} = \{-1, 0, +1\}$ states. Actually, there are, but just two of them- specifically, $m_{\ell} = +1$, which is what we call left circularly polarized light, and $m_{\ell} = -1$, which is right circularly polarized light. **But there is no m**_l = 0 state!

Now here is the question- why is that the case? Here are two figures for right and left circularly polarized light that will help you, where you can see how the electric field rotates around the axis of propagation: (5 pts)



Hint: In the $m_{\ell} = 0$ case, the photon rotates by moving forward and backward in line with the direction of propagation.

8. The solution to Ampere's Law in 3D: $\frac{\partial^2 \vec{E}}{\partial x^2} + \frac{\partial^2 \vec{E}}{\partial y^2} + \frac{\partial^2 \vec{E}}{\partial z^2} = \frac{1}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2}$ is: $\vec{E} = f(x) \cdot f(y) \cdot f(z) \cdot f(t)$,

where the time dependent function is: $f(t) = \sin \left(2\pi \cdot c \cdot \frac{t}{\lambda}\right)$

a. What does c t represent? **b.** What are the units of $\mathbf{c} \cdot \frac{\mathbf{t}}{\lambda}$? **c.** Why is there a 2π ?

d. Now, summarize why the argument of the sine function: $2\pi \cdot \mathbf{c} \cdot \frac{\mathbf{t}}{\lambda}$ makes sense. (8 pts)

9. Here we will calculate the population distribution of COVID patients as a function of the number of low-income citizens (NP). The map shown here will help you understand the variables.

a. First, it is determined that the number of COVID cases changes with the geographic location (**x**, **y**), the population (**pop**), area A and number of low-income people (NP) according to the following:

 $Cases(\mathbf{x}, \mathbf{y}, \mathbf{pop}) = f(\mathbf{x}) \cdot f(\mathbf{y}) \cdot f(\mathbf{pop})$

$$= \sin\left(\frac{\mathbf{n}_{\mathbf{x}}\boldsymbol{\pi}}{\sqrt{\mathbf{A}}} \cdot \mathbf{x}\right) \cdot \sin\left(\frac{\mathbf{n}_{\mathbf{y}}\boldsymbol{\pi}}{\sqrt{\mathbf{A}}} \cdot \mathbf{y}\right) \cdot \sin\left(\frac{2\boldsymbol{\pi}}{\mathbf{NP}} \cdot \mathbf{pop}\right)$$



A city is divided into neighborhoods via the n_x and n_y boundaries. The wealthy and lowincome areas have different numbers of COVID patients and hospital bed availabiltiy.

Here, n_x and n_y represent the number of boundaries between the rich and poor COVID patients and neighborhoods. The function Cases(**x**, **y**, **pop**) is the solution to the following differential equation:

$$\frac{\partial^2}{\partial \mathbf{x}^2} \text{Cases}(\mathbf{x}, \mathbf{y}, \mathbf{pop}) + \frac{\partial^2}{\partial \mathbf{y}^2} \text{Cases}(\mathbf{x}, \mathbf{y}, \mathbf{pop}) = \frac{\partial^2}{\partial \mathbf{pop}^2} \text{Cases}(\mathbf{x}, \mathbf{y}, \mathbf{pop})$$

Please use this differential equation and the formula for Cases to demonstrate:

$$n_x^2 + n_y^2 = \frac{4 \cdot A}{NP^2}$$

Hint: the first term is: $\frac{\partial^2 \text{Cases}}{\partial x^2} = \frac{\partial^2 \sin(\frac{n_x \pi}{\sqrt{A}} \mathbf{x})}{\partial x^2} \cdot f(\mathbf{y}) \cdot f(\mathbf{pop}) = -\left(\frac{n_x^2 \pi^2}{A}\right) \cdot f(\mathbf{x}) \cdot f(\mathbf{y}) \cdot f(\mathbf{pop})$

b. We can simplify the result from pt. a: $n_x^2 + n_y^2 = \frac{4 \cdot A}{NP^2}$ as: $n^2 = \frac{4 \cdot A}{NP^2}$. Next, we learn from the County Health office that the number of hospital beds available to the population is:

$$\operatorname{Beds}(n) = \left(\frac{1}{4}\right) 2\pi n \cdot \partial n$$

Can you convert this into the number of beds available as a function of the size of the low-income population? Meaning, convert Beds(n) into Beds(NP) given that $n^2 = \frac{4 \cdot A}{NP^2}$? (7 pts)

Hint: You need to use a Jacobian: $\partial n = \left| \frac{\partial n}{\partial NP} \right| \partial NP$.

c. When you multiply the number of available hospital beds: Beds(NP) with the average number of COVID patients as a function of the size of the low-income population: $\langle P(NP) \rangle = \frac{1}{NP \cdot (e^{1000}/NP - 1)}$ you arrive at the COVID patient distribution:

$$Beds(NP) \cdot \langle P(NP) \rangle = \frac{2\pi \cdot A}{NP^3} \frac{1}{NP \cdot \left(e^{1000/NP} - 1\right)} \partial NP$$
$$= \frac{2\pi \cdot A}{NP^4 \left(e^{1000/NP} - 1\right)} \partial NP$$



(7 pts)

A graph of the above distribution is shown. Can you describe why the graph rises and falls as it does? Please explain the answer as though you were speaking to a middle school student. For example, don't you already know how COVID affects low-income earners disproportionately? What kind of access to medical care to low-income people have? Discuss how these are related to the equations developed. (5 pts)

d. What would integrating the result in pt. c yield? Note you don't have to actually integrate it, just describe what the numerical

result would mean as though you were speaking to a middle school student. (3 pts)

10. Now let's repeat what we did with problem #9 for lightbulbs. We determined that the Boltzmann equation's normalizer for the blackbody radiator problem is:

Norm =
$$\left\{1 - e^{\frac{-hc}{\lambda \cdot k_{B}T}}\right\}^{-1}$$

Please evaluate $(k_B T)^2 \frac{\partial \ln(Norm)}{\partial(k_B T)}$ to show that it is the same as the average energy. (10 pts)

Hint: You have the correct equation for the average energy from class and Ch. 12 of "Free Energy". Also you will need to use the following identity: $\frac{\partial}{\partial} \ln \left(1 - e^{\frac{-a}{x}}\right) = -\frac{a}{(\frac{a}{x})}$

following identity:
$$\frac{\partial}{\partial x} \ln \left(1 - e^{\frac{-a}{x}} \right) = -\frac{a}{x^2 \left(e^{\frac{a}{x}} - 1 \right)}$$



(3 pts)

11. When people were first working on the blackbody radiator problem they thought to use the Equipartition theorem to calculate the energy of a photon:

$$\langle E \rangle = \frac{k_B T}{2} \cdot \text{degrees of freedom}$$

The number of degrees of freedom is 2 for a photon because they can be left- or right-circularly polarized. Consequently, the blackbody intensity distribution would be:

$$Modes(\lambda) \cdot \langle E \rangle = \frac{8\pi L^3}{\lambda^4} \cdot k_B T \cdot \partial \lambda$$

This is called the Rayleigh-Jeans law, which isn't correct as can be demonstrated by calculating the total energy output of the object via integration:

$$Total \ energy = \int_{0}^{\infty} \frac{8\pi L^{3}}{\lambda^{4}} \cdot k_{B}T \cdot \partial\lambda$$

a. What do you get when you evaluate $\int_0^\infty \frac{8\pi L^3}{\lambda^4} \cdot k_B T \cdot \partial \lambda$?

You may need to use an on-line integrator:

https://www.wolframalpha.com/widgets/view.jsp?id=8ab70731b1553f17c11a3bbc87e0b605

FYI, if the on-line thing states "does not converge", then the answer is ∞ .

b. The problem encountered with the answer with pt. a was called the "Ultraviolet Catastrophe". Why do you think they called the result that? (3 pts)

12. There is an idea that quantum mechanical expressions should turn into classical ones under some limit. For example, the quantum Planck distribution: $\frac{8\pi L^3}{\lambda^5} \cdot \frac{hc}{\left(e^{\frac{hc}{\lambda k_B T}}-1\right)}$ should turn into the classical Rayleigh-Jeans one: $\frac{8\pi L^3}{\lambda^4} \cdot k_B T$. But how?

a. First, look at the $e^{hc/\lambda k_BT}$ term, and use this identity: $e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!}$... to simplify it to the 2nd term (i.e. do this: $e^x \approx 1 + x$). This simplification is valid if λ is very very long. (7 pts)

b. Now plug in your answer above into
$$\frac{8\pi L^3}{\lambda^5} \cdot \frac{hc}{\left(e^{hc}/\lambda k_B T_{-1}\right)}$$
 and simplify it- what do you have? (7 pts)

c. What one finds is that all quantum mechanical equations have "h" in them, but classical equations never do. Thus, the Rayleigh-Jeans law is "classical" because it doesn't have Planck's constant. It also correctly describes the lightbulb for long wavelengths, but not short ones as shown here. Now, you may be wondering what the question is. There isn't one- did you

(nts)

notice how many points this question is worth?



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