5 Fixed vs. periodic boundary conditions

The energy eigenstates of a single electron in an infinite cubic potential well with sides \( L \) are superpositions of
\[
\psi(x) = A e^{i k \cdot x}
\]
where \( A \) is a normalization constant and \( k \) a wavevector. The energy associated with this eigenstate is:
\[
E(k) = \frac{\hbar}{2m} k^2
\]
where \( m \) is the mass of the electron.

It is common to assume periodic boundary conditions for a single electron wavefunction in a cubic infinite well with sides \( L \):
\[
\psi(x, y, z) = \psi(x + L, y, z) \\
\psi(x, y, z) = \psi(x, y + L, z) \\
\psi(x, y, z) = \psi(x, y, z + L).
\]

These imply that
\[
k_x = \frac{2\pi}{L} n_x \quad k_y = \frac{2\pi}{L} n_y \quad k_z = \frac{2\pi}{L} n_z
\]
where \( n_x, n_y \) and \( n_z \) are any (positive or negative) integers.

In this problem, you will consider the more familiar alternative of fixed boundary conditions
\[
\psi(0, y, z) = \psi(L, y, z) = 0 \\
\psi(x, 0, z) = \psi(x, L, z) = 0 \\
\psi(x, y, 0) = \psi(x, y, L) = 0.
\]

The aim is to compare results for the Fermi energy and the total energy for the two boundary conditions.
a) Show that energy eigenstates of the form

$$\psi(x) = A \sin(k_x x) \sin(k_y y) \sin(k_z z)$$

satisfy the fixed boundary conditions provided that

$$k_x = \frac{\pi}{L} n_x \quad k_y = \frac{\pi}{L} n_y \quad k_z = \frac{\pi}{L} n_z$$

where $n_x, n_y, n_z = 1, 2, 3, \ldots$

b) Consider, for a moment, the two dimensional case. Indicate the 10 lowest energy eigenstates in the $k_x$ and $k_y$ plane.

c) Consider the three dimensional case. Suppose that a large number, $N$, of electrons are placed in the cubic infinite well. Verify that the region containing the filled states is a section of a sphere and describe this section. Determine the radius, $k_F$, of this section of the sphere in terms of the electron density $n = N/V$ where $V$ is the volume of the well.

d) Determine the corresponding Fermi energy, $E_F$. How does this compare to the value obtained using the periodic boundary conditions?

e) Determine an expression for the density of states per unit volume, $g(E)$. Note that this could be different to the expression for the periodic boundary condition case.

f) Determine the total energy per unit volume, $E$. How does this compare to the value obtained using periodic boundary conditions?