

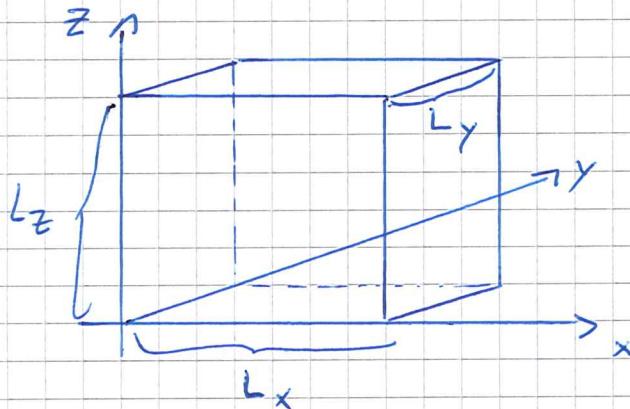
THREE-DIMENSIONAL BOX

Q8.1, H.52, G.531

Energy levels

3D infinite well:

$$V(x, y, z) = \begin{cases} 0, & 0 < x < L_x, 0 < y < L_y, 0 < z < L_z \\ \infty, & \text{otherwise.} \end{cases}$$



Since the Schrödinger equation separates,

$$\hat{H}\psi = -\frac{\hbar^2}{2m} \nabla^2 \psi = -\frac{\hbar^2}{2m} (\partial_x^2 + \partial_y^2 + \partial_z^2) \psi = E\psi$$

$$= (E_x + E_y + E_z) \psi;$$

We can use the solution from the 1D case of the infinite square well:

$$\psi_{n_x}(x) = \sqrt{\frac{2}{L_x}} \sin k_x x, \quad k_x = \frac{n_x \pi}{L_x}, \quad n_x = 1, 2, \dots$$

$$E_{n_x} = \frac{\hbar^2 k_x^2}{2m}.$$

For the 3D case, we therefore get

$$\psi_{n_x n_y n_z}(x, y, z) = \sqrt{\frac{8}{L_x L_y L_z}} \sin \frac{n_x \pi x}{L_x} \sin \frac{n_y \pi y}{L_y} \sin \frac{n_z \pi z}{L_z}$$

$$E_{n_x n_y n_z} = \frac{\hbar^2 c^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

Degeneracy due to symmetry

From the energy levels we notice that if two or more of the sides of the box are the same, e.g. $L_x = L_y$, we get degenerate eigenvalues, for instance $E_{211} = E_{121}$. The system has a symmetry which leads to degeneracy! If all sides are the same, we get even more degeneracy.

In quantum mechanics, what we mean when we say that the system has a symmetry, is that the Hamiltonian is unchanged by some transformation.

In this case, if $L_x = L_y = L_z$, the Hamiltonian is unchanged by $\frac{\pi}{2}$ rotations about the x, y or z axes.

We might take a more formal look at this at a later point.

Density of states

Important application of the 3D box is the description of ideal gases, including "gases" of electrons. In solids, the loosely-bound outermost valence electrons in each atom can become detached, roaming around throughout the material without interacting. This is denoted the "free electron gas". The gases are "free" or "ideal" in the sense that we neglect interactions.

In a macroscopic volume, $V = L_x L_y L_z$, the energy levels, $E_n \sim \frac{n^2}{L^2}$, become closely spaced. In the statistical treatment of systems with many particles, the number of quantum states per unit energy plays an important role: the density of states. (DOS)

To calculate the DOS we will use the wavevector $\vec{k} = (k_x, k_y, k_z)$, with

$$k_x = \frac{\pi n_x}{L_x}, \quad k_y = \frac{\pi n_y}{L_y}, \quad k_z = \frac{\pi n_z}{L_z}, \quad n_i = 1, 2, \dots$$

(We could also calculate it in terms of the integers n_i , see lecture notes).

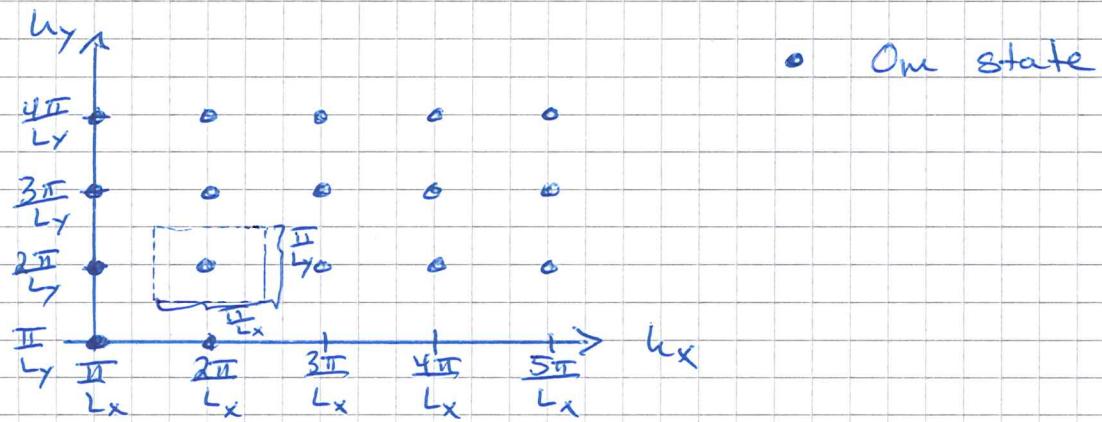
The energy is then given by

$$E_{\vec{k}} = \frac{\hbar^2}{2m} \vec{k}^2$$

The possible wavenumber values are

$$k_i = \frac{\pi}{L_i}, \frac{2\pi}{L_i}, \frac{3\pi}{L_i}, \dots$$

where each combination (k_x, k_y, k_z) represents one possible quantum state. In 2D the grid of possible states looks like



The volume occupied by one state is

$$\frac{\pi}{L_x} \cdot \frac{\pi}{L_y} \cdot \frac{\pi}{L_z} = \frac{\pi^3}{V}.$$

Hence, we find one state per "k-space" volume $\pi^3 V$, and the density of states in \vec{k} -space is

$$g(\vec{k}) = \frac{\text{number of states}}{\text{Volume}}$$

$$= \frac{1}{(\pi^3/V)} = \frac{V}{\pi^3}.$$

We are, however, interested in the density of states in energy-space.

We begin by calculating the number of states with energy less than E . We only include states such that

$$E_{\vec{h}} = \frac{\hbar^2}{2m} |\vec{k}|^2 < E \Rightarrow |\vec{k}| = \sqrt{h_x^2 + h_y^2 + h_z^2} < \sqrt{\frac{2mE}{\hbar^2}}$$

We call the maximum wavenumber

$$h_{\max} = \frac{\sqrt{2mE}}{\hbar}$$

The number of states is then given by

$$N = \underbrace{\frac{1}{8} \int_0^{h_{\max}} dh}_{\text{Volume in } \vec{h}\text{-space}} \cdot \underbrace{g(\vec{h})}_{\text{density of states in } \vec{h}\text{-space}}$$

$$\int d\vec{h} = \int_0^{h_{\max}} \int_0^{\pi} \int_0^{2\pi} d\vec{q} \sin\theta$$

$$= \frac{1}{8} \frac{4\pi}{3} h_{\max}^3 \cdot \frac{V}{\pi^3} = \frac{V}{6\pi^2} h_{\max}^3$$

Insert for h_{\max} ,

$$N(E) = \frac{V}{6\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{3/2}$$

We can now calculate the DOS

$$g(E) = \frac{\# \text{ states in energy interval}}{\text{energy interval}}$$

$$= \lim_{\Delta E \rightarrow 0} \frac{N(E + \Delta E) - N(E)}{\Delta E} = \frac{dN}{dE}$$

$$= \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}$$

In 2D we instead get:

$$\begin{aligned}
 N^{(2D)} &= \frac{1}{4} \int_0^{k_{\max}} d\tilde{h} \cdot g(\tilde{h}) \\
 &= \frac{1}{4} \pi k_{\max}^2 \cdot \frac{V}{\pi^2} = \frac{V k_{\max}^2}{4\pi} \\
 &= \frac{\sqrt{2mE}}{4\pi\hbar^2} = \frac{\sqrt{m}}{2\pi\hbar^2} E
 \end{aligned}$$

$$\Rightarrow g^{(2D)}(E) = \frac{dN^{(2D)}}{dE} = \frac{\sqrt{m}}{2\pi\hbar^2},$$

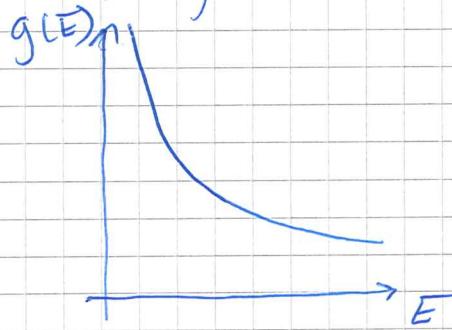
a constant! Now $V = L_x L_y$.

Finally, in 1D

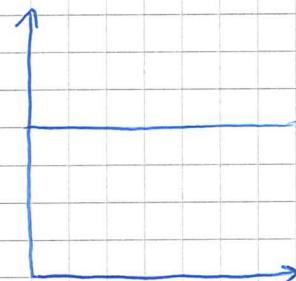
$$\begin{aligned}
 N^{(1D)} &= \frac{1}{2} \int_0^{k_{\max}} d\tilde{h} \cdot g(\tilde{h}) \\
 &= k_{\max} \cdot \frac{L_x}{\pi} = \frac{\sqrt{2mE}}{\hbar\pi} \cdot L_x
 \end{aligned}$$

$$\rightarrow g^{(1D)}(E) = \frac{dN^{(1D)}}{dE} = \frac{\sqrt{2mL}}{2\pi\hbar} \frac{1}{E}.$$

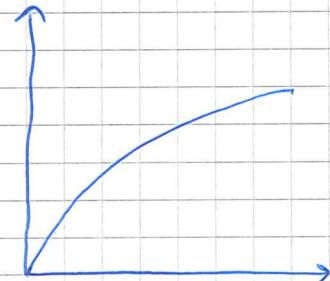
We therefore have:



1D



2D



3D

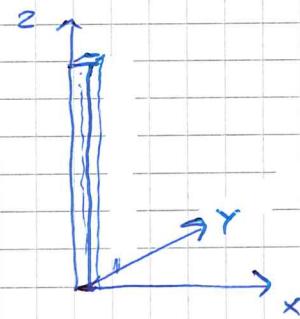
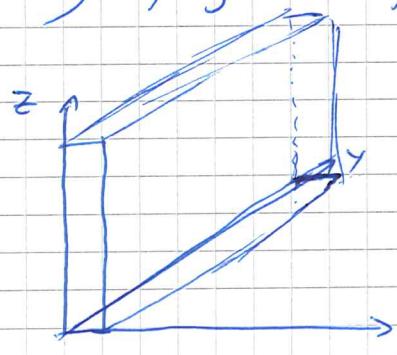
Note: 1D or 2D systems are not purely theoretical constructs. Look at the energy

$$E_{n_x n_y n_z} = \frac{\pi^2 \hbar^2}{2m} \left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right]$$

If we choose L_x very small, $L_x \ll L_y, L_z$, the energy $\pi^2 \hbar^2 / 2m L_x^2$ then becomes much larger than the other two, and we may never excite particles to states with $n_x > 1$. The x -dep. part of the wavefunction is then locked to the lowest state, $\psi_x(x) \approx \sin \frac{\pi x}{L_x}$.

Nothing happens with the motion in the x -direction! It's much "cheaper" to excite the system to higher n_y, n_z , and the physical processes will go on in the y, z directions — the system is effectively 2D!

To make the system effectively 1D, one can choose for instance $L_x, L_y \ll L_z$, limiting physical processes to the z direction.



PERIODIC BOUNDARY CONDITIONS

[Ch 8.1.d, H52.3, G230]

In some cases it is natural to treat a particle as a free particle, even though it is contained in a finite volume. This can for instance be the case if we do not care about effects due to the boundaries of the volume.

If we treat the particles as free, we should have a wavefunction

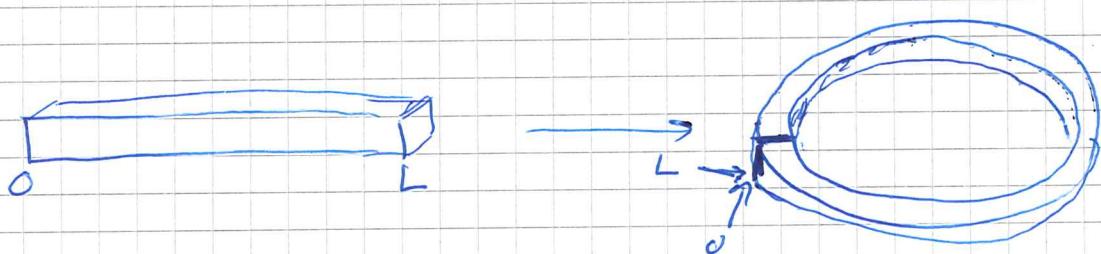
$$\psi(x) \sim e^{ikx},$$

a traveling wave with momentum hk .

For a particle in a box we used the boundary conditions

$$\psi(0) = \psi(L) = 0.$$

What are the appropriate boundary conditions in this case? We imagine that we connect the boundaries of the box:



For the wavefunction to be unique, we require

$$\psi(x) = \psi(x+L),$$

that is, the wavefunction has to be periodic. Hence, we must have

$$e^{ikx} = e^{ik(L+x)} \rightarrow e^{ikL} = 1.$$

$$\Rightarrow kL = 2\pi \cdot n, \quad n = 0, \pm 1, \pm 2, \pm 3, \dots$$

Hence, the allowed wavenumbers and energies

$$k = \frac{2\pi n}{L}, \quad n \in \mathbb{Z}$$

$$E = \frac{\hbar^2 k^2}{2m} = \frac{(2\pi n)^2}{2m L^2} n^2$$

We also need to determine the prefactor A of the wavefunction $\psi = Ae^{ikx}$. We require orthonormality:

$$\begin{aligned} I &= \int_0^L dx \psi_n^* \psi_{n'} = |A|^2 \int_0^L dx e^{i(k-k')x} \stackrel{!}{=} S_{nn'} \\ &= \left[|A|^2 \frac{e^{i(k-k')x}}{i(k-k')} \right]_0^L = |A|^2 \frac{e^{i(k-k') \cdot L} - 1}{i(k-k')}, \quad k \neq k' \\ &\quad |A|^2 \int_0^L dx = |A|^2 L, \quad k' = k \end{aligned}$$

$$\text{We now use } k = 2\pi n/L \Rightarrow e^{i(k-k') \cdot L} = 1$$

$$\Rightarrow I = |A|^2 L \stackrel{!}{=} S_{nn'}$$

$$\Rightarrow A = \frac{1}{\sqrt{L}}$$

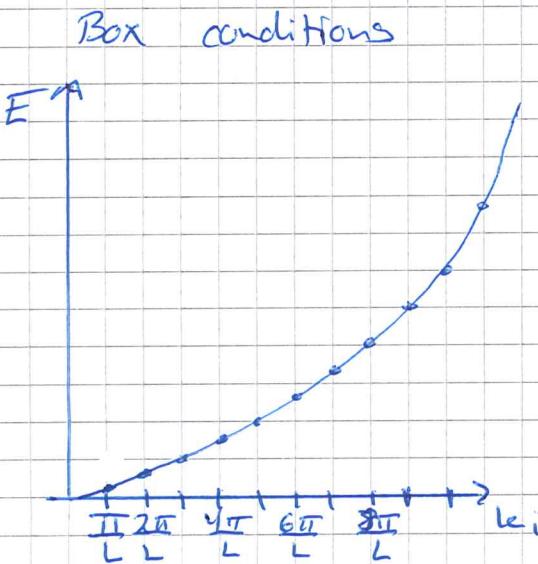
Generalizing to 3D, we have in a Volume $V = L_x L_y L_z$

$$\psi = \frac{1}{\sqrt{V}} e^{i \vec{k} \cdot \vec{r}}, \quad k_i = \frac{2\pi n_i}{L_i}, \quad n_i \in \mathbb{Z}, \quad i = \{x, y, z\}$$

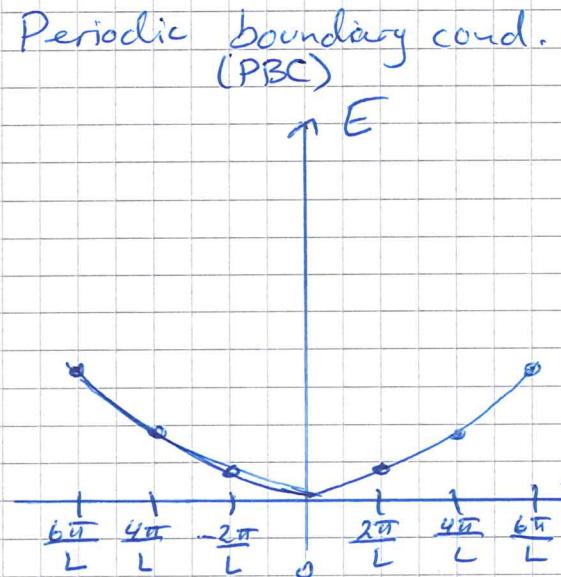
Density of states

The periodic boundary conditions give the same density of states as box conditions!

Along one direction



$$k = \frac{\pi n}{L}$$



$$k = \frac{2\pi n}{L}$$

PBC wavenumbers are half as densely spaced, but we have two branches, for positive and negative k . With PBC each state occupies a volume $\frac{(2\pi)^3}{V}$, and we therefore get the total number of states with energy less than E :

$$N = \int_0^{k_{\max}} dk \stackrel{\text{PBC}}{g(k)} = \frac{4\pi k^3}{3} \cdot \frac{V}{(2\pi)^3}$$

2 additional $\frac{1}{8}$

no factor $1/8$ since we include negative k -values.

$$= \frac{V}{6\pi^2} k_{\max}^3$$

$$\Rightarrow N(E) = \frac{V}{6\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{3/2} \Rightarrow g(E) = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{E}$$

Non-interacting fermions in a volume V

[Q8.2, G53.1]

We fill up a volume V (assumed large) with N noninteracting fermions.

Due to the Pauli principle, they cannot all occupy the same state.*

The ground state of the system is the state with lowest possible energy, and the fermions will therefore fill up the $\frac{N}{2}$ states with lowest energy. \uparrow spin, assuming spin $\frac{1}{2}$

Using periodic boundary conditions, each state occupies a volume $\frac{(2\pi)^3}{V}$, and we get the requirement

$$\frac{N}{2} = \frac{4}{3}\pi k_F^3 \cdot \frac{V}{(2\pi)^3},$$

where k_F is the radius of the sphere in k -space. This corresponds to the magnitude of the wavevector of the filled state with highest energy. This is often called the Fermi wavenumber.

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3} = (3\pi^2 \rho)^{1/3},$$

where we define the particle density $\rho = \frac{N}{V}$.

The corresponding energy is called the Fermi energy

$$E_F = \frac{\hbar^2}{2m} k_F^2 = \frac{\hbar^2}{2m} (3\pi^2 \rho)^{2/3}$$

The total energy can be calculated by summing over all states weighted by their energy. In the macroscopic limit, this can be approximated by

$$\begin{aligned} E_{\text{tot}} &= \int_0^{E_F} dE \cdot E \cdot g(E) \\ &\quad \xrightarrow{\text{energy}} \quad \xrightarrow{\text{number of states per energy interval}} \\ &= 2 \cdot \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^{E_F} dE E^{3/2} \\ &\quad \xrightarrow{\text{spin}} \\ &= \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{2}{5} E_F^{5/2} \\ &= \frac{V}{5\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \left(\frac{\hbar^2}{2m} \right)^{5/3} (3\pi^2 \rho)^{5/3} \\ &= \frac{\hbar^2 V}{10m\pi^2} \left(\frac{3\pi^2 N}{V} \right)^{5/3} = \frac{\hbar^2 (3\pi^2 N)^{5/3}}{10\pi^2 m} V^{-2/3} \end{aligned}$$

Could also calculate this using an integral in k-space with energy $E(\vec{k})$.

This energy is analogous to internal thermal energy of an ordinary gas. Notice that if the volume increases, the total energy decreases. The fermion gas exerts a pressure on the walls. The change in energy dE is spent doing work on the system, $dW = P dV$. Hence, the pressure is

$$P = -\frac{\partial E}{\partial V} = \frac{2}{3} \frac{E_{tot}}{V}.$$

$$= \frac{\frac{\hbar^2}{15\pi^2 m}}{(3\pi^2\rho)^{5/3}} = \frac{(3\pi^2)^{2/3} \hbar^2}{5m} \rho^{5/3}.$$

This pressure is often called degeneracy pressure, and is simply due to the Pauli principle and therefore strictly quantum mechanical! The classical pressure goes to zero as $T \rightarrow 0$.

White dwarfs: stabilized by degeneracy pressure. Add more weight (above Chandrasekhar limit $\sim 1.4 M_\odot$), the white dwarf would collapse to a neutron star.