Bohr Atom and Specific Heats of Gases and Liquids

S Uma Sankar

Department of Physics
Indian Institute of Technology Bombay
Mumbai, India

Kirschhoff's Law

Kirchhoff proved the following theorem based on thermodynamic arguments: If $e(\nu)$ is the emissivity (power emitted per unit area per unit frequency) and $A(\nu)$ is the fraction of incident power absorbed per unit area per unit frequency, then

$$e(\nu) = J(\nu, T)A(\nu),$$

where $J(\nu, T)$ is a **universal** function.

The above equation is valid for anybody which is thermal equilbrium with radiation.

A blackbody (which is an idealization) absorbs all the energy which falls on it. For a blackbody $A(\nu) = 1$. A large number of materials, behave like blackbodies when heated.

Stefan's Law

Based on an experimental study of different blackbodies, Stefan established that the total power, per unit area, emitted by a blackbody overall the frequencies, is given by

$$e_{\text{total}} = \int_0^\infty e(\nu) d\nu = \int_0^\infty J(\nu, T) d\nu = \sigma T^4,$$

where σ is a universal constant whose value is $\sigma = 5.67 \times 10^{-8}\ \mathrm{W - m^{-2} - K^{-4}}$.

Note that Stefan's Law, which is based on experimental observations, is consistent with Kirschhoff's equation, which is derived from thermodynamic considerations.

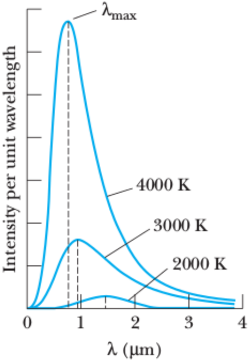
The universal function $J(\nu, T)$ introduced by Kirschhoff can be related to $u(\nu, T)$, the energy per unit volume per unit frequency carried by the blackbody, as

$$J(\nu, T) = \frac{c}{4} u(\nu, T).$$

Since $J(\nu, T)$ is a universal function, so is $u(\nu, T)$.

Wein's Exponential Law

Experimental measurements showed $u(\nu, T)$ to have the form

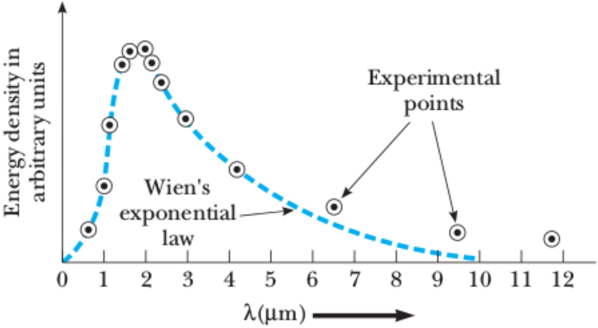


Wien made a guess that

$$u(\nu, T) = A\nu^3 \exp\left(-B\nu/T\right),$$

where A and B are universal constants. Called Wien's exponential law.

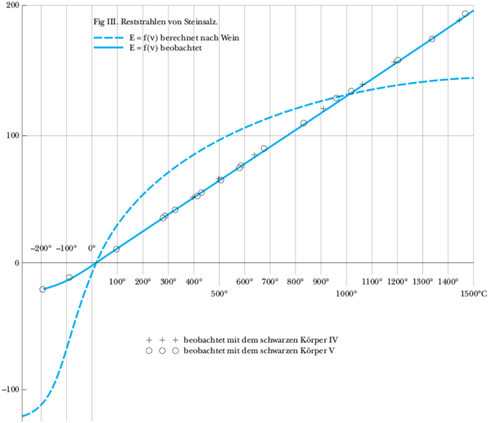
Wien’s Exponential Law



Fits well at low wavelengths but does not match experiments at large wavelengths.

Energy Density vs Temperature

Mismatch at large λ is more dramatic when the temperature dependence of $u(\nu, T)$ is studied:



$u(\nu, T) \propto T$ for large $\lambda = 51.2\ \mu\mathrm{m}$.

Rayleigh-Jeans Law

Maxwell showed that an oscillating charge emits radiation of the same frequency as that of the oscillation.

Rayleigh and Jeans assumed that the blackbody consists of a large number of oscillators (each of its own frequency) in thermal equilibrium with the radiation surrounding it.

From Statistical Mechanics, one can show that the probability, of an oscillator at temperature T to have energy E, is $P(E) \propto \exp(-E/kT)$.

Hence the average energy of an oscillator in Rayleigh-Jeans model is

$$\langle E \rangle = \frac{\int_0^\infty EP(E)dE}{\int_0^\infty P(E)dE} = \frac{\int_0^\infty E\exp(-E/kT)dE}{\int_0^\infty \exp(-E/kT)dE} = kT.$$

Rayleigh-Jeans Law

If $n(\nu)d\nu$ is the number of oscillators per unit volume, oscillating with frequencies between ν and $\nu + d\nu$, then

$$u(\nu, T) = kT \; n(\nu)d\nu.$$

Rayleigh-Jeans calculated

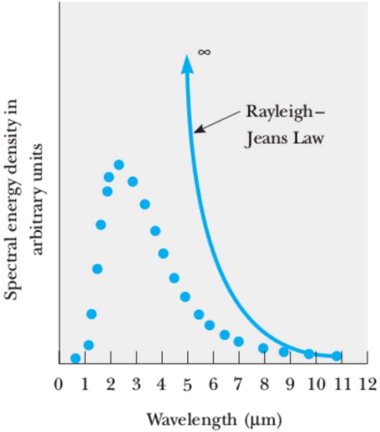
$$n(\nu)d\nu = \frac{8\pi\nu^2}{c^3}d\nu,$$

based on thermal equilibrium between the oscillators and the radiation.

Hence we get the Rayleigh-Jean's formula

$$u(\nu, T)d\nu = kT\frac{8\pi\nu^2}{c^3}d\nu.$$

Rayleigh-Jeans Law



Fits well at large wavelengths but is a disaster at low wavelengths.
Matches $u(\nu, T) \propto T$ observed for large wavelengths.

Planck's Hypothesis

Max Planck also assumed that the oscillators in the blackbody are in thermal equilibrium with the radiation, just as Rayleigh-Jeans did. So he had the same expression for $n(\nu)d\nu$.

Rayleigh-Jeans assumed that the energy E emitted or absorbed by an oscillator can take any positive real value between 0 and ∞.

This is a natural assumption to make, given how energy was viewed in classical physics.

Planck's Hypothesis

Planck made **two** important assumptions:

1. The energy emitted or absorbed by the oscillator of frequency ν is proportional to ν. This is a radical departure from the classical picture.
2. The energy is emitted or absorbed in integer units or **Quanta** of $h\nu$, where he introduced a new fundamental constant h (now called Planck's constant).

Now the probability of an oscillator having energy $E = nh\nu$ is $\propto \exp\left(-nh\nu/kT\right)$, where n is a natural number.

Planck's Hypothesis

Using Planck's hypothesis, we calculate the average energy of an oscillator in the balckbody to be

$$\begin{aligned}\langle E\rangle &= \frac{\sum_{n=0}^{\infty} nh\nu e^{-(nh\nu/kT)}}{\sum_{n=0}^{\infty} e^{-(nh\nu/kT)}} \\ &= \frac{h\nu}{e^{(h\nu/kT)}-1}.\end{aligned}$$

Substituting this formula, in stead of kT, in the expression for $u(\nu, T)$, we get

$$u(\nu, T) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{(h\nu/kT)}-1},$$

which fits the blackbody spectrum over the full range of wavelengths.

In the limit $h\nu/kT \ll 1$, we recover Rayleigh-Jeans law.
In the limit $h\nu/kT \gg 1$, we obtain Wein's exponential law.

Cosmic Microwave Background Radiation (CMBR)

In the early universe, matter was in the form of a plasma which was equilibrium with radiation. The universe could be considered to be a blackbody and the radiation, with a Planckian spectrum, filled the whole universe.

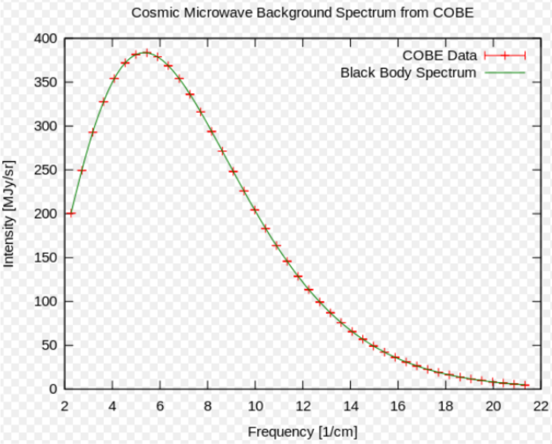
As the universe expanded, it cooled. When the temperature of the universe fell below 10^4K ($kT < 10\ \mathrm{eV}$), protons and electrons combined to form hydrogen. At this point, the radiation and matter stopped interacting.

Further expansion of the universe red-shifted the radiation with Planckian spectrum. George Gamow and his students, who bulit up this picture of universe in 1948, estimated its current temperature to be about 10K. (Fred Hoyle, who built a rival picture of universe, derisively called Gamow's picture The Big Bang Theory),

In 1964, two engineers from Bell Labs bulit a very sensitive antenna and were extremely puzzled when they found that it was always giving a noise whose frequency peaked at 160 GHz. This noise was isotropic. From every direction it was the same noise.

Cosmic Microwave Background Radiation (CMBR)

Cosmologists at Princeton University interpreted this noise to be the CMBR predicted by Gamow and his students.

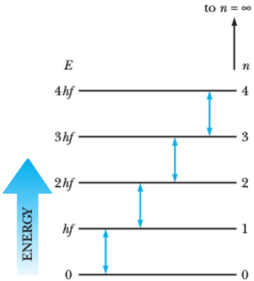


The temperature of the radiation is measured to be 2.7K.

Quantization of Oscillators

Planck assumed that an oscillator, of frequency ν, emits or absorbs energy in quanta of $h\nu$.

Why should it be so? Because the oscillator has discrete energy levels labelled by $nh\nu$ with $n = 0, 1, 2, \ldots.$



Hydrogen Spectral Lines

As soon as the science of spectrography developed, it was observed the light emitted by atoms is in the form of spectral lines

Spectroscopy was used to identify elements and discover new elements. For example, Helium was first observed in the spectral study of sunlight. Later it was found to exist on earth.

In studying the Hydrogen spectral lines in the visible region, Balmer obtained a simple formula for the wavelengths of the observed emissions

$$\lambda_n^{\mathrm{Balmer}} = C_2 \left(\frac{n^2}{n^2 - 4} \right) \text{ with n} = 3, 4, 5...$$

Later a whole range of spectral lines were observed. The expression for the wavelength of the emissions is modified to

$$\frac{1}{\lambda_{mn}} = R \left(\frac{1}{n^2} - \frac{1}{m^2} \right) \text{ with m} > \text{n},$$

where R is the Rydberg constant.

Hydrogen Spectral Lines

Here again radiation is labelled by integers. Is it due to quantization?

Yes!

But here the frequency and, by Planck's hypothesis, the energy depend on $\propto 1/n^2$.

This energy quantization seems to be different from Planck's quantization. How is it possible to get the above quantization?

Answer: (as given by Neils Bohr) Quantize the angular momentum in integer units of Planck constant.

Planetary Model of Atom

α particle scattering experiments of Geiger and Marsden and their analysis by Rutherford showed that atoms contain a nucleus which contains all the mass and carried positive charge.

A number of electrons orbit the nuclues, much the way same way planets orbit the sun.

Problem again! An orbiting electron has acceleration. Classical electromagnetic theory says that accelerating charges should radiate energy! It says that the electron should crash into the nucleus in 10^{-22} sec.

It is the same theory which predicted that oscillating charges should radiate energy, which Hertz used to design his experiments that produced radio waves.

Bohr Quantization

Undoubtedly we exist and atoms exist too! Electrons in atoms are not crashing into nuclei.

But why should the electrons in atoms get an exemption to the rule that accelerating charges should radiate? Note that in Hertz's experiment, radio waves were produced by electrons oscillating in an applied electric field.

Bohr resolved this issue by hypothesizing that atoms contain stable orbits in which electrons can stay indefinitely if they are undisturbed.

These orbits are identified by the Bohr quantization condition that the angular momentum of the electron in these orbits is an integer multiple of Planck's constant.

$$mvr = n\hbar \ (\hbar = h/2\pi)$$

Note that the dimensions of the Planck's constant are the same as those of angular momentum.

Bohr Quantization

Why should we believe in Bohr's crazy idea? For the same reason we should believe in Planck's crazy idea.

Planck's quantization hypothesis led to a derivation of the blackbody radiation formula and the calculation of Stefan's constant in terms of more fundamental universal constants.

Similary Bohr's quantization condition led to a derivation of $E_n = -R/n^2$ for an orbit with angular moment $n\hbar$ and the calculation of Rydberg constant in terms of more fundamental universal constants

$$R = \left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{m_e e^4}{2\hbar^2}.$$

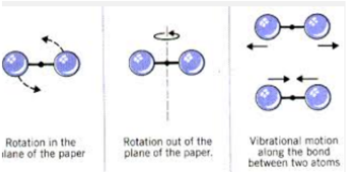
It is said that Einstein, when he heard of Bohr's work, commented, "That is an enormous achievement".

Specific Heat of Diatomic Gases

The variation of the specific heat of diatomic gases with temperature can be explained using quantization of the angular momentum due to rotation (Bohr hypothesis) and quantization of energy due to vibration (Planck hypothesis).

Consider the diatomic molecule to be shaped like a dumbell (two identical spheres connected by a long thin spring).

It has three independent translations (in x, y and z directions), two independent rotations (about the two axes perpendicular to the connecting spring) and one vibration (along the direction of the spring).



Rotation in the lane of the paper

Rotation out of the plane of the paper.

Vibrational motion along the bond between two atoms

Specific Heat of Diatomic Gases

We apply angular momentum quantization condition to rotations and energy quantization condition to vibration.

If angular momentum takes values $mh/(2\pi)$ ($m = 0, 1, 2, ...$), then rotational kinetic energy $E_{\rm rot}$ takes values $m^2h^2/(8\pi^2 I)$, where I is the moment of Inertia of the diatomic molecule about its center.

The vibrational energy $E_{\rm vib}$ takes discrete values $nh\nu_{\rm vib}$ (where $n = 0, 1, 2, ...$).

In almost all the cases, $E_{\rm rot} \ll E_{\rm vib}$.

It takes very little energy to make the molecule move. So at low temperatures, only the three translational motions occur. The two rotations and the vibration do not occur because

$$kT \ll E_{\rm rot} \ll E_{\rm vib}.$$

Therefore, the internal energy is $U = 3N(1/2)kT$ and the specific heat $C_V = 1.5R$.

Specific Heat of Diatomic Gases

At room temperature, we have

$$E_{\mathrm{rot}} \ll kT \ll E_{\mathrm{vib}}.$$

So the thermal energy is large enough to excite the rotations but is not enough to excite the vibration. So the internal energy is $U = 5N(1/2)kT$ and the specific heat is $C_V = 2.5R$.

At high temperatures, when

$$E_{\mathrm{rot}} \ll E_{\mathrm{vib}} \ll kT,$$

the vibration is also excited, which adds another NkT to the internal energy (half from kinetic energy and half from potential energy). So the specific heat becomes $3.5R$.

Number of Vibrations of a Solid

Classical theory of heat predicted that the specific heat of all solids should be $3R$ at all temperatures.

Experimentally, it was found that $C \rightarrow 0$ as $T \rightarrow 0$.

Einstein explained this feature based on Quantization of vibrations.

The number of atoms, N, in a solid is of the order of Avagadro number. Each atom has, in principle, three degrees of freedom (it can move in three independent directions). So the number of degrees of freedom is 3N.

The solid, as a mass, has three translational degrees of freedom and three rotation degrees of freedom (A famous theorem of Euler).

Hence the number of vibrational degrees of freedom in the solid (that is, the number of independent ways the atoms in the solid can vibrate) is $3N - 6 = 3N$, because the 6 can be neglected when N is of the order of Avagodro number.

Einstein's explanation of Specific heat of Solids

Classically, each independent vibrational mode gets **average** energy kT (half due to kinetic energy and half due to potential energy).

If the vibrational modes are quantized, this average energy for the model with frequency ν is $h\nu/(e^{(h\nu/kT)}-1)$. Hence the internal energy of the solid is

$$U = \frac{3Nh\nu}{e^{(h\nu/kT)}-1}.$$

For $h\nu/kT \ll 1$ (or for large T), this reduces to the classical formula.

For low temperatures, we have $h\nu/kT \gg 1$ and the internal energy becomes

$$U = 3Nh\nu e^{-(h\nu/kT)},$$

and the specific heat is

$$C = \frac{\partial U}{\partial T} = 3R\left(\frac{h\nu}{kT}\right)^2 e^{-(h\nu/kT)},$$

leading to $C \to 0$ as $T \to 0$.