Performing the inner differentiation we obtain

$$\frac{\partial}{\partial x}\left[A\left(\frac{\ell\pi}{L_x}\right)\cos\left(\frac{\ell\pi x}{L_x}\right)\sin\left(\frac{m\pi y}{L_y}\right)\sin\left(\frac{n\pi z}{L_z}\right)\right]$$

Differentiating again,

$$\frac{\partial^2\psi_{\ell,m,n}(x,y,z)}{\partial x^2} = -A\left(\frac{\ell\pi}{L_x}\right)^2\sin\left(\frac{\ell\pi x}{L_x}\right)\sin\left(\frac{m\pi y}{L_y}\right)\sin\left(\frac{n\pi z}{L_z}\right) = -\left(\frac{\ell\pi}{L_x}\right)^2\psi_{\ell,m,n}(x,y,z)$$

Similarly,

$$\frac{\partial^2\psi_{\ell,m,n}(x,y,z)}{\partial y^2} = -\left(\frac{m\pi}{L_y}\right)^2\psi_{\ell,m,n}(x,y,z) \qquad \frac{\partial^2\psi_{\ell,m,n}(x,y,z)}{\partial z^2} = -\left(\frac{n\pi}{L_z}\right)^2\psi_{\ell,m,n}(x,y,z)$$

Finally, adding these second partial derivatives as they appear in eqn. IIIA-2a,

$$\left\{-\left[\left(\frac{\ell\pi}{L_x}\right)^2+\left(\frac{m\pi}{L_y}\right)^2+\left(\frac{n\pi}{L_z}\right)^2\right]+\frac{8\pi^2m^*}{h^2}\varepsilon\right\}\psi_{\ell,m,n}(x,y,z) = 0$$

Since this product equals zero, either the quantity within brackets equals zero or $\psi(x,y,z)$ equals zero. The latter possibility is ignored since it implies that $P(x,y,z) = |\psi(x,y,z)|^2$ equals zero for all x,y, and z. This is to say that the probability that the particle at a point is zero for <u>all</u> points within the box. The alternative is that the bracketed terms equal zero. This gives an expression for the allowed values of the energy. See eqn. IIIA-4 below.

We have verified that the assumed wave function, eqn. IIIA-3, is a valid solution for the free particle in a box subject to the specified restrictions on the energy. This function can be used to predict the position probability of the particle in terms of its energy. Neither the wave function nor the position probability is necessary for the statistical determination of the thermodynamic properties. Yet some students may find a more thorough investigation of the character of eqn. IIIA-3, especially as it relates to our macroscopic experience, helpful in understanding its meaning. Such an elaboration is presented in Appendix IIIA-A.

In Exmp. 2 we found that the free particle in a box could acquire only certain discrete energy magnitudes.

$$\varepsilon_{\ell,m,n} = \frac{h^2}{8m^*}\left[\left(\frac{\ell}{L_x}\right)^2+\left(\frac{m}{L_y}\right)^2+\left(\frac{n}{L_z}\right)^2\right] \qquad \text{(IIIA-4)}$$

where $\ell,m,n = 1,2,3,\ldots$, and all possible combinations. The possible energies of the particle, ε, are written as $\varepsilon_{\ell,m,n}$ to emphasize that they are discrete, or quantized. We call the values ascribed to ℓ,m, and n for any specific $\varepsilon_{\ell,m,n}$ the *quantum numbers of that energy state*. Furthermore, the specified energy states $\varepsilon_{\ell,m,n}$ are the only possible states for the particle and the corresponding $\psi_{\ell,m,n}(x,y,z)$ are the only possible wave functions. These energy states and wave functions are called the *allowed* energies and wave functions.