Quantum Physics PY1T20/PYU11P20

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Lecture 8: Thermal phenomena

Key to the historical development of quantum mechanics:

- Thermal effects which were inconsistent with classical physics
- led to the Planck hypothesis: the energy of an electromagnetic wave of frequency ω is quantized:

$$E = n\hbar\omega$$

<u>Specific Heats</u>

- Classical model, failure at low temperature
- Einstein model

<u>Black Body radiation</u>

- Classical model, 'UV catastrophe'
- Planck model
- Wien & Stefan laws

Photoelectric effect revisited

Thermal properties: primer

- We will need some facts from thermodynamics and statistical mechanics (to be covered in detail later in your course):
- A body at a temperature T has energy, due to the thermal motion of the constituents (atoms, photons, etc.)
- This energy is fluctuating* : there is a probability distribution of energy.
- The probability that the energy is E is $\propto e^{-E/k_b T}$
- In classical physics the average energy can be more simply calculated using 'the principle of equipartition [of energy]'.

* These fluctuations are negligible for a large object but important if we're thinking of a few particles -- be they classical or quantum.

Specific heat C_v of solids

Solid is N atoms coupled, each having 3 position degrees of freedom

Classically Energy = $k_b T$ per oscillator

(equipartition principle – $k_b T/2$ per deg of freedom, oscillator has 2, PE & KE)

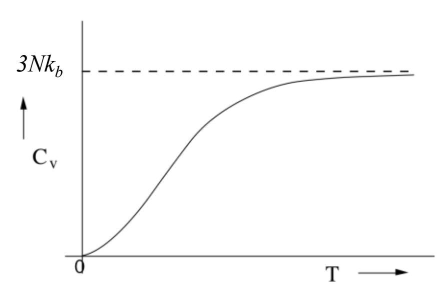
Total energy $U = 3Nk_b T$ *(N is number of atoms, k_b Boltzmann const)*

Now $C_v = dU/dT$ So $C_v = 3Nk_b$ *(or 3R/mole, Dulong & Petit)*

i.e. a constant, independent of temperature T…

Experimental observation:
OK at high T
BUT…
C_v falls *(towards zero)* at low temperatures…

Why is classical result wrong?



Specific heat of solids *(cont.)*

Planck - Assumed energy of oscillators is quantised!

$E = n\hbar\omega$ where n is a positive integer

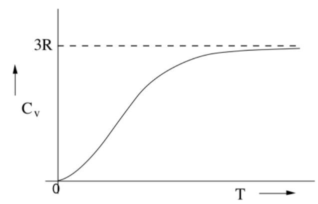
Probability of an energy E is $P(E) \propto e^{-E/k_bT} = e^{-n\hbar\omega/k_bT}$

Mean energy is $\langle E \rangle = \dfrac{\sum_n E\, P(E)}{\sum_n P(E)}$

So total Energy U is $3N\langle E \rangle = \dfrac{3N\sum_n (n\hbar\omega)e^{-n\hbar\omega/k_bT}}{\sum_n e^{-n\hbar\omega/k_bT}} = 3Nk_bT\left[\dfrac{\hbar\omega/k_bT}{e^{\hbar\omega/k_bT-1}}\right]$

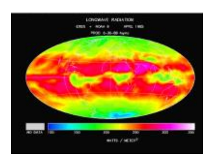
i.e. Quantum term on R.H.S. freezes out energy exchange at low temperature.
Happens because the finite gap between states, $\hbar\omega$ becomes greater than k_bT
Similar 'quenching' effect for molecule modes

$$\Rightarrow C_v = \left(\frac{\partial U}{\partial T}\right) = Nk_b\left(\frac{\hbar\omega}{k_bT}\right)^2 \frac{e^{\hbar\omega/k_bT}}{(e^{\hbar\omega/k_bT-1})^2}$$



Einstein formula for specific heat

Blackbody Radiation

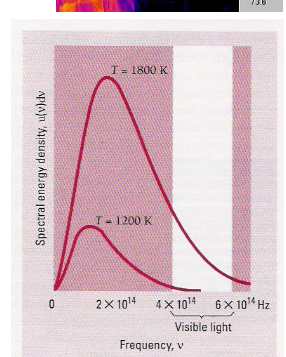


At finite temperature matter "glows"
i.e. emits radiation with a continuous spectrum.

e.g Infrared imaging of people, planet etc.

Surface dependent (*emissivity, silvery, black, etc.)*

Blackbody = <u>ideal</u> 100% emitter/absorber
in thermal equilibrium with its surroundings.
Practical realisation is a <u>thermal cavity</u>.



Measure: spectrum energy density *u(ω)*
Observe that increasing temperature
(1)increases *u* overall
(2) shifts peak emission to higher frequencies

i.e. colour and intensity of hot objects vary with T
Examples – Bar fire, molten iron, stars, universe μwave background…..

Rayleigh-Jeans model

Classical – cavity walls in thermal equilibrium with waves inside.

Assumptions: (1) Oscillators in walls emit/absorb EM waves

(2) Walls are perfect reflectors $\Rightarrow$ standing waves

(3) Equipartition of Energy

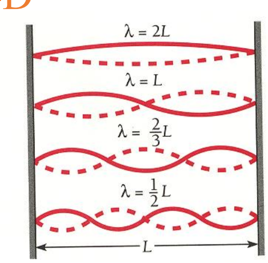
i.e. $< E > = k_b T/2$ *per degree of freedom, So* $\boldsymbol{k_b T}$ ***per oscillator/wave***

Problem to solve is –
How many waves/oscillators,
and at what wavelengths?

Waves in boxes: 1-D & 3-D

1-D box size L with Standing waves where $j = 1,2,3\ldots.$

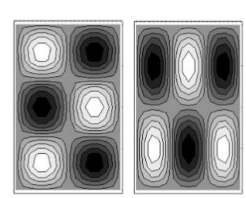
$$2L/\lambda = j$$



For 3-D: cube of side $L \Rightarrow j_x, j_y, j_z$
$= 1,2,3\ldots$ independently for each axis

Standing waves, nodes at walls, modes of cavity
Wave equation solution shows $j^2 = j_x^2 + j_y^2 + j_z^2$

Next question:
How many such waves in cavity have wavelengths between λ and $\lambda+d\lambda$?

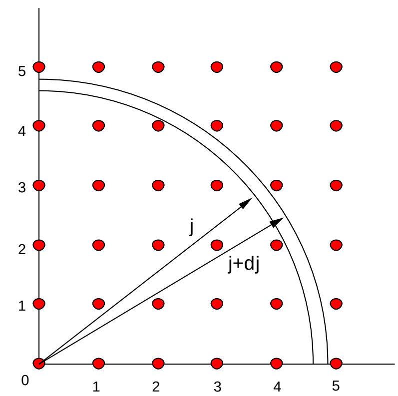


Examples in a 2-D box
2,3 and 3,2 wave patterns

j-space calculation

j values of possible waves are a cubic grid of points with separation 1
values 1,2,3 etc. on each axis *This is* **'j-space'**

So *g(j)dj* - the number of waves in range λ to λ +d λ is
the number of points in *j*-space in a spherical shell radii *j* to *j*+d*j*
Assume *j* large, so *j* is (almost) continuous
so $$g(j)dj = 4\pi j^2 dj$$



Relate $g(\lambda)$ to $g(j)$
Need 2 modifications:
λ is +ve octant only, so <u>*reduce*</u> by factor 8
2-polarisation modes, so *increase* by x2
Overall, *reduce* by x4

$$g(\lambda)d\lambda = \frac{1}{4} g(j)dj = \pi j^2 dj$$

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Number of waves & energy

$$g(\lambda)d\lambda = \pi j^2 dj$$ Now $$j = \frac{2L}{\lambda} \qquad dj = \frac{2L}{\lambda^2} d\lambda$$

So $$g(\lambda)d\lambda = \pi \left(\frac{2L}{\lambda}\right)^2 \frac{2L}{\lambda^2} d\lambda = \frac{8\pi L^3}{\lambda^4} d\lambda$$ *Note λ^{-4} dependence*

Energy $$E(\lambda)d\lambda = k_b T \frac{8\pi L^3}{\lambda^4} d\lambda$$

Energy *density* in cavity $$u(\lambda)d\lambda = \frac{1}{L^3} k_b T \frac{8\pi L^3}{\lambda^4} d\lambda = \frac{8\pi k_b T}{\lambda^4} d\lambda$$

Convert to frequency $$\lambda = \frac{c}{f} = \frac{2\pi c}{\omega} \qquad d\lambda = \frac{2\pi c}{\omega^2} d\omega$$

$$\Rightarrow \quad \boxed{u(\omega)d\omega = \frac{8\pi k_b T \omega^4}{(2\pi)^4 c^4} \frac{2\pi c}{\omega^2} d\omega = \frac{k_b T \omega^2}{\pi^2 c^3} d\omega}$$

Classical result, diverges at high ω – **the 'Ultraviolet catastrophe'!**

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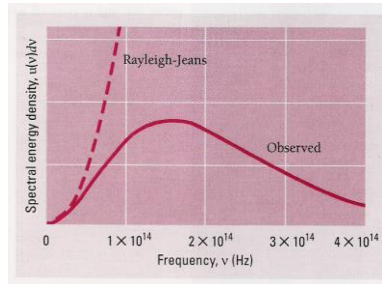
Comparison with experiment?

$$u(\omega)d\omega = \frac{k_b T \omega^2}{\pi^2 c^3} d\omega$$

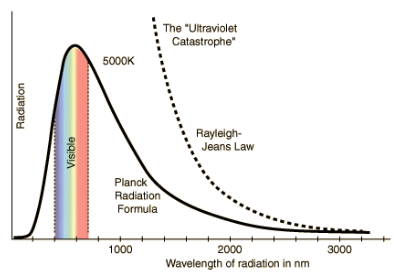
OK at low frequency.
Fails at high frequency
The 'U-V' catastrophe"
(of classical physics!)



u vs. $\omega\uparrow$ vs. $\lambda\downarrow$

Empirical 'fit' for high frequency by Wien, but no theory….

The 'big problem' for classical physics at end of C19



Planck's Blackbody Expression

Planck: oscillators can only emit energy in "packets" of $\hbar\omega$
- the original quantum hypothesis!

The only possible energy levels of the oscillators are $E=n\hbar\omega$
Emission is the result of <u>transitions</u> between these levels.

See specific heats for statistical analysis…
$\Rightarrow$ multiply classical result by $\dfrac{\hbar\omega/k_b T}{e^{\hbar\omega/k_b T}-1}$

$\Rightarrow$ $$u(\omega)d\omega = \frac{\hbar\omega^3}{\pi^2 c^3}\frac{1}{e^{\hbar\omega/k_b T}-1}$$

Planck Blackbody radiation formula – agrees with experiment
First important success of quantum theory

Why does this quantum model work and the classical not?

Classical:

Any oscillator has energy $k_B T$ no matter how high frequency. High frequencies can have some amplitude and hence some energy, so the total energy diverges with the number of states and frequency.

Quantum:

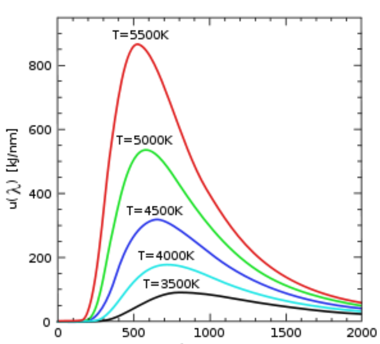
Each oscillator exchanges energy only in discrete amounts $\hbar\omega$ so at higher frequencies where $k_B T$ is much smaller than $\hbar\omega$ the states are not excited and thus do not contribute to the energy. Only lower energy (longer wavelength) modes contribute.

This prevents the divergence and causes intensity to fall off at higher frequencies.

Analogy with specific heats.

Generally, expect macroscopic quantum phenomena to be more readily visible at lower temperatures.

Results derived from Planck Equation - 1



Wien's Displacement Law

Wavelength of maximum energy

$\lambda_{max} \propto 1/T$

(or $\omega_{max} \propto T$)

(i.e. more blue when hotter… stars, furnace, etc.)

To find ω_{max}, differentiate Planck expression $\frac{d}{d\omega} u(\omega) d\omega = 0$

(Exercise!)

Find $\hbar\omega_{max}/k_b T = 2.8214$ Correct result, agrees with experiment

Results derived from Planck Equation - 2

Stefan – Boltzmann Law: For Blackbody *(perfect emitting surface)*
Total energy R emitted/unit area $\propto T^4$ $(=ST^4)$

R related to integral of Planck expression over all frequencies

$$U = \int_0^\infty u(\omega)d\omega = \frac{\hbar}{\pi^2 c^3}\int_0^\infty \frac{\omega^3}{e^{\hbar\omega/k_b T}-1}d\omega$$

With $\alpha = \hbar\omega/k_b T$ becomes $U = \frac{8\pi k_b^4}{h^3 c^3} T^4 \int_0^\infty \frac{\alpha^3}{e^\alpha - 1} d\alpha$

Integral = $\pi^4/15$ So $U = \frac{8\pi^5 k_b^4}{15 h^3 c^3} T^4 = aT^4$ *S-B Law!*

Can show that $S = 5.67 \times 10^{-8}\ W\,m^{-2}\,K^{-4}$

Photoelectric Effect Revisited

Einstein did not "solve" the photoelectric effect by introducing "photons" to match the experiment. In fact, he predicted what the experiment should be! Confirmation of his prediction came in 1916.

Actually, Einstein applied classical idea of entropy, as understood for a gas, to radiation.

For a gas, $\Delta S = Nk_b(\Delta V/V)$ where N is number of molecules
For radiation, $\Delta S = [E/\hbar\omega]k_b(\Delta V/V)$
$\Rightarrow$ $[E/\hbar\omega]$ is number of radiation "particles" *(Wien formula)*

Or $\hbar\omega$ is the energy of light (waves) "particle"!
An example of "Quasi-history"