Question #84295, Physics / Molecular Physics | Thermodynamics |

A particle of mass m moves in a three dimensional box with dimensions a , b , c . Calculate the allowed energy values. For a=b=c=L give the first five eigenvalues of the energy and the coresponding degenerate energy levels

Hint:

Consider solution of this kind: Ψ(x , y , z)=Ψx (x)Ψy (y)Ψ z(z) with energy E and solve for Ψx ,Ψy ,Ψz with energies Ex , Ey ,Ez where E=Ex+Ey+Ez

Solution

The potential for the particle inside the box

$$V(\vec{r}) = 0 \tag{1}$$

- $0 \leq x \leq L_x$
- $0 \leq y \leq L_y$
- $0 \leq z \leq L_z$
- $L_x < x < 0$
- $L_y < y < 0$
- $L_z < z < 0$

r→ is the vector with all three components along the three axes of the 3-D box: $r = L_x x + L_y y + L_z z$ When the potential energy is infinite, then the wavefunction equals zero. When the potential energy is zero, then the wavefunction obeys the Time-Independent Schrodinger Equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r) + V(r)\psi(r) = E\psi(r) \tag{2}$$

Since we are dealing with a 3-dimensional figure, we need to add the 3 different axes into the Schrondinger equation:

$$-\frac{\hbar^2}{2m}\left(\frac{d^2\psi(r)}{dx^2} + \frac{d^2\psi(r)}{dy^2} + \frac{d^2\psi(r)}{dz^2}\right) = E\psi(r) \tag{3}$$

The easiest way in solving this partial differential equation is by having the wavefunction equal to a **product** of individual function for each independent variable (e.g.,the separation of variables technique):

$$\psi(x, y, z) = X(x)Y(y)Z(z) \tag{4}$$

Now each function has its own variable:

- X(x) is a function for variable *x* only
- Y(y) function of variable *y* only
- Z(z) function of variable *z* only

Now substitute Equation (4) into Equation (3) and divide it by the product: xyz:

$$\frac{d^2\psi}{dx^2} = YZ\frac{d^2X}{dx^2} \Rightarrow \frac{1}{X}\frac{d^2X}{dx^2} \tag{5}$$

$$\frac{d^2\psi}{dy^2} = XZ\frac{d^2Y}{dy^2} \Rightarrow \frac{1}{Y}\frac{d^2Y}{dy^2} \tag{6}$$

$$\frac{d^2\psi}{dz^2} = XY\frac{d^2Z}{dz^2} \Rightarrow \frac{1}{Z}\frac{d^2Z}{dz^2} \tag{7}$$

$$\left(-\frac{\hbar^2}{2mX}\frac{d^2X}{dx^2}\right) + \left(-\frac{\hbar^2}{2mY}\frac{d^2Y}{dy^2}\right) + \left(-\frac{\hbar^2}{2mZ}\frac{d^2Z}{dz^2}\right) = E \tag{8}$$

E is an energy constant, and is the sum of x, y, and z. For this to work, each term must equal its own constant. For example,

$$\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2}\varepsilon_x X = 0 \tag{9}$$

Now separate each term in Equation (8) to equal zero:

$$\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2}\varepsilon_x X = 0$$

$$\frac{d^2Y}{dy^2} + \frac{2m}{\hbar^2}\varepsilon_y Y = 0$$

$$\frac{d^2Z}{dz^2} + \frac{2m}{\hbar^2}\varepsilon_z Z = 0$$

Now we can add all the energies together to get the total energy:

$$\varepsilon_x + \varepsilon_y + \varepsilon_z = E \tag{10}$$

Do these equations look familiar? They should because we have now reduced the 3D box into three particle in a 1D box problems!

$$\frac{d^2X}{dx^2} + \frac{2m}{\hbar^2}E_x X = 0 \approx \frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi \tag{11}$$

Now the equations are very similar to a 1-D box and the boundary conditions are identical, i.e.,

$$n = 1, 2, ..\infty \tag{12}$$

Use the normalization wavefunction equation for each variable:

$$\psi(x) = \sqrt{2/L_x}\sin n\pi x/L_x \tag{13}$$

$$Limit: 0 \leq x \leq L \tag{14}$$

$$\psi(x) = 0 \tag{15}$$

$$Limit: L < x < 0 \tag{16}$$

Normalization wavefunction equation for each variable

$$X(x) = \sqrt{\frac{2}{L_x}}\sin\left(\frac{n_x\pi x}{L_x}\right) \tag{17}$$

$$Y(y) = \sqrt{\frac{2}{L_y}}\sin\left(\frac{n_y\pi y}{L_y}\right) \tag{18}$$

$$Z(z) = \sqrt{\frac{2}{L_z}}\sin\left(\frac{n_z\pi z}{L_z}\right) \tag{19}$$

The limits of the three quantum numbers

- $n_x = 1, 2, 3, \ldots\infty$
- $n_y = 1, 2, 3, \ldots\infty$
- $n_z = 1, 2, 3, \ldots\infty$

For each constant use the de Broglie Energy equation:

$$\varepsilon_x = \frac{n_x^2 h^2}{8mL_x^2} \tag{20}$$

with $n_x = 1 \ldots \infty$

Do the same for variables n_y and n_z. Combine Equation 4 with Equations 17-19 to find the wavefunctions inside a 3D box.

$$\psi(r) = \sqrt{\frac{8}{V}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right) \tag{21}$$

with

$$V = \underbrace{L_x \times L_y \times L_z}_{\text{volume of box}} \tag{22}$$

To find the Total Energy, add Equation 20 and Equation 10.

$$E_{n_x,n_y,n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) \tag{23}$$

The energy of the particle in a 3-D cube (i.e., $a = L, b = L$, and $c = L$) in the *ground state* is given by Equation 23 with $n_x = 1, n_y = 1$, and $n_z = 1$. This energy ($E_{1,1,1}$) is hence

$$E_{1,1,1} = \frac{3h^2}{8mL^2} \tag{24}$$

The ground state has only one wavefunction and no other state has this specific energy; the ground state and the energy level are said to be **non-degenerate**. However, in the 3-D cubical box potential the energy of a state depends upon the sum of the squares of the quantum numbers (Equation 21). The particle having a particular value of energy in the excited state *MAY* has several different stationary states or wavefunctions. If so, these states and energy eigenvalues are said to be **degenerate**.

For the first excited state, three combinations of the quantum numbers ($n_x,\ n_y,\ n_z$) are $(2,\ 1,\ 1),\ (1, 2, 1),\ (1, 1, 2)$. The sum of squares of the quantum numbers in each combination is same (equal to 6). Each wavefunction has same energy:

$$E_{2,1,1} = E_{1,2,1} = E_{1,1,2} = \frac{6h^2}{8mL^2} \tag{25}$$

Corresponding to these combinations three different wavefunctions and **three** different states are possible. Hence, the first excited state is said to be three-fold or triply degenerate. The number of independent wavefunctions for the stationary states of an energy level is called as the **degree of degeneracy** of the energy level. The value of energy levels with the corresponding combinations and sum of squares of the quantum numbers

$$n^2 = n_x^2 + n_y^2 + n_z^2 \tag{26}$$

the first five eigenvalues of the energy and the corresponding degenerate energy levels

Total Energy (E_{n_x,n_y,n_z})	Degree of Degeneracy
$\frac{3h^2}{8mL^2}$	1
$\frac{6h^2}{8mL^2}$	3
$\frac{9h^2}{8mL^2}$	3
$\frac{11h^2}{8mL^2}$	3
$\frac{12h^2}{8mL^2}$	1