8. Micro & Nanoscale Phenomena
8.1 Classical size effects
In section 7, the characteristic length of the box is much longer than the mean free path Λ. Therefore, the collisions between molecules and the wall are neglected in our derivation and thermal conductivity is regarded as the bulk property of the gas. However, there are many applications in which Λ becomes comparable or larger than the size of the system. The classical size effects occur in such situations.

Example 1: $\Lambda > d$ for a disk drive   Example 2: $\Lambda \sim d$ or $\Lambda > d$ for thin films
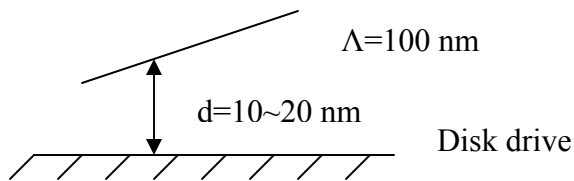
Λ=100 nm

d=10~20 nm

Disk drive

Thin film k
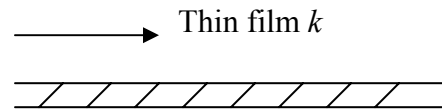
In example 2, we can further reduce the film thickness to enhance the size effects. With measured data for k and specific heat c, the mean free path in silicon can be estimated by

$$k = \frac{cv\Lambda}{3},$$

where v is sound velocity. The approximated mean free path Λ is around 40 nm, while the actual value is around 300 nm. The size effects occur for silicon films with thickness less than Λ.

Note: in some thermal insulation applications, we also use porous materials whose pore sizes are comparable to or less than Λ. The thermal conductivity of the air trapped in the pores will be significantly reduced.

8.2 Quantum size effects
According to quantum mechanics, electrons and phonons are also material waves; the finite size of the system can influence the energy transport by altering the wave characteristics, such as forming standing waves and creating new modes that do not exist in bulk materials.

For example, electrons in a thin film can be approximated as standing waves sitting inside a potential well of infinite height. The condition for the formation of such standing waves is that the wavelength, λ, satisfies the following relation
$D = \lambda n / 2$ (n=1,2,…),
where D is the width of the potential well. According to the de Broglie relation, the wavelength is
$\lambda = h / p$,

where h is Planck constant (h=6.6x10^{-34} Js), p is momentum. The energy of the electron is thus E=p^2/2m or $E = \dfrac{p^2}{2m} = \dfrac{h^2}{8m}(\dfrac{n}{D})^2$.

n=2

n=1

D
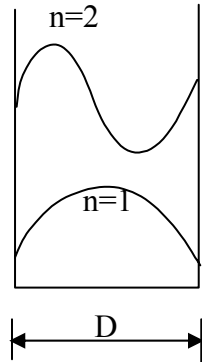
1) For a free electron, D=1 mm, we have

$$E = \dfrac{n^2}{8 \times 9.1 \times 10^{-31}}(\dfrac{6.6 \times 10^{-34}}{10^{-3}})^2 \sim 10^{-34} n^2 << k_B T = 4.14 \times 10^{-21} J \text{ at room temperature.}$$

2) For D=1e-8 m, we calculate $E > k_B T$. Further reducing D results in more observable E.

8.3 Fast transport

For many materials, we have $\tau = 10^{-12} - 10^{-11} s$. Laser pulse can be as short as a few femtosecond, we cannot use diffusion theory when the time scale is shorter than the relaxation time.

Chapter 2 Material Waves & Energy Quantization

2.1 Basic wave characteristics

2.1.1 Traveling wave

First consider a harmonic wave (such as an electric or a magnetic field) represented by a sine function traveling along the positive x-direction,

$$\vec{\Phi} = A\sin(2\pi ft - \dfrac{2\pi x}{\lambda})\hat{y}$$

$$= A\sin(\omega t - kx) ,$$

where $\omega = 2\pi f$ denote angular frequency, $k = 2\pi / \lambda$ denote wavevector magnitude, $\hat{y}$ is a unit vector in the y-coordinate direction. Here $2\pi ft$ is the time term, while $\dfrac{2\pi x}{\lambda}$ is the spatial term.

For constant phase, i.e., $\omega t - kx = const$, we have

$$\dfrac{dx}{dt} = \dfrac{\omega}{k} = f\lambda = v_p ,$$

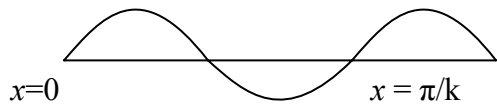where v_p is phase velocity. It indicates how fast the wave phase is propagating.

Note: for light we have a linear relationship $\omega = ck$.

2.1.2 Complex representation

It is convenient to use the complex representation of the sine and cosine functions, e.g.

$$A\,e^{-i(\omega t - kx)} = A\left[\cos(\omega t\text{-}kx) - i\sin(\omega t - kx)\right].$$

2.1.3 Standing wave

$x=0$ $x = \pi/k$

We can create a standing wave by superimposing two traveling waves along the positive and negative x-directions (assuming that the problem is linear such that the superposition principle applies),

$$\mathbf{\Phi} = A\left[\sin(\omega t - kx) - \sin(\omega t + kx)\right]\hat{y} = -2A\cos(\omega t)\sin(kx)\,\hat{y},$$

which has fixed nodes in space such that $\mathbf{\Phi}=0$. These nodes are similar to the string ends of a guitar.

The energy of a wave is typically $U \propto |\mathbf{\Phi}|^2$.

2.2 Wave-particle duality
2.2.1 Electromagnetic (EM) wave

Quantum mechanics started with the explanation for blackbody radiation and the absorption spectra of gases. Isaac Newton (1642-1727) believed that radiation was particle-like in nature rather than wave-like, as we are more familiar with today. It was the discovery and explanation of interference and diffraction phenomena, from the work of Christian Huygens (1629-1695), Thomas Young (1773-1829), Augustin Jean Fresnel (1788-1827), and others, followed by Maxwell (1831-1879) and his celebrated equations that solidified the foundation of the wave nature of the electromagnetic field.

The Maxwell equations, however, fail to explain the emission and absorption processes, such as the experimentally observed fine spectra of absorption in various gases, and the blackbody radiation.
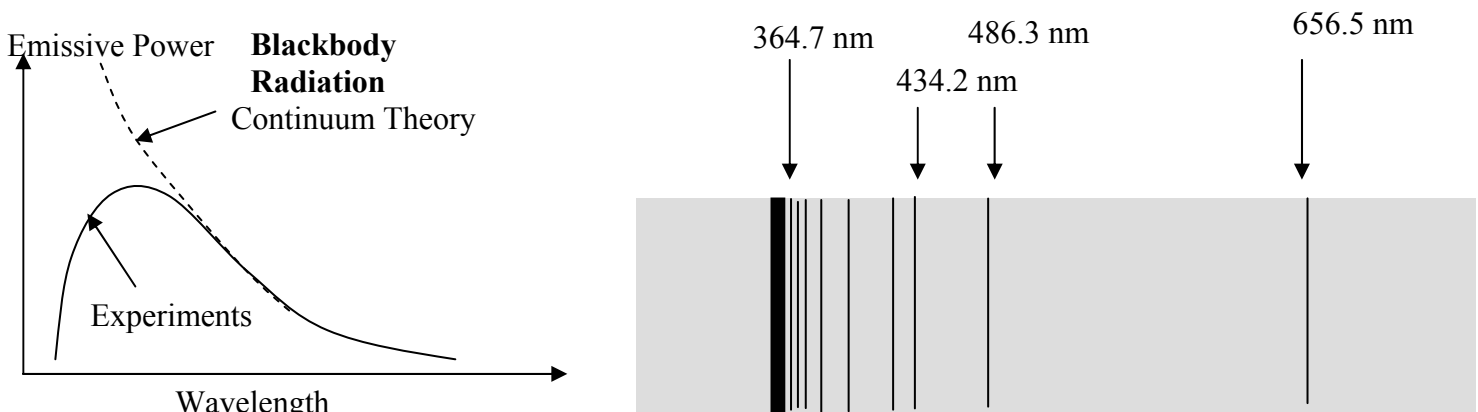
To explain the blackbody radiation, Max Planck (1858-1948) introduced a radical hypothesis that the allowable energy of the electromagnetic field at a frequency ν is not continuous, but is a multiple of the following basic energy unit

$E = nh\nu$,

in which h is called the Planck constant and has a value h=6.6x10^{-34} J·s.

According to the relativity theory, we have

$E = mc^2$.

Thus the momentum is

$p = mc = E/c = h\nu/c = h/\lambda$.

After 1926, people used the term "photon" to name the quantum with $E = h\nu$, $p = h/\lambda$.

Einstein used the corpuscular characteristics of electromagnetic radiation to explain some puzzling results from the basic photoelectricity experiment in the following figure. Based on the photon particle concept, Einstein reasoned that one photon can excite an electron out of the metal surface only when the photon energy is higher than the work function A (=E_v-E_f), which is the energy difference between electrons at the vacuum level, E_v, and inside the metal, E_f, i.e.,

$h\nu_p \geq E_v$-E_f.
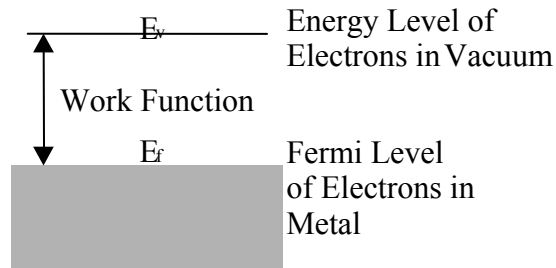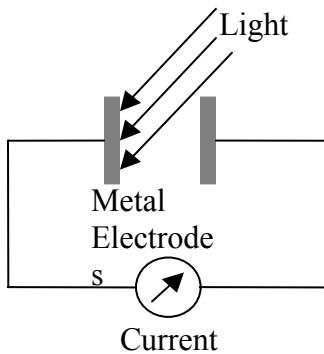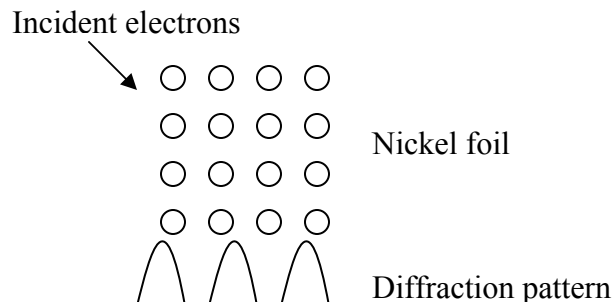

2.2.2 Material wave

The wave-particle duality of light triggered de Broglie to postulate that a material particle also has wave properties. Based on an analogy to the Planck-Einstein relations, he proposed that the wavelength of any particle is

λ=h/p,

where p is the magnitude of the particle momentum.

An electron with a velocity 1 m/s and a mass of 9.1×10^{-31} kg yields 0.7×10^{-3} m, a quite long wavelength. The first proof of the wave properties of particles came from the electron diffraction experiment, in which peak signals are observed in specified incident angles.

Transmission Electron Microscope (TEM)
A TEM uses thermal excitation or applying a high voltage to draw electrons from the tip end. The electrons are then accelerated by the strong electrical field to gain a large momentum p (small $\lambda \sim 1$ Å). Since the resolution is normally comparable to wavelength λ, high resolution is obtained with electron energy as high as MeV magnitude. The electrons penetrate through the sample (less than 200 nm thick) and the diffraction/transmission is observed from the detector.
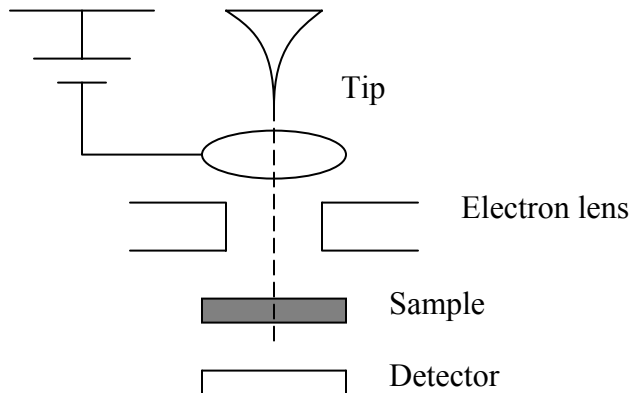
Scanning Electron Microscope (SEM)
Different from a TEM, a SEM only observes the surface and electrons do not penetrate the sample. Electrons have lower energy in a SEM.

2.2.3 Mathematical Description of Waves
Two basic methods have been developed to describe the materials waves. The first was the matrix method developed by Heisenberg (1925). Shortly after, Schrödinger developed the famous equation that bears his name. These two descriptions are equivalent among themselves, so we will focus on the Schrödinger equation (Schrödinger, 1926). The equation states that the wavefunction of any matter obeys the equation,

$$ -\frac{\hbar^2}{2m}\nabla^2\Psi_t + U\Psi_t = i\hbar\frac{\partial \Psi_t}{\partial t}, $$

where m is the mass, t is the time, U is the potential energy (related to b.c), and Ψ_t is called the wave function of the matter, $\hbar = h/2\pi$. If $U=0$, the Schrödinger equation becomes

$$ -\frac{\hbar^2}{2m}\nabla^2\Psi_t = i\hbar\frac{\partial \Psi_t}{\partial t}, $$

which is similar to heat conduction equation $k\nabla^2 T = \rho c \frac{\partial T}{\partial t}$ but the magic imaginary unit "i" really gives rise to wave behavior.

Schrödinger himself did not come up with a correct explanation for the meaning of wavefunction. The right explanation was given by Born, who suggested that Ψ_t itself is not an observable quantity, but $\Psi_t \Psi_t^*$ is the probability density function to find the particle at location x, where "*" means complex conjugate. The normalization requirement for the probability function is then

$$\int \Psi_t^* \Psi_t dV = 1 .$$

The expectation value of any quantity (such as energy, momentum, location, etc.) can be calculated from

$$< \Omega >= \int \Psi_t^* \Omega \Psi_t dV .$$

In quantum mechanics, quantities such as location, energy, and momentum of matter should be understood in terms of probability values. These quantities are expressed by operators, such as position operator:
$$\Omega = \mathbf{r}$$
time operator:
$$\Omega = t$$
momentum operator:
$$\mathbf{\Omega} = \mathbf{p} = -i\hbar\nabla$$

$$= -i\hbar\left(\frac{\partial}{\partial x}\hat{\mathbf{x}} + \frac{\partial}{\partial y}\hat{\mathbf{y}} + \frac{\partial}{\partial z}\hat{\mathbf{z}} \right) = p_x\hat{\mathbf{x}} + p_y\hat{\mathbf{y}} + p_z\hat{\mathbf{z}}$$

and the energy operator

$$\Omega = H = \frac{\mathbf{p}\bullet\mathbf{p}}{2m} + U = \frac{\mathbf{p}^2}{2m} + U$$

$$= -\frac{\hbar^2}{2m}\nabla^2 + U = -\frac{\hbar^2}{2m}\left(\frac{\partial}{\partial x^2} + \frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2} \right) + U$$

Note: in equation $< \Omega >= \int \Psi_t^* \Omega \Psi_t dV$, you cannot switch Ψ_t^* and Ψ_t if Ω contains the gradient operator ∇ and the Laplace operator ∇^2.

Standard deviation:
Similar to

$$\Delta x = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x- <x>)^2} ,$$

in quantum mechanics we have

$$< \Delta q >= \sqrt{\int \Psi_t^*(q- <q>)^2\Psi_t dV} .$$

Heisenberg uncertainty principle states

$$< \Delta p >< \Delta x >\geq \frac{\hbar}{2} ; < \Delta t >< \Delta E >\geq \frac{\hbar}{2} .$$

From the Schrödinger equation, we can derive

$$\frac{\partial |\Psi_t|^2}{\partial t} + \nabla \cdot \vec{J} = 0,$$

where the first term means the changing rate of density, the second flux term is

$$\vec{J} = \frac{i\hbar}{2m}(\Psi_t \nabla \Psi_t^* - \Psi_t^* \nabla \Psi_t).$$

Note: please compare this to continuity equation $\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = 0$.

Separation of variables:
Assuming $\Psi_t(\mathbf{r},t) = \Psi(\mathbf{r})Y(t)$ and substituting into the Schrödinger equation, we get

$$\frac{1}{\Psi}\left[-\frac{\hbar^2}{2m}\nabla^2\Psi + U\Psi \right] = i\hbar\frac{1}{Y}\frac{dY}{dt} = E,$$

where E is a constant (eigenvalue) since Ψ depends on $\mathbf{r}$ only and Y depends on t only. Its meaning will be explained later ($\langle H \rangle = E$). Solving for Y leads to

$$Y = C_1 \exp\left[-i\frac{E}{\hbar}t \right] = C_1 \exp[-i\omega t].$$

And the governing equation for $\Psi(r)$ is called the steady-state Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + (U - E)\Psi = 0.$$

This is an eigen equation with the eigenvalue E and eigenfunction Ψ determined by the potential profile U and the boundary conditions.