

Introduction:

Why Quantum Mechanics in Chemical & Biological Engineering?



Quantum : Background & History

Reference:

McEvoy, Zarate, Introducing Quantum Theory, Icon Books (1996)

What is the definition of “classical” (고전)?

By **classical** (고전) is meant those late 19th century scientists nourished on an academic diet of Newton's mechanics (뉴턴 역학) and Maxwell's electromagnetism (맥스웰의 전자기론)-the two most successful syntheses of physical phenomena in the history of thought.

Just before the turn of 20th century, scientists were so absolutely certain of their ideas about the nature of matter and radiation that any new concept which contradicted their **classical** picture would be given little consideration.



Fundamental assumptions of classical mechanics (고전 역학)

1. The universe was like a giant machine set in a framework of absolute time and space. Complicated movement could be understood as a simple movement of the machine's inner parts, even if these parts can't be visualized.
2. The Newtonian synthesis implied that all motion had a **cause (원인)**. If a body exhibited motion, one could always figure out what was producing the motion. This is simply **cause and effect (원인과 결과)**, which nobody really questioned.
3. If the state of motion was known at one point it could be determined at any other point in the future or even the past. Nothing was uncertain (불확실성), only a consequence of some earlier cause. This is **determinism (결정론)**.
4. The properties of light are **completely described** by Maxwell's electromagnetic **wave** theory (맥스웰의 전자기파) and confirmed by the interference patterns observed in a simple double-slit experiment by Thomas Young in 1802.

5. There are two physical models to represent energy in motion: one a **particle** (입자), represented by an impenetrable sphere like a billiard ball, and the other a **wave** (파), like that which rides towards the shore on the surface of the ocean. They are mutually exclusive, i.e. energy must be either one or the other.
6. It was possible to measure to any degree of accuracy (정확하게 측정 가능) the properties of a system, like its temperature or speed. Simply reduce the intensity of the observer's probing or correct for it with a theoretical adjustment. Atomic systems were thought to be no exception.

Classical scientists believed all these statements to be **absolutely true**. But **all** six assumptions would eventually prove to be **in doubt**.

—————> How did the quantum theory come about?

Background : thermodynamics

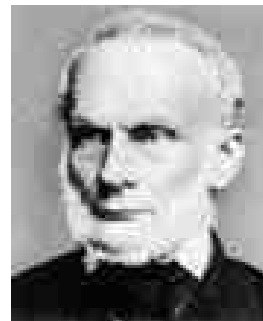
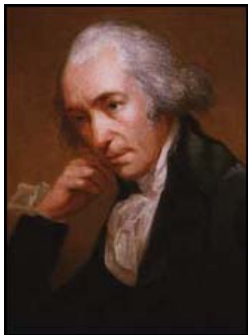
The movement of heat, which always flows from a body of higher temperature to a body of lower temperature, until the temperatures of the two bodies are the same (**thermal equilibrium**).

Heat is correctly described as a **form of vibration**...

1st law: **law of the conservation of energy** (James Watt (1736-1819, steam engine), James Prescott Joule (1819-89, heat → mechanical work), Herman von Helmholtz (1821-94, 1st law)

2nd law: **entropy** (Rudolf Clausius (1822-88))

cf. “energy” means “containing work” in Greek



Background : the existence of atoms

Democritus (460-370 BC, Greek philosopher): first propose the concept of atoms (means “indivisible”)

John Dalton (1766-1844): used the atomic concept to predict the chemical properties of elements and compounds in 1806

But it was not until a century later to accept the existence of atoms as a fact. However, during the 19th century, even without physical proof of atoms, many theorists used the concept.

근대적 원자론의 실험적 출발: **Robert Boyle** (1627-1691)



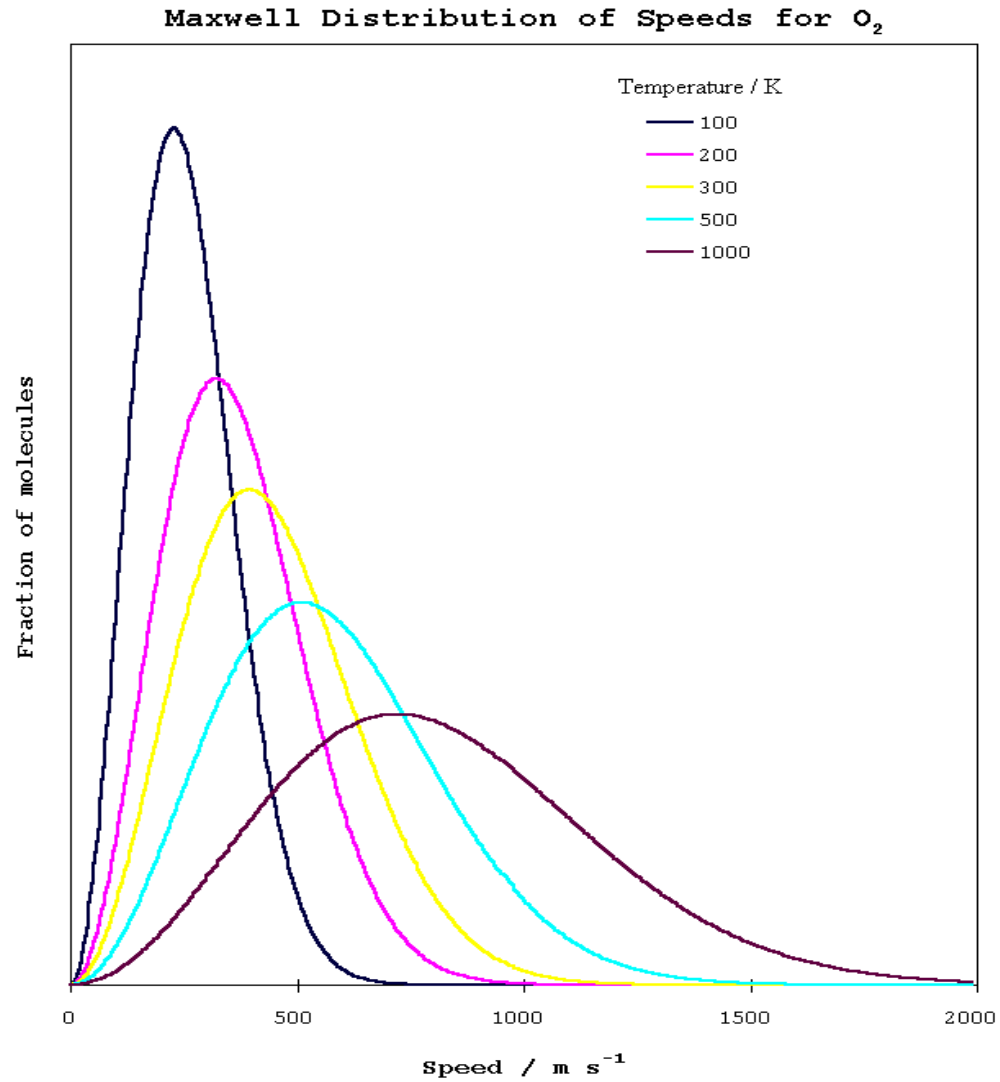
Background : Maxwell's kinetic theory

J. C. Maxwell, a confirmed atomist, developed kinetic theory of gases (기체운동론) in 1859: he pictured the gas to consist of billions of molecules moving rapidly at random, colliding with each other and with the walls of the container; **statistical averages** to see if the macroscopic properties could be predicted from a microscopic model for a collection of gas molecules.

Maxwell's analysis, based on Newton's mechanics, showed that temperature is a measure of the microscopic **mean squared velocity** of the molecules. Heat is thus caused by the ceaseless random motion of atoms.

Maxwell distribution: The real importance of Maxwell's theory is the prediction of the **probable velocity** distribution of the molecules; this gives the **range** of velocities. This is the use of probabilities when an exact calculation is impossible in practice.

Maxwell distribution



Background : statistical mechanics (통계역학)

Ludwig Boltzmann (1844-1906): general probability distribution law

Statistical mechanics: the properties of macroscopic bodies are predicted by the statistical behavior of their constituent microscopic parts: it is impossible to calculate the motion of billions and billions of particles. But the probability method can give direct answers for the most probable state.

These **new ideas-using probabilities and statistics** of microscopic systems to predict the macroscopic properties which can be measured in the laboratory (like temperature, pressure...)- underlie all of what was to come in quantum theory.



1900-1930: quantum vs. classical mechanics

Three critical experiments in the pre-quantum era which could not be explained by a straightforward applications of classical mechanics

1. Black body radiation & the UV catastrophe

2. The photoelectric effect

3. Optical spectra

and so on

Triple birth of the new quantum theory

1925-1926 **three** distinct and independent developments of a complete quantum theory were published... and then shown to be **equivalent**.

- Matrix mechanics by Werner Heisenberg (1901-76)
- Wave mechanics by Erwin Schrödinger
- Quantum algebra by Paul Dirac

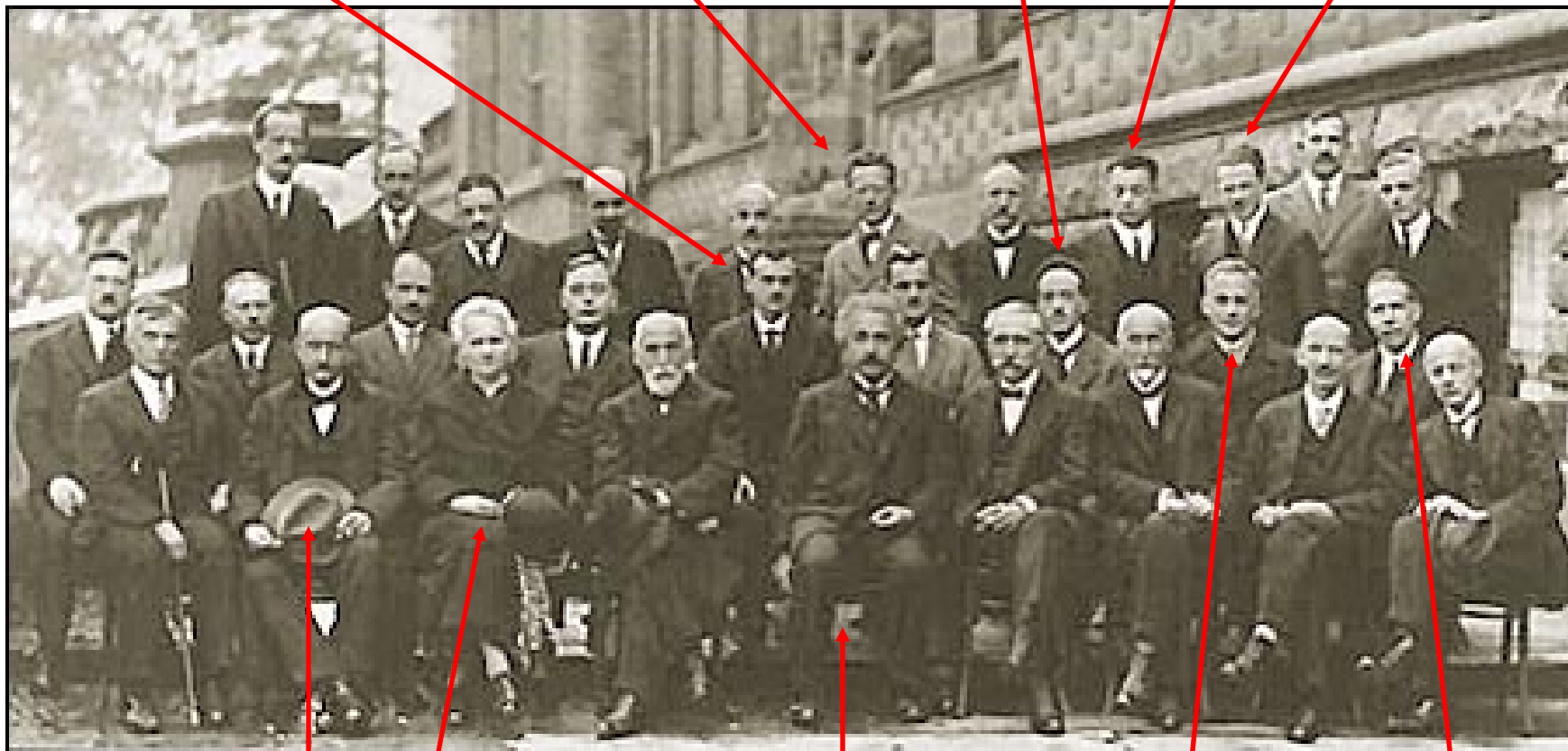
Paul Dirac
(1902-84)

Erwin Schrödinger
(1887-1961)

Louis de Broglie (1900-58)
(1892-1987)

Wolfgang Pauli

Werner Heisenberg
(1901-76)



Max Planck(1858-1947)

Max Born(1882-1970)

Marie Curie(1867-1934)

Albert Einstein(1879-1955)

Niels Bohr
(1885-1962)

Basic Classical Mechanics

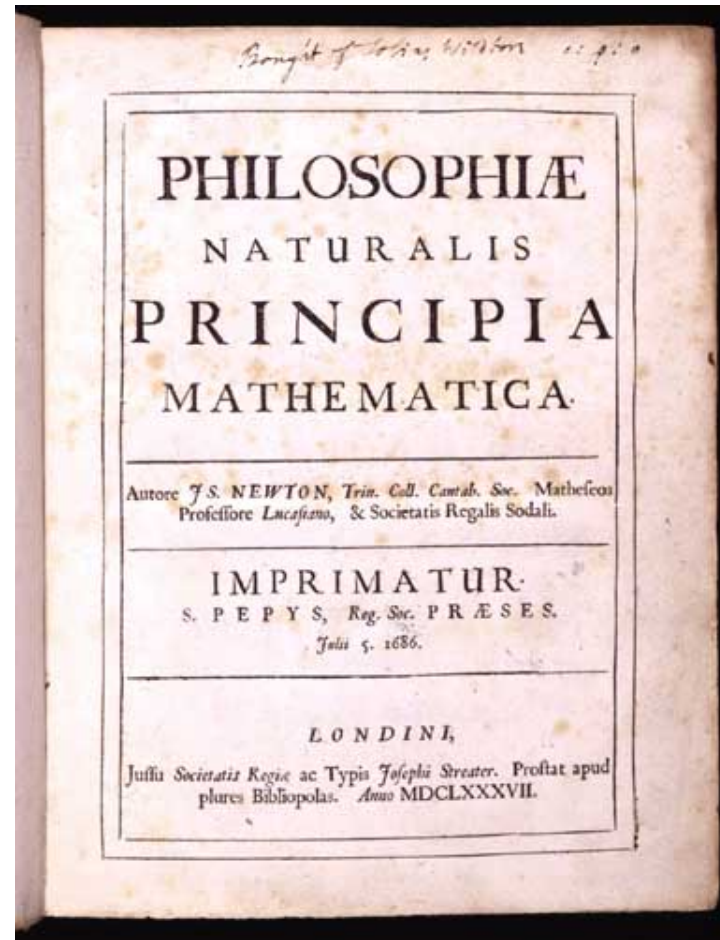
Reading: Atkins, Appendix 3 (pp. 979-984)

17 C, Isaac Newton

→ successful at explaining the motion of everyday objects and planets

→ failed at very small particles (20th century)

Newton's Mechanics



1. Main features

- 1) Trajectory (궤적) is completely determined → deterministic
cf) quantum mechanics: probability
- 2) Energy can take any non-negative value → allows the translational, rotational, and vibrational modes of motion to be excited to any energy simply by controlling the forces
cf) Q. M.: discrete
- 3) Measurement of dynamic variables can be made as precisely as we wish → no inherent limitation in accuracy
cf) Q. M.: uncertain

2. Total energy

Total energy of a particle : $E = E_k + V(x)$

E_k : kinetic energy (from the motion)

$V(x)$: potential energy (from the position)

Force $F = -(dV(x)/dx)$

→ The direction of the force is towards decreasing potential energy

$$E_k = (1/2)mv^2 = p^2/2m \text{ (since } \mathbf{p} = m\mathbf{v}, \text{ linear momentum)}$$

Total energy $E = p^2/2m + V(x)$

→ Particle has a definite trajectory, or define position and momentum at each instant

e.g.) $V = 0, v = (dx/dt)$

$$v = (dx/dt) = (2E_k/m)^{1/2}$$

$$\Rightarrow x(t) = x(0) + (2E_k/m)^{1/2}t$$

$$p(t) = mv(t) = m(dx/dt) = (2mE_k)^{1/2}$$

If we know initial position & momentum, we can predict all later positions & momenta exactly

3. Newton's 2nd law of motion

the rate of change of momentum = the force acting on the particle

$$\mathbf{F} = d\mathbf{p}/dt = d(m\mathbf{v})/dt = m(d^2\mathbf{r}/dt^2) = m\mathbf{a}$$

$$\mathbf{r} = \mathbf{r}(x, y, z)$$

e.g.) 1-dimension, $F = m(d^2x/dt^2)$ (d^2x/dt^2) : acceleration of particle

trajectory: $\mathbf{r} = \mathbf{r}(t, \mathbf{v}_0, \mathbf{r}_0)$, $\mathbf{p} = \mathbf{p}(t, \mathbf{v}_0)$

E_k ; $0 \rightarrow E_k = F^2\tau^2/(2m)$ by $t = 0 \rightarrow t = \tau$; any energy value available

4. Rotational motion

angular momentum J

$$\mathbf{J} = I\boldsymbol{\omega}$$

$\boldsymbol{\omega}$: angular velocity (radians/s),

I : moment of inertia ($I = mr^2$)

To accelerate a rotation, it is necessary to apply a torque
torque T , a twisting force

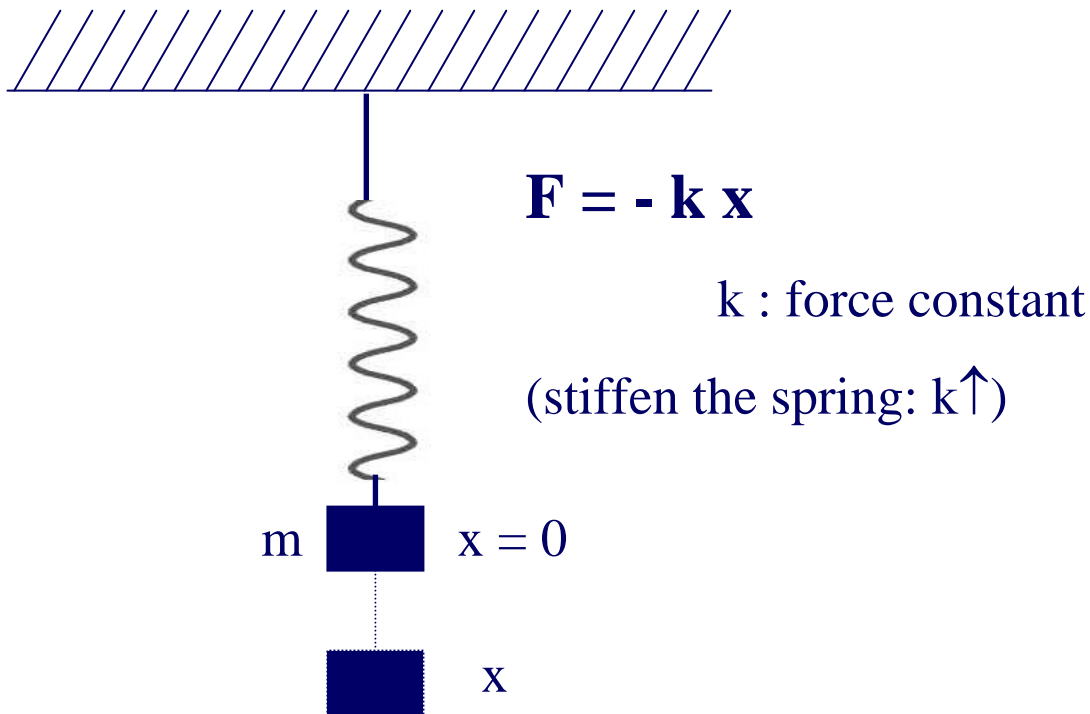
$$T = dJ/dt$$

Rotation energy

$$0 \rightarrow E_k = T^2\tau^2/2I \text{ by time } 0 \rightarrow \tau$$

→ arbitrary rotational energy available

5. Harmonic oscillator → vibration



-: force direction → opposite to displacement

$$F = -kx$$

k: force constant

$$m(d^2x/dt^2) = -kx$$

$$d^2x/dt^2 + \omega^2x = 0$$

where $\omega = \sqrt{(k/m)}$; angular frequency

$$\rightarrow \omega = 2\pi\nu, \text{ frequency } \nu = \omega/2\pi = (1/2\pi)\sqrt{(k/m)}$$

$$x(t) = A\sin\omega t \quad (A: \text{amplitude})$$

$$p(t) = m\omega A\cos\omega t \quad (\text{since } p = mv = m(dx/dt))$$

$$E_k = p^2/2m = 1/2m\omega^2A^2\cos^2\omega t = 1/2kA^2\cos^2\omega t$$

$$F = -kx = -dV/dx$$

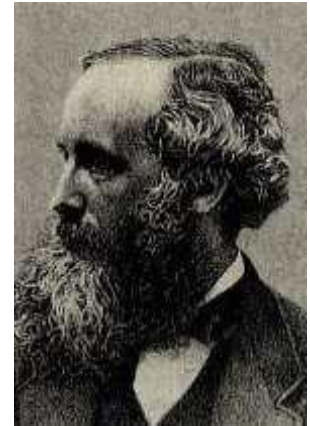
$$V = 1/2kx^2 = 1/2kA^2\sin^2\omega t$$

$$\text{Total } E = E_k + V = 1/2kA^2\cos^2\omega t + 1/2kA^2\sin^2\omega t = 1/2kA^2$$

→ any vibrational energy available (amplitude (A) governs the energy, independent of frequency)

Classical mechanics: agree with everyday experience → **does not** extend to very small particles, such as individual atoms

Electromagnetic Theory of Radiation



Electromagnetic field

- In classical physics, electromagnetic radiation is understood in terms of electromagnetic field
 - An oscillating electric and magnetic disturbance (even in vacuum) (electric field + magnetic field)
- travel at constant speed: “speed of light” (c)
- wavelength λ (lambda),
frequency ν (nu, Hz) $\lambda \nu = c$
wavenumber ($\tilde{\nu}$) (nu tilde, cm^{-1}):

$$\tilde{\nu} = \nu / c = 1 / \lambda$$

Electromagnetic radiation

Travelling x-direction

$$\text{Electric field } E(x,t) = E_0 \cos[2\pi \nu t - (2\pi/\lambda)x + \phi]$$

$$\text{Magnetic field } B(x,t) = B_0 \cos[2\pi \nu t - (2\pi/\lambda)x + \phi]$$

E_0 & B_0 : the amplitudes of the fields

ϕ : phase of the wave ($-\pi$ to π): two waves $\phi = 0 \rightarrow$ constructive

$\phi = \pi$ or $-\pi \rightarrow$ destructive

E & B: plane polarized

Differentiation

$$\left(\frac{\partial^2}{\partial x^2}\right)\Psi(x,t) = -(4\pi^2/\lambda^2)\Psi(x,t), \quad \left(\frac{\partial^2}{\partial t^2}\right)\Psi(x,t) = -4\pi^2\nu^2\Psi(x,t)$$

$\Psi(x,t)$: either $E(x,t)$ or $B(x,t)$

Intensity of electromagnetic radiation \propto square of the wave amplitude
(energy) E_0^2 or B_0^2

The Failures of Classical Mechanics (Physics)

Reading: Atkins, ch. 8 (p. 244-252)

e.g., black-body radiation
heat capacity of solid
photoelectric effect
atomic spectra etc

1. Black-body radiation

- hot object emit electromagnetic radiation
e.g., iron bar: red \rightarrow yellow \rightarrow blue \rightarrow ...; $T \uparrow \rightarrow$ wavelength $\lambda \downarrow$,
frequency $\nu \uparrow$

- black-body: ideal emitter, perfect absorber & perfect emitter
many times absorption & emission → thermal equilibrium at temperature T
→ leaking out through pinhole

$T \uparrow$ color shifts toward the blue

- **Wien's law** (Wien's displacement law, 1893)

$$T\lambda_{\max} = \text{const.} = 1/5c_2, c_2 = 1.44 \text{ cm}\cdot\text{K}$$

λ_{\max} : maximum distribution wavelength at T

e.g., at 1000 K $\rightarrow \lambda_{\max} \sim 2900 \text{ nm}$

Sunlight peak at $\sim 500 \text{ nm} \rightarrow T = 5800 \text{ K}$

- **Stefan-Boltzman law** (1879)

Total energy density ϵ , ($\epsilon = E/V$, radiation energy per unit volume)

$$\epsilon = aT^4$$

or

excitance M , (radiation power per unit surface, the brightness of the emission)

$$M = \sigma T^4$$

σ (Stefan-Boltzman constant): $5.67 \times 10^{-8} \text{ Wm}^{-2}\text{K}^{-4}$

e.g., 1 cm^2 surface at 1000 K radiate about 6 W (cf. $\text{W} = \text{J/s}$)

- Rayleigh-Jeans law

19 C, Rayleigh → classical approach: electromagnetic field as a collection of a oscillators of all possible frequencies

→ energy distribution calculation from mean energy $\langle E \rangle = kT$ for each oscillator

Rayleigh-Jeans law

$$d\varepsilon = \rho d\lambda, \quad \rho = (8\pi \langle E \rangle / \lambda^4) d\lambda = (8\pi kT / \lambda^4) d\lambda$$

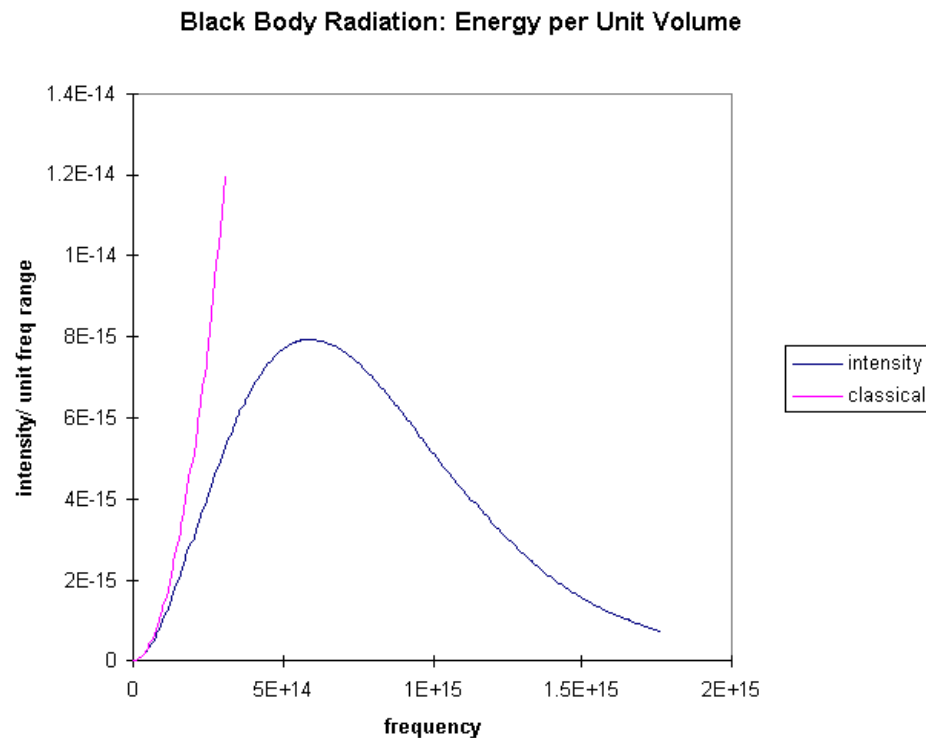
ε : energy density, ρ : proportionality constant,

k : Boltzmann constant ($1.381 \times 10^{-23} \text{ JK}^{-1}$)

⇒ quite successful at long λ

⇒ but it fails at lower λ (UV, X-rays...) “Ultraviolet catastrophe”(자외선 파탄)

$$\text{or } \lambda = c/\nu, \lambda\nu = c \rightarrow d\nu = -c(d\lambda/\lambda^2) \rightarrow d\lambda = -\lambda^2 d\nu/c$$
$$d\varepsilon = (8\pi\nu^2 kT/c^3) d\nu$$



- classical mechanics: even cool objects should radiate in the visible and UV regions → no darkness even at low T (?)

- **The Planck distribution**

- In 1900, Max Planck propose each oscillator is not continuous →
energy quantization

(proposing that the energy of each oscillator is limited to discrete values and cannot be varied arbitrarily)

cf) classical mechanics: all possible energies are allowed

$E = h\nu, 2h\nu, 3h\nu, \dots$ (integer multiples of $h\nu$)

$E = nh\nu, n = 0, 1, 2, 3, \dots$

h : Planck constant, 6.626×10^{-34} J·s

$\lambda\nu = c$, λ : wavelength, ν : frequency

- classical mechanics
average energy $\langle E \rangle$

- Planck
average energy $\langle E \rangle$

- Short λ

- long λ

2. Heat capacity

- Dulong & Petit's law (19 C)

monatomic solid: $\langle E \rangle = kT$ for each direction $\rightarrow 3kT$ for 3-D

N atoms: molar internal energy $U_m = 3N_A kT = 3RT$

constant volume heat capacity

$$C_{V,m} = (\partial U_m / \partial T)_V = 3R (= 24.9 \text{ JK}^{-1}\text{mol}^{-1})$$

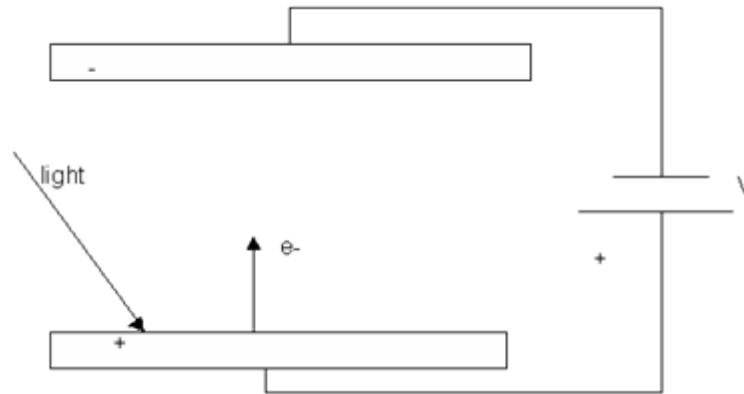
Deviation at low temperature: $T \rightarrow 0 \Rightarrow C_{V,m} \rightarrow 0$

- Einstein formula (1905)
 - all the atoms oscillate with the same frequency → at low T, few oscillators possess energy to oscillate; T ↑, enough energy for all the oscillators
 - using Planck's hypothesis ($E = nh\nu$)
all $3N$ atomic oscillators → vibrational energy of crystal: $3N\langle E \rangle$

- still poor in experimental data since Einstein assumed all the atoms oscillate with the same frequency

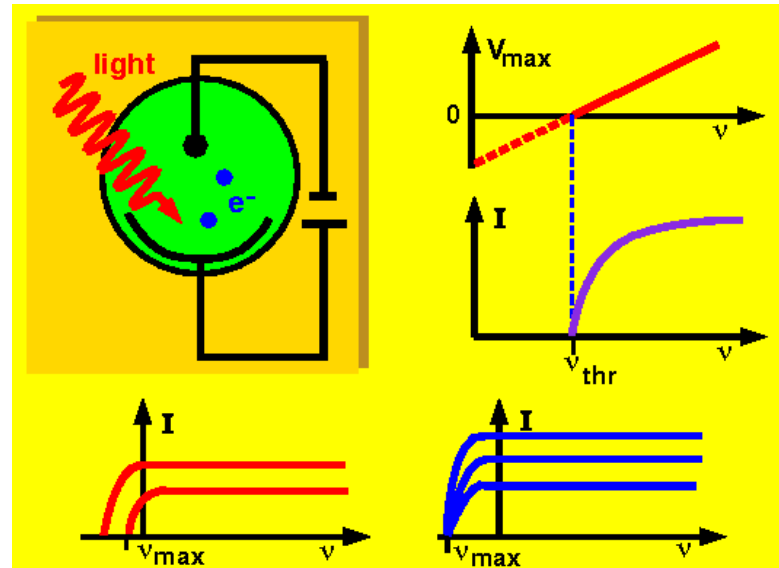
3. The photoelectric effect

Philipp Lenard (1862-1947): the light ejects electrons from the metal (**photoelectron**)



Classical viewpoint would assume that the light waves beat on the metal surface like ocean waves and the electrons are distributed like pebbles on a beach. **More intense illumination (i.e. brighter) would deliver more energy to the electrons.** However,.....

1902 Lenard: the electron energy were entirely independent of the light intensity. Further, there was a certain threshold frequency below which no photoelectron were ejected, no matter how bright the light beam.



Albert Einstein (1905) showed that the puzzle of photoelectric effect are easily explained once the illuminating radiation is a collection of particles (photons): qV (kinetic energy of electron) = $h\nu$ (energy of the incoming photon) – P (work to get out of the metal)

- Einstein (1905-6)

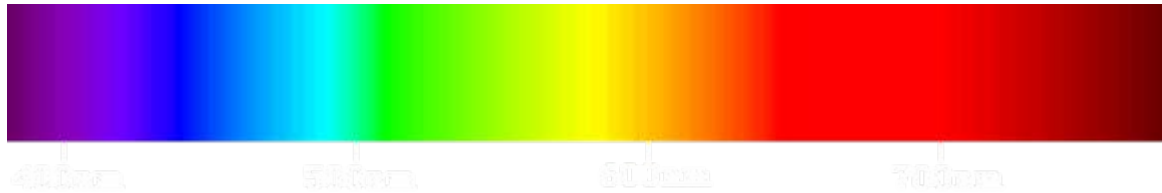
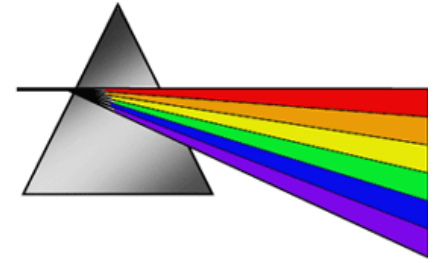
- $\nu < \nu_0$ (threshold ν): no emission, even at strong radiation intensity
 $\nu > \nu_0$: electron emission even at very low intensity

- kinetic energy of ejected electron $\propto \nu$, independent of radiation intensity
if $h\nu > \Phi$ (work function): electron emission

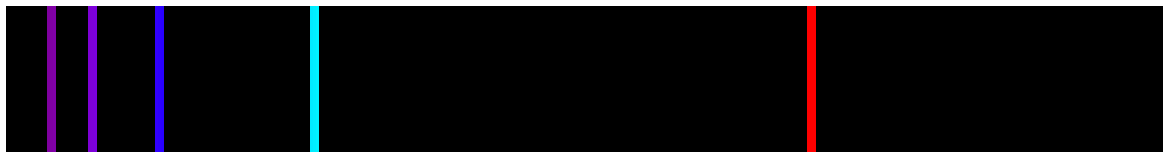
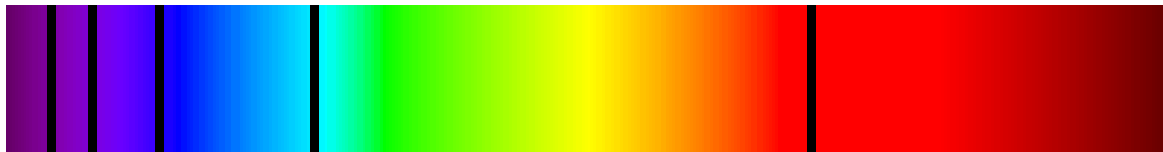
$$\frac{1}{2}m_e v^2 = h\nu - \Phi$$

- Φ : the energy required to remove an electron from the metal to infinity
→ energy depended on the frequency of the incident light $\Rightarrow nh\nu$

4. Atomic & molecular spectra



1862 A. J. Angstrom (1814-74) : hydrogen



What do these lines mean? All this was very puzzling!

- spectrum: radiation absorbed or emitted by atoms & molecules

→ radiation is emitted or absorbed at a series of discrete frequencies
→ energy of atoms/molecules is confined to discrete values

- Balmer (1885): visible spectrum of atomic hydrogen
 $1/\lambda = R_H(1/2^2 - 1/n^2)$, $n = 3, 4, \dots$; empirical expression
 R_H : Rydberg const ($= 1.09678 \times 10^5 \text{ cm}^{-1}$)

Lyman: UV series, $1/\lambda = R_H(1/1^2 - 1/n^2)$,

Paschen: IR, $1/\lambda = R_H(1/3^2 - 1/n^2)$,

- Why lines? \Rightarrow Bohr (1913): Planck quantum hypothesis + classical mechanics
- Bohr's hypothesis
 - (1) electrons exist in a discrete set of stable, stationary orbits in the atom
 - cf) perfect orbit: different from that in quantum mechanics
 - (2) transition between orbits: $\Delta E = h\nu \rightarrow$ frequency $\nu = \Delta E/h$
 - (3) dynamical equilibrium between proton and electron
 - electrostatic attraction force = centrifugal force
 - (4) angular momentum of orbital: quantized

⇒ Energy is quantized

- Only explain hydrogen (one-electron) spectra
 - 1) fail to explain the spectra of atoms more than one electron
 - 2) incorrect to regard the electrons in atoms as discrete particles with precise positions and velocities