Particle in a Box

We will now explore the quantum mechanical "particle in the Box". This will justify a result I quoted earlier

$$\sum_{\text{States}} \longrightarrow \int \frac{dx\,dp}{h}$$

i.e. that the sum over states becomes an integral over classical phase space

The Energy Levels and eigen-functions are:

$$\boxed{\begin{aligned} \mathcal{E}_n &= \frac{\hbar^2 \pi^2}{2mL^2} n^2 \equiv \frac{p_n^2}{2m} \quad \text{with} \quad p_n \equiv \left(\frac{\hbar \pi}{L}\right) n \\ &\equiv \mathcal{E}_1 n^2 \quad \text{with} \quad \mathcal{E}_1 \equiv \frac{\hbar^2 \pi^2}{2mL^2} \\ &\text{with} \quad n = 1, 2, 3, \ldots \end{aligned}}$$

this is the magnitude of the momentum of the n-th state

The wave functions are

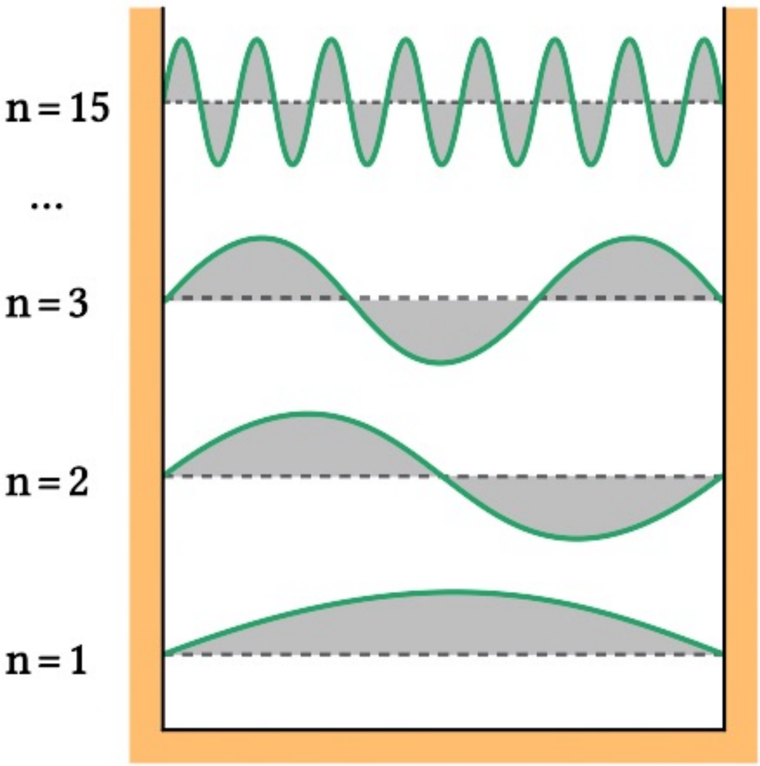
$$\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{p_n x}{\hbar}\right)$$

$\Leftarrow$ These are shown below

$$\propto e^{ip_n x/\hbar} - e^{-ip_n x/\hbar}$$

each box state is a superposition of a right moving wave (+) and a left moving wave (−)

The partice in box wave fcns



For example: the wavelength of the $n=3$ mode (state) is $\lambda_3 = \frac{2}{3L}$ so:

$$p_3 = \frac{h}{\lambda_3} = \frac{2\pi\hbar}{\lambda_3}$$

$$= \left(\frac{\hbar\pi}{L}\right) 3$$

and

$$\mathcal{E}_3 = \mathcal{E}_1 \cdot 3^2 = 9\,\mathcal{E}_1$$

- The quantum number n counts how many half-wavelengths fit in the box. For a typical box $L \sim 1\text{m}$ and typical atom $\lambda \sim 1\,\text{Å} \sim 10^{-10}\,\text{m}$, n is huge, $n \sim 10^{10}$!

- So n (which labels the momentum $p_n = \hbar\pi n/L$) is practically continuous, except at low temperatures of boxes of order an atomic length.

Particle-In-Box: Stat Mech

$$Z = \sum_{n=1}^{\infty} e^{-\beta \varepsilon_n} = \sum_{n=1}^{\infty} e^{-\beta \varepsilon_1 n^2}$$

Now the partition function can't be evaluated in closed form (at this level). But, we know that n is nearly continuous and very large. We can replace the sum with an integral.

$$\sum_{n=1}^{\infty} \longrightarrow \int_0^{\infty} dn = \int_0^{\infty} \frac{L\,dp}{\pi \hbar} = \int_{-\infty}^{\infty} \frac{L\,dp}{2\pi\hbar}$$

one is very small $n \sim 10^{10}$

we used $p = \frac{\hbar \pi}{L} n$

Then instead of integrating over the momentum magnitude $p = 0 \ldots \infty$, we integrate over the momentum itsself, $p = -\infty \ldots \infty$ inserting a factor of 2.

So we see that for $n \gg 1$

$$\boxed{\sum_n \longrightarrow \int \frac{dx\,dp}{(2\pi\hbar)} = \int \frac{dx\,dp}{h}}$$

So then the quantum treatment just reproduces the classical result in this limit:

$$\varepsilon_n = \frac{p_n^2}{2m} \Rightarrow \frac{p^2}{2m}$$ approximately continuous

$$\sum_n \rightarrow \int \frac{dx\,dp}{h}$$

Then

$$Z \simeq \int \frac{dx\,dp}{h}\, e^{-\beta p^2/2m} = \frac{L\,(2\pi m kT)^{1/2}}{h} = \frac{L}{\lambda_{th}}$$

The approximation is good when $n \gg 1$. This means since $\varepsilon_n = \varepsilon_1 n^2 \sim kT$ that we must have

$$\boxed{\sqrt{\frac{kT}{\varepsilon_1}} \gg 1 \quad \text{or} \quad \frac{L}{\lambda_{th}} \gg 1}$$

note: $L/\lambda_{th} = \frac{\sqrt{\pi}}{2}\left(\frac{kT}{\varepsilon_1}\right)^{1/2}$, the numerical factor $\sqrt{\pi}/2$ is irrelevant when making an estimate or posing a condition. If L/λ is large, so is $(kT/\varepsilon_1)^{1/2}$.

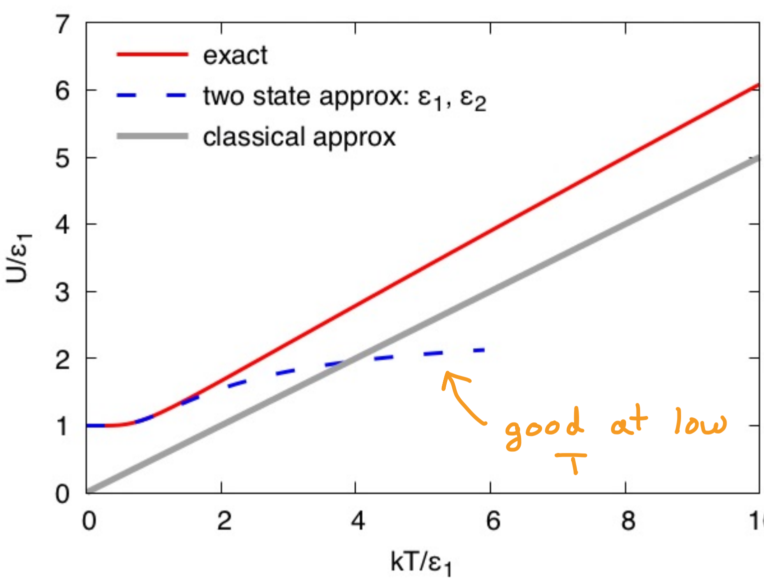
Summary

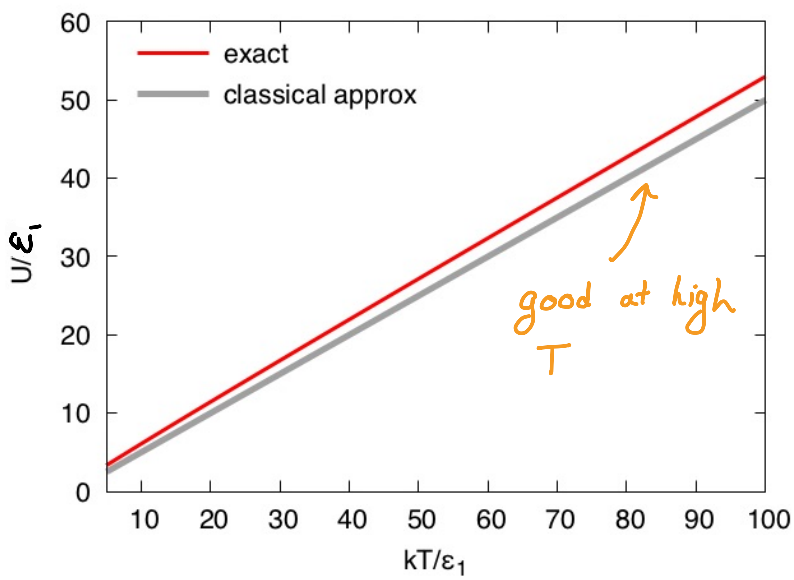
$$Z = \sum_{n=1}^{\infty} e^{-\beta\varepsilon_1 n^2} \simeq \begin{cases} e^{-\beta\varepsilon_1} + e^{-4\beta\varepsilon_1} & \text{small } T,\ \beta\varepsilon_1 \gg 1 \\ \dfrac{L}{\lambda_{th}} = \dfrac{\sqrt{\pi}}{2}\left(\dfrac{kT}{\varepsilon_1}\right)^{1/2} & \text{large } T \\ & \text{classical approx} \end{cases}$$

At small temperatures we can approximate Z by just including the first two terms in the sum. At high T the classical approximation is good. Then we compute:

$$U = \langle \varepsilon \rangle = -\frac{\partial \ln Z}{\partial \beta}$$

This is shown below with the low and high T limits:





More Dimensions

The classical approximation $\sum_{\text{state}} \to \int d^3x\, d^3p / h^3$ works in more dimensions

In 3D the PIB energy levels are

$$\mathcal{E}_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right) = \frac{p_{n_x}^2}{2m} + \frac{p_{n_y}^2}{2m} + \frac{p_{n_z}^2}{2m}$$

with $n_x = 1, \ldots \infty$ and similary for n_y and n_z. For each direction we define a momentum component:

$$p_{n_x} \equiv \frac{\hbar \pi}{L} \cdot n_x$$ = magnitude of momentum in the x direction, with similar notation in y and z directions.

The sum over states is

$$\sum_{\text{states}} = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \simeq \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z$$

$$= \int_0^\infty \frac{L\, dp_x}{\pi \hbar} \int_0^\infty \frac{L\, dp_y}{\pi \hbar} \int_0^\infty \frac{L\, dp_z}{\pi \hbar}$$

$$= \int_{-\infty}^{\infty} \frac{dx\, dp_x}{(2\pi\hbar)} \int_{-\infty}^{\infty} \frac{dy\, dp_y}{(2\pi\hbar)} \int_{-\infty}^{\infty} \frac{dz\, dp_z}{2\pi\hbar} = \int \frac{d^3\vec{r}\, d^3\vec{p}}{(2\pi\hbar)^3}$$