The Thermodynamic Interaction of Light with Matter

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Abstract

Light is electromagnetic radiation that could be shown in a spectrum with a wide range of wavelengths. Blackbody radiation is a type of thermal radiation and is an important topic to explore due to it being an ideal body that materials' properties are often described in comparison to it. Therefore, it helps in understanding how materials behave on the quantum level. One must understand its interaction with light spectrum and how electron excitation happens. Thus, concepts such as Planck's law, energy quantization and band theory will be discussed to try to grasp of how light interacts with materials.

Keywords: Blackbody radiation, Stefan-Boltzmann law, Planck's law, Quantization, Band theory, Optical properties, Conductivity

Introduction

Thermal radiation is the generation of electromagnetic waves from particles in matter and all matters that are greater than absolute zero in temperature emits thermal radiation.

Thermal radiation can occur between the ultraviolet range at 400 nm and infrared borderline microwave range at 10^4 nm. While visible light takes place at the visible range between 400-800 nm.

Human beings as all bodies at room temperature also emit thermal radiation, however, this emission happens at a very low frequency. Our body uses thermal radiation as an additional way to cool off which is emitted in the infrared range and therefore can be detected by an IR camera. Thermal radiation is also one of the main methods of heat transfer. In order to study how light

interacts with materials, it is also important to first look into blackbody radiation and its spectrum since many of the parameters, like emissivity, are calculated in reference to blackbody radiation. However, at the time of discovering this, classical physics was not prepared with the right tools to be able to explain this phenomenon properly. There were problems with classical electromagnetism that it could not account for blackbody radiation and the data would only work for the longer wavelengths but not the short ones. That is when modern physics and quantum mechanics came to explain blackbody radiation with a more developed math and thus the age of quantum mechanics was initiated.

Moreover, in order to understand materials, why they look the way they do and understand their optical properties, it is important to consider to study how light interacts with matter because it is a crucial factor in material's behavior and structure. After the revolutionary explanation of the photoelectric effect, the quantization of energy and the wave-particle duality, the behavior of light and atoms became clearer.

Blackbody Radiation: (vibrational energies of atoms in solid produce BB radiation)

An ideal blackbody is a perfect emitter and absorber of thermal radiation. It absorbs and emits electromagnetic radiation of all wavelengths uniformly in all directions. This electromagnetic radiation that is emitted is called blackbody radiation. Since a blackbody does not reflect any radiation and is not sufficiently hot to appear self-luminous on its own, therefore, it appears entirely black[1]. The naming comes originally from Gustav Kirchhoff in 1860, "...the supposition that bodies can be imagined which, for infinitely small thicknesses,

completely absorb all incident rays, and neither reflect nor transmit any. I shall call such bodies *perfectly black*, or, more briefly, *black bodies*." [2]

In order for a blackbody to maintain its consistency, say for example it should be in thermal equilibrium with its surroundings, it needs to emit all the radiation that was absorbed because losing energy in any other way risks a change in temperature. Therefore, the radiation emitted from a blackbody has greater energy at any given wavelength than any other body at the same equilibrium temperature regardless of its material or size.[1] Thus, comes the quality of it being ideal, it prominently absorbs all incident light on it at a specific temperature and then emits it completely.

It was Kirchhoff who first introduced this concept in 1859-1860. He proposed that based on the second law of thermodynamics, a perfect blackbody of temperature T at thermal equilibrium emitting electromagnetic radiation over all wavelengths has a universal function for its emissive power that depends solely on temperature and radiative wavelength.[3] His universal character was shown as emission e and coefficient of absorption e, in this ratio that equal the spectral radiance K,

$$\frac{e}{a} = K \tag{1.1}$$

His postulation is known as Kirchhoff's law of thermal radiation and it was a simple postulation that needed the mathematical support in order to lead to the discovery of quantum mechanics. Since a blackbody in thermal equilibrium is a perfect absorber and does not reflect any radiation off, it has an emissivity of 1, e = I which means its surface emits radiation perfectly.[4] However, surfaces in reality can not reach up to the qualities of a blackbody because they can not absorb all of the incident energy upon them so efficiently. Thus, real materials emit energy only

at a fraction of what a blackbody emits. Therefore, the emissivity is calculated relative to the blackbody radiation by dividing the energy radiated from an object's surface to the energy of a blackbody that is radiated at the same temperature.[5]

The quest for creating a material that could be as close as possible of a blackbody's emissivity is still on to this day. In fact, researchers at Rice University in 2008 have reported carbon nanotubes with an absorptivity of 99.955% of visible radiation.[6] Also, Surrey Nanosystems in the UK, created a nearly perfect black material called dark chameleon dimers or Vantablack, with absorptivity of 99.96% in 2015.[7]

In order to study and realize a blackbody, it is thought of as a hole in a cavity or a box, with blackened walls [8]. This small hole would allow one to observe the radiation that emerges for studying. Radiation entering the cavity through will not be reflected, except under special conditions, and thus photons are bouncing back and forth between the walls of the cavity defining the cavity's temperature. The little peephole allows one to observe the emerging light which is considered to be blackbody radiation or as how Kirchhoff referred to it as, cavity radiation.[1][9] Figure-1 shows an isothermal cavity.[10]

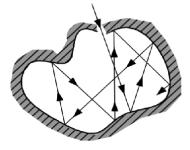


Figure [1]: An isothermal cavity as an analogy of blackbody radiation [10]

Stefan-Boltzmann

Trying to find mathematical solutions for the Kirchhoff's universal function, the scientific community was intrigued. Experiments were being produced in the 1870s which lead Joseph Stefan in 1879 to empirically deduce the proportionality between total emissive power of an object and its absolute temperature raised to the fourth power [10].

Later on in 1884, it was Ludwig Boltzmann who derived the same law theoretically using classical thermodynamics principle. Therefore it was called the Stefan-Boltzmann law, shown in eq (1.2) which states that the total energy radiated from the surface of a blackbody per unit time per unit area is proportional to the fourth power of its temperature.[1] Thus, udv = u(v,T)dv is the differential density of energy of radiation of a blackbody at temperature T and frequency v[4],

$$\underline{M_b^e} = \int_0^\infty u(vT)dv = \sigma T^4$$
 (1.2)

Where M_b^e is the total radiant exitance and σ is the Stefan-Boltzmann constant, $\sigma = 5.67E - 8$ W/m2·K4 [10]

Wien displacement law

However finding the relation between the total energy emitted by a blackbody and its temperature was not fully sufficient, looking at the energy distribution through a spectrum was much needed. Therefore, at the end of the nineteenth century, a spectrum was experimentally produced showing the radiation emitted from a blackbody as a function of wavelength, however, it still needed a mathematical form of it.[1]

The spectral radiant exitance is related to the total energy emitted by a body within a wavelength interval. It was Wilhelm Wien in 1894 who discovered that a wavelength λ can be identified using the spectral radiant exitance. Wien concluded the equation theoretically in,

$$M_{e,\lambda}^b(\lambda,T) = \frac{1}{\lambda^5} F(\lambda T) \tag{1.3}$$

Equation 1.3 shows that even though that Wien had an unknown function F that yet need to be solved, he found a relation. It shows that Kirchhoff's law that is T and λdependant, can be minimized into this single variable function F that is equal to the product of temperature and wavelength.[1] He came to the conclusion that a body in an equilibrium state, will maintain its state if a very slow expansion is applied on it and therefore the unknown function is replaced by another unknown function. This meant that once the spectral radiant exitance is known at one temperature, its value at another known temperature can be determined or in another way, the energy/frequency is a function of the other invariant frequency/temperature. In order to get the equation that is more used today, the law was derived and solved for zero, it was also used as a deduction to Stefan-Boltzmann law which results in this equation,

$$\lambda_{max}T = b \tag{1.4}$$

Where b is a constant and this equation shows that the spectral radiance of a blackbody will peak at a λ_{max} which is inversely proportional to temperature. Therefore, this helped foresee the shape of the blackbody spectrum where there is a shift for each spectrum's peak showing that different temperature spectrums peak at different wavelengths and is known by Wien's Displacement Law. For detailed derivation, see <u>Blackbody radiation</u> text[1]. Figure [2] shows a blackbody radiation spectrum with Wien's Displacement Law.

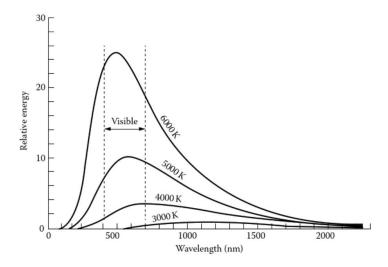


Figure [2]: Blackbody radiation spectrum as a function of wavelength. It shows Wien's displacement law where λ_{max} shifts to the left as the temperature increases.[11]

Eventually, Wien came to the result of a formula for the radiation in the form of,

$$\underline{M_{e,\lambda}^b(\lambda,T) = c_1 \lambda^{-5} exp(-\frac{c_2}{\lambda T})}$$
 (1.5)

Even Though Wien's formula had a close fit to the experimental data, it was yet very limited. As it turned out when compared to the spectrum, Wien's approximation described the spectral radiant exitance accurately within 1%. However, this was held true only for shorter wavelengths when $\lambda T \leq 3100 \,\mu$ m K.[13]

In June 1900, Lord Rayleigh also tried to work on this problem and modified Wien's law into,,

$$\underline{M_{e,\lambda}^b(\lambda,T) = c_1 \lambda^{-4} exp(-\frac{c_2}{\lambda T})}$$
 (1.6)

Where constants C were yet to be determined, he then derived it into its final form as,[1]

$$\underline{M_{e,\lambda}^b(\lambda, T) = c_I \lambda^{-4} T} \tag{1.7}$$

Lord Rayleigh however, knew that his formula would only be accurate for longer wavelengths and would fall short for shorter ones in the ultraviolet range. After four years of publishing the equation, Rayleigh contacted his colleague James Jean at Cambridge University about it and the later noted an error by a factor of eight.[14] Therefore, for that help the law was named Rayleigh-Jean. Experimentation showed that the Rayleigh-Jean approximation was only accurate 1% when $\lambda T \geq 7.2 \times 10^5 \ \mu \text{m·K.}[13]$

This showed a substantial flaw in the mathematical support for the distribution spectrum, one that Rayleigh knew of but yet couldn't explain it. Equation (1.7) assumed that at short wavelengths as the function approaches zero, the intensity increases infinitely and it would radiate all the heat instantaneously which contradicts the laws of physics for bodies in thermal equilibrium.[1] The naming of the "ultraviolet catastrophe" comes from Paul Ehrenfest.[13]

So at the end of the 19th century, the failure of classical physics to solve the problem of blackbody radiation still intrigued physicist and was full of attempts for solving it. It wasn't until 1900 until Planck came up with a whole new concept that not only solved the shortcomings in Wien and Rayleigh's formulas, but only paved the way for a new concept as well. Figure [3] shows the comparison in deviation of Wien, Rayleigh, and Planck.

After three years of struggling with the study of the blackbody problem, Planck wrote the form of the distribution law continuing Wien's work and furthering some of his postulations. In 1900, Planck successfully wrote the distribution equation.

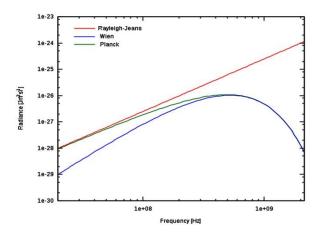


Figure [3]: A comparison of spectral radiance graph to Rayleigh-Jeans, Planck and Wien's formulas.[13]

He did this by working on a combination of Wien's radiation law which was known to be true for shorter wavelengths but deviates at longer wavelengths, along with Lord Rayleigh's result that worked well for longer wavelengths and fell short for the shorter ones. This way Planck had written a functioning equation for the spectral radiant exitance,

$$\underline{M_{e,\lambda}^b(\lambda,T)} = \frac{2\pi hc^2}{\lambda^5 \left[exp\left(\frac{he}{K_h\lambda T}\right) - I\right]}$$
(1.8)

Where what Wien's formula formally had two C and c as radiation constants, here it was calculated that the constants are $C = 2hc^2$ and $C = \frac{hc}{k_b}$ where c is the speed of light, h is Planck's constant and k_b is Boltzmann constant.[12]

After Planck derived a mathematical formula for the radiation form, he then had to provide an explanation for it. Therefore, he came up with the resolution about light, that is a bit distant from the classical Maxwell description of light being distinctive electromagnetic wave which is continuous. He came to the conclusion that the energy emitted from a blackbody is rather discrete and comes in quantized form. This discrete packets of quantized energy are called

"quanta".[9] Moreover, he realized that in order to have the theoretical aspect in agreement with the experimental part, one needs to assume that the blackbody's radiated energy could only be a multiple of integers and is proportional to the frequency[15],

$$E = nhv ag{1.9}$$

Where h is the Planck constant, v is the frequency of the radiation and n is a positive integer. Therefore, Planck's Law for thermal radiation have been tested theoretically and experimentally and was held true for both aspects. Due to his realization of the relation between frequency and energy and how it cannot exist in all values since its quantized, a new branch of physics was developed with the help of Einstein, called quantum mechanics.

Photoelectric effect

However, Planck's hypothesis was not accepted initially, not until Einstein came in 1905 and explained the photoelectric effect using equation (1.9). The photoelectric effect is described as the ejection of electrons from a metal surface when a light beam is shone on it. This happens if the photons of the incident light which is absorbed by the metal surface has sufficient energy to make the electrons in an excited state to be emitted from the metal [15]. This phenomenal does not depend on the intensity of the light but rather on its frequency threshold.

For the reason that light, as explained in the photoelectric effect, exhibited some properties of particles, scientists had to explain the particle like behavior of waves.

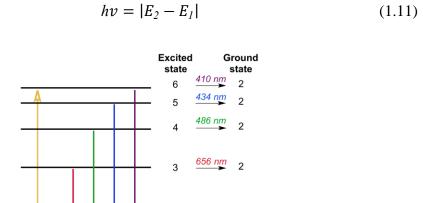
Frequency dependence/Atom model & electron excitation

More experimental evidence was being gathered proving that energy is quantized. One of those experiments was Bohr's model of the Hydrogen atom. While classical descriptions of the

atom had inconsistencies with electrodynamic theory and turned out to be flawed, Bohr model solved those problems by explaining the atom structure using quantum mechanics. He pictured the small, heavy nucleus in the middle with negative electrons orbiting around it that do not have accelerating momentum like the classical theory but where electrons have a set of specific allowed values [16]. When the atom absorbs energy from the electromagnetic field, electrons at a certain energy level, for example at E1, absorbs a photon that is equivalent to the difference between energy levels in order to move to a higher energy level (E2) and be in an excited state.

$$\Delta E = E(n_{high}) - E(n_{low}) \tag{1.10}$$

Since the excited state is not stable for the atom, a transition to a state lower in energy occurs and thus light is emitted [15]. This electron's transition is shown in figure [4]. Since that transition emits a photon that has a specific discrete wavelength and frequency, it is for that reason frequency is found directly proportional to the energy of photons and it is quantized which is shown in equation 1.11 [15]

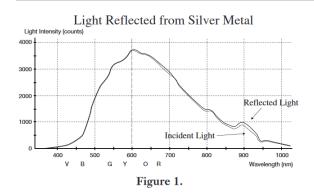


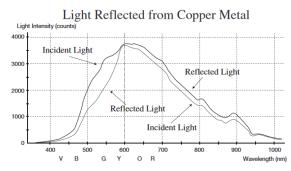
Energy absorbed Energy emitted Energy level Figure [4]: The electron transition between energy levels through absorption and emission/excitation and de-excitation in relation to λ in the visible region of an hydrogen atom. [19]

Why we see colors

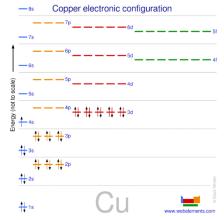
This quantum nature of the energy levels and transitions can help explain how different materials with different electron configuration have different colors. The apparent color of materials depends on the surface properties of the atoms that make up the object such as reflection, transmittance, absorption, and emission. As known, white color looks white because it reflects all wavelengths of light and absorbs none, and black absorbs all wavelengths of color and reflects none. Also, colored objects absorb all colors except for their apparent color of which they reflect. For example, the dye molecules in a red shirt makes it look red by absorbing wavelengths at the violet/blue range and reflecting that range's complementary color which is red.

To have a deeper understanding of this process at the quantum level, one can look at copper which appears as a reddish color while metals are normally of a silver color. This happens because metals normally do not absorb the incident light and most of it is reflected, which causes a slight distortion and gives it that silver shade since the incident light curve almost entirely overlaps with the reflected light in its spectra as seen in figure 4. On the other hand, copper actually absorbs the blue-green wavelength of the incident light and reflects its complementary color which is red-orange. This happens due to the exception with the electron configuration of copper where instead of the expected [noble gas]d9 s2 configuration, it has [Ar]3d10 4s1 shown in figure [6]. It is due to the low energy difference between d subshell and the higher s subshell [17]. When the 3d electron gets excited by absorbing energy, it moves to the 4s energy level, this energy needed to transition is equivalent of the blue-green light energy which it absorbs. In order to maintain its stability, the electron attempts to move back to its original energy state which is lower in level, so it loses its energy in the red-to-infrared region.





Figure[5]: A comparison in the light spectra of a silver metal and copper[17]



Figure[6]: Electron configuration of copper metal [25]

Where the IR energy is lost in the form of heat and the reflected light therefore is reddish in the 600 nm region[17].

This electron transition can also help explain Wien's displacement law and why when objects are heated up they radiate a different color. When an object increases in temperature, it gains more energy according to the first law of thermodynamics. Thus it absorbs more energy for the

electrons to move to a higher energy levels which in transitioning back produce a higher frequency photons and for example goes from a red radiation color to blue.

Optical properties of materials:

The previous description of light interacting with materials that allows us to see in colors describes one type of optical property which is opacity. There are three classifications of matter's appearance when interacting with light which are, opaque, translucent, and transparent. The reason we are able to see colors as they are and not see through them is because they are opaque which means that when interacting with light, the electrons absorb all the incident light and transition from ground state to excited-higher in energy unoccupied states and later on reemit those photons. Translucent materials are somewhere in between, where they can transmit light while having some photons scattered and thus not forming a clear image therefore objects seen through it look somewhat unclear while a transparent material allows for objects to be seen through it more clearly. Transparent materials, on the other hand, are the opposite of opaque. They relatively have almost no interaction with incident light where most of it is neither absorbed nor reflected, but passes through the atoms, or in other words, it transmits light. Transmittance happens because light photons pass through without exciting electrons because they do not have enough energy to give for the electrons to transition to higher energy levels due to their big band gaps, which will be explained later on.

A selective surface on the other hand can selectively transmit specific wavelengths and absorb other wavelengths. For example, glass as it appears transparent to our eyes, it however is opaque to most ultraviolet and infrared radiation. This happens because glass is originally made up of a crystal structure of silicon oxides but when heated up and cooled, those molecules lose energy which allows the crystal structure to freely fill any gaps in it since it doesn't have an ordered

form anymore. The glass's atomic structure shows a big gap between its occupied energy levels and the empty energy levels which means the light's photons-in the visible range- do not have enough energy to excite electrons to higher energy levels, therefore they transmit light in the visible range from 400-800nm. However, in the glass is opaque in the near infrared range and ultraviolet as shown in Figure 7 where the cutoff is almost below 400 and over 2000 nm where transmittance drops to zero. This happens because the UV radiation causes the glass's molecules to vibrate and the radiation's photons give enough energy for electron excitation and thus its absorbed. The glass's transparency to UV and IR can be increased by increasing the silica content in it [24]. To read more on the vibrational transition in the UV and IR spectrum, see *Quantum Chemistry and Spectroscopy* (Engel, 2015).

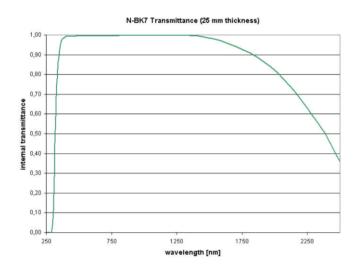


Figure [7]: Glass's transmittance in the UV, visible and IR ranges [23].

Band Theory

All atoms have discrete energy levels where electrons orbit around the nucleus. When the atoms are arranged together to form a molecule or a solid, the atomic orbitals of each atom overlap with each other and form a molecular orbital which makes up an energy band in a solid. This energy

band is thus considered an energy continuum. The highest occupied molecular orbital (HOMO) is called the valence band as well and the lowest unoccupied molecular orbital (LUMO) is considered the conduction band [15]. Since electrons can transfer between energy levels at an atomic sublevel, they also have the ability to move in solids between energy levels whether they were in the same band or in different bands depending on the amount of energy they're absorbing from light[22]. Different materials have different spacings between bands which partially decide their properties whether they are transparent or opaque or whether they are conductive or insulating.

Semiconductors & Conduction band

Thermodynamics serves as a tool to help with understanding different applications such as semiconductors. A semiconductor has an electrical conductivity that lies between an insulator and a conductor. In insulators the forbidden area between the valence and conduction band, which is called the band gap, is so large and there are no specific allowed values for the total energy or what is known in quantum mechanics as eigenvalues. Insulators like glass and diamonds with a big band gap have their valence band or HOMO, filled with electrons and it's far away from its LUMO, this distance translates into a higher energy to overcome, and therefore electrons cannot reach the conduction band. On the other hand, conductors have electrons that are free to move within their conduction band. As for the semiconductor, they have a narrow gap between the valence and conduction bands, therefore it can actually have conduction properties if there was a production of an excited state for electrons which could be done by light absorption, doping or heating [21]. It could have some photons transmitted through and some absorbed.

Conclusion

Thermal radiation and blackbody radiation are important topics in thermodynamics. The quest of finding an appropriate explanation with the right mathematical support for the blackbody spectrum lead physicists to develop and create a new field in physics, statistical and quantum mechanics. This was due to the efforts of many different scientists such as Kirchhoff, Boltzmann, Wien and Planck who set one of the most important laws in physics, the Planck's law. Understanding how light interacts with matter is very important the material's properties and predict their reactions. Light was understood in many ways over the years where it was thought of as only waves but after the postulations and the constant discoveries of scientists they realized that light is made of particles as well when Einstein revealed his paper on the photoelectric effect and proved the wave-particle duality. This all helped in understanding light and how it relates to materials and have a strong effect in making them what they are. For example, photons absorbed from light is what makes objects look a certain color when a specific amount of energy is absorbed from a light photon. Moreover, it can help explain why a material can conduct electricity or is insulating or even why they look opaque or translucent. This deep understanding of light and atoms and how they react together has helped scientists to find different application and create different tools to help humanity in many different fields.

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