University of Washington
Department of Chemistry
Chemistry 453
Winter Quarter 2015

Lecture 15. 02/13/15
Recommended Text Reading; Atkins DePaula: 9.4

A. Particle –in-a-Box: Two and Three Dimensions

- Electronic energies in cyclic systems like benzene and cyclobutadiene may be approximated with two dimensional particle-in-a-box.
- For a two dimensional box with side a, b, length the energy is a sum of two terms:

$$E = E_x + E_y = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right) \qquad (15.1)$$

the wave function is a product of two terms:

$$\Psi_{n_x,n_y}(x,y) = \psi_{n_x}(x)\psi_{n_y}(y) = \sqrt{\frac{4}{ab}}\sin\left(\frac{n_x \pi x}{a}\right)\sin\left(\frac{n_y \pi y}{b}\right) \qquad (15.2)$$

where $n_{x,y}$=1,2,3,4…

- Note the probability of finding a particle with energy quantum numbers n_x and n_y within a region: $x_a \le x \le x_b$ and $y_a \le y \le y_b$ of a two dimensional box with side lengths a and b is expressed by the double integral:

$$P_{xy}(n_x, n_y) = \frac{2}{a}\int_{x_a}^{x_b}\sin^2\frac{n_x \pi x}{a}dx \times \frac{2}{b}\int_{y_a}^{y_b}\sin^2\frac{n_y \pi y}{b}dy$$

  where we solve each integral using the standard form: $\int \sin^2 ax\,dx = \frac{x}{2} - \frac{1}{4a}\sin 2ax + \text{constant}$
- Note equations 15.1 and 15.2 indicate occurrence of degeneracy: different wave functions with the same energy. For example, the energies

$$E(1,2) = \frac{h^2}{8m}\left(\frac{1^2}{a^2} + \frac{2^2}{b^2}\right) \text{ and } E(2,1) = \frac{h^2}{8m}\left(\frac{2^2}{a^2} + \frac{1^2}{b^2}\right) \qquad (15.3)$$

  are different if $a \neq b$. But if the box is square i.e. a=b=L, the energies are the same:

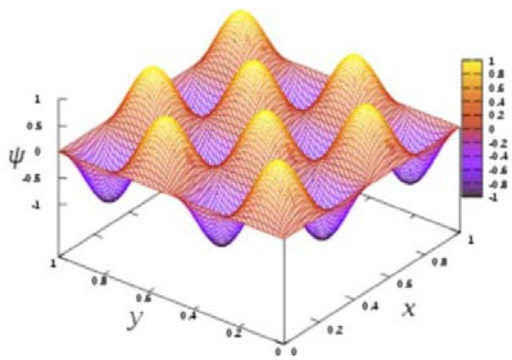
$$E(1,2) = E(2,1) = \frac{h^2}{8mL^2}\left(2^2 + 1^2\right) = \frac{5h^2}{8mL^2}$$

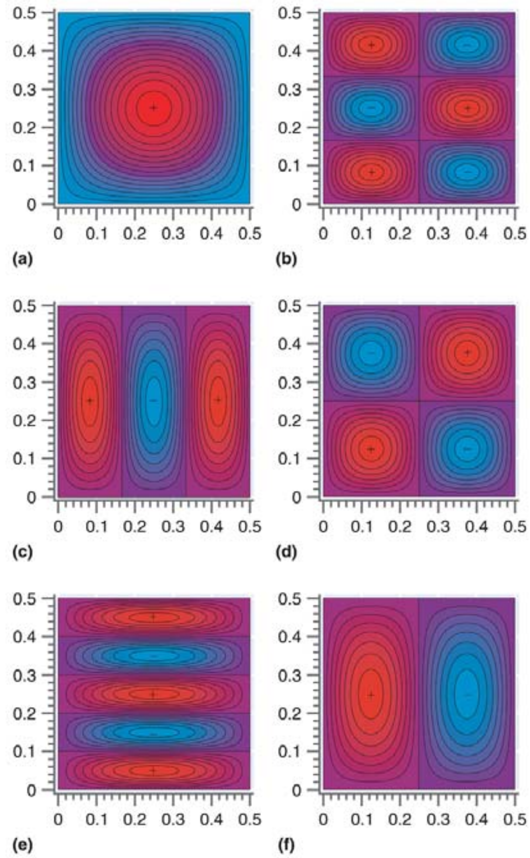
- The two wave functions corresponding to these identical energies differ in their spatial distribution of density. We say this energy is two-fold degenerate.

$$\psi_{n_x=1}(x)\psi_{n_y=2}(y) = \sqrt{\frac{4}{ab}}\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{2\pi y}{b}\right) \text{ versus } \psi_{n_x=2}(x)\psi_{n_y=1}(y) = \sqrt{\frac{4}{ab}}\sin\left(\frac{2\pi x}{a}\right)\sin\left(\frac{\pi y}{b}\right)$$

(15.4)

Figure 15.1: Wave functions for particle in a Square Box: a=b. Bottom left: three dimensional perspective for wave function $n_x=n_y=4$. Bottom right shows contour plots for
a) $n_x=n_y=1$; b) $n_x=2$, $n_y=3$
c) $n_x=3, n_y=1$; d) $n_x=n_y=2$
e) $n_x=1$; $n_y=5$; f) $n_x=2$, $n_y=1$





- For a three dimensional box with sides a, b, c in length the energy is a sum of three terms:

$$E = E_x + E_y + E_z = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \qquad (15.5)$$

the wave function is a product of two terms:

$$\Psi_{n_x,n_y,n_z}(x,y,z) = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z) = \sqrt{\frac{8}{abc}}\sin\left(\frac{n_x \pi x}{a}\right)\sin\left(\frac{n_y \pi y}{b}\right)\sin\left(\frac{n_z \pi y}{c}\right) \qquad (15.6)$$

where $n_{x,y,z}$=1,2,3,4…

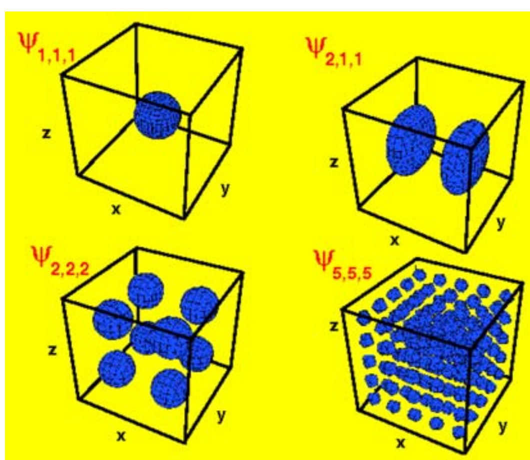


Figure 15.2:
$\Psi_{n_x,n_y,n_z}(x,y,z)$ for a particle in a cubic box.

D. The Quantum Translational Partition Function; Translational U and S

- Particle-in-Box energies can be used to calculate thermodynamic properties for ideal monatomic gases, and other quantum particles undergoing translational motions. Use particle-in-a-3D-box energies in a single particle partition function expression:

$$q_{trans} = \sum_{n_{x,y,z}=1}^{\infty} e^{-\varepsilon(n_x,n_y,n_z)/k_BT} = \sum_{n=1}^{\infty} \exp\left[-\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right)\frac{h^2}{8mk_BT}\right] \qquad (15.7)$$

- Now assume it is a big box so that $\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right)\frac{h^2}{8mk_BT}$ <<1. Then we can replace the triple summation with a triple integral

$$q_{trans} = q_X q_Y q_Z \approx \int_1^{\infty} dn_x \int_1^{\infty} dn_y \int_1^{\infty} dn_z \exp\left[-\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right)\frac{h^2}{8mk_BT}\right]$$

$$\approx \int_0^{\infty} dn_x \exp\left[-\left(\frac{n_x^2}{a^2}\right)\frac{h^2}{8mk_BT}\right]\int_0^{\infty} dn_y \exp\left[-\left(\frac{n_y^2}{b^2}\right)\frac{h^2}{8mk_BT}\right]\int_0^{\infty} dn_z \exp\left[-\left(\frac{n_z^2}{c^2}\right)\frac{h^2}{8mk_BT}\right] (15.8)$$

$$= \frac{abc}{h^3}\left(2\pi mk_BT\right)^{3/2} = \frac{V}{h^3}\left(2\pi mk_BT\right)^{3/2}$$

- Note this result is obtained by changing the partition function from a summation to an integral. In doing so we assumed the energy level spacing for a particle in a box $\Delta E << k_BT$ where for a 1D box:

$$\Delta E = E_{n+1} - E_n = \left[\left(n+1\right)^2 - n^2\right]\frac{h^2}{8mL^2} = \left(2n+1\right)\frac{h^2}{8mL^2} << k_BT \qquad (15.9)$$

- For a large box this condition is fulfilled. See homework.
- Using equation 15.8 we calculate the molar translational internal energy.

Assuming $Q_{trans} = \frac{q_{trans}^N}{N!}$

$$U_{trans} = N_A k_B T^2 \frac{\partial \ln q_{trans}}{\partial T} = \frac{Nk_BT^2}{q_{trans}}\frac{\partial q_{trans}}{\partial T} = N_A k_B T^2 \frac{h^3}{\left(2\pi mk_BT\right)^{3/2}}\frac{\left(2\pi mk_B\right)^{3/2}}{h^3}\frac{\partial T^{3/2}}{\partial T} \qquad (15.10)$$

$$= N_A k_B T^2 \frac{3}{2}\frac{T^{1/2}}{T^{3/2}} = \frac{3N_Ak_BT}{2} = \frac{3RT}{2}$$

- This is the same result obtained from the kinetic theory of gases. We obtained the same result because we assumed $\Delta E << k_BT$ and calculated q $_{rans}$ with an integral.
- Using 15.8 we can also obtain the entropy of translation:

$$S_{trans} = \frac{U_{trans}}{T} + k_B \ln Q_{trans} = \frac{3Nk_BT}{2T} + k_B \ln\left(\frac{q_{trans}^N}{N!}\right)$$

$$= \frac{3Nk_B}{2} + k_B\left(N \ln q_{trans} - N \ln N + N\right) = \frac{5Nk_B}{2} + Nk_B \ln\left(\frac{q_{trans}}{N}\right) \quad (15.11)$$

$$= Nk_B \ln\left(\frac{q_{trans} e^{5/2}}{N}\right) = Nk_B \ln\left(\frac{V\left(2\pi m k_B T\right)^{3/2} e^{5/2}}{Nh^3}\right) = Nk_B \ln\left(\frac{k_B T\left(2\pi m k_B T\right)^{3/2} e^{5/2}}{Ph^3}\right)$$

- The last line of equation 15.11 goes by the name Sakur-Tetrode equation . Note we get equation 15.11 to obtain entropy changes for ideal gases:

$$\Delta S = Nk_B \ln\left(\frac{V_2\left(2\pi m k_B T_2\right)^{3/2} e^{5/2}}{Nh^3}\right) - Nk_B \ln\left(\frac{V_1\left(2\pi m k_B T_1\right)^{3/2} e^{5/2}}{Nh^3}\right)$$

$$= Nk_B \ln V_2 T_2^{3/2} - Nk_B \ln V_1 T_1^{3/2} = Nk_B \ln\frac{V_2}{V_1} + Nk_B \ln\frac{T_2^{3/2}}{T_1^{3/2}} = Nk_B \ln\frac{V_2}{V_1} + \frac{3}{2} Nk_B \ln\frac{T_2}{T_1} \quad (15.12)$$