The Particle in a Box Model

In this model, a particle is placed inside a box with walls defined by infinite potential energy (*1–3*). Within the limits of the box, the potential energy zeroes, as represented in the picture below for the one-dimensional case.

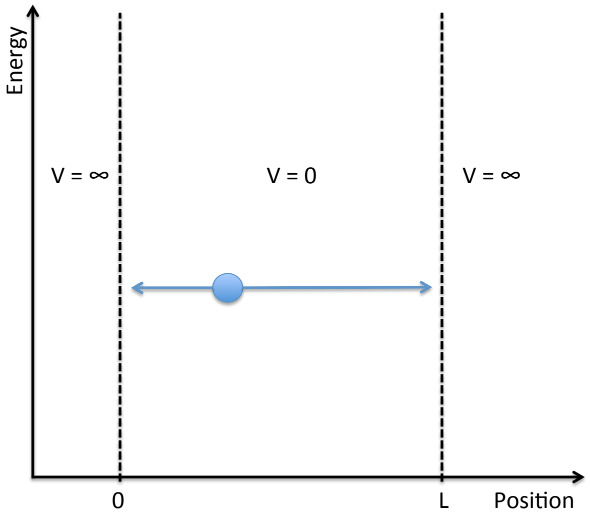

Figure 1: Scheme for the one-dimensional particle in a box. V is the potential energy, which is infinity outside the box's limits.

The respective Schrödinger equation is given by

$$-\frac{\hbar^2}{2m}\nabla\Psi+V\Psi = E\Psi \tag{1}$$

where V=∞ outside the length of the box (usually between 0 and L) and V=0 inside the length of the box. Since the particle's energy must be defined for all the space available to it, we only consider the zero-potential energy region for the differential equation we must solve. This means that only the kinetic energy terms survive. Using Cartesian coordinates the differential operator is separable, which means that we may treat each dimension of space independently of one another. For a N_{dim}-dimensional space we thus get

$$-\frac{\hbar^2}{2m}\nabla\Psi = -\frac{\hbar^2}{2m}\sum_i^{N_{dim}}\frac{\partial^2}{\partial x_i^2}\Psi = \sum_i^{N_{dim}}E_i\Psi = E\Psi \tag{2}$$

In going from a one-dimensional Schrödinger equation into the N_{dim}-dimensional case one must add the respective energy terms, as demonstrated above. The global wavefunction for the N_{dim}-dimensional system can be calculated by multiplying the respective one-dimensional wavefunctions. Isolating the coordinate specific terms into their respective equations and making the dependence on a generic one-dimensional coordinate x we finally reach

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x) = E_x\Psi(x) \tag{3}$$

The general solution for this differential equation is the function

$$\Psi(x){=}Asin(kx){+}Bcos(kx) \tag{4}$$

By taking the second derivative of this function, we obtain the energy for the many possible states,

$$E{=}\frac{\hbar^2k^2}{2m} \tag{5}$$

where from the boundary conditions $\Psi(0) = \Psi(L) = 0$

$$k{=}\frac{n\pi}{L}, \qquad n{\in}\mathbb{N} \tag{6}$$

The boundary conditions also allow us to determine that $B{=}0$, zeroing out the contribution from the cosine. The only thing left to define is thus the constant A. Because the probability of finding the particle somewhere in the available space must be 1, then by integrating the square of the wavefunction we obtain

$$A{=}\sqrt{\frac{2}{L}} \tag{7}$$

Therefore, for a one dimensional box, the Schrödinger equation can be solved to get the wavefunction

$$\Psi(x){=}\sqrt{\frac{2}{L}}sin(\frac{n\pi x}{L}) \tag{8}$$

For the energy of the particle in the box to be zero, then the quantum number n must also be zero. In that case, one can no longer determine the particle's position from its wavefunction, in agreement with the Heisenberg uncertainty principle. In the description above, the wavefunction describes the translation of a particle in a box. The energy of this particle depends on the quantity k, which is determined by the quantum number of translation n. In the N_{dim}-dimensional case the energy is dependent on N_{dim} translational quantum numbers. Since different combinations of the quantum numbers n_i can lead to the same energy, we are directed to the definition of degeneracy: Two different states are degenerate if they have the same energy.

According to the Copenhagen school of quantum mechanics, the square of the absolute value of the wavefunction is a probability density function

$$D(x) = |\Psi(x)|^2{=}\frac{2}{L}sin^2(\frac{n\pi x}{L}) \tag{9}$$

It is interesting to note the behaviour of the probability density function. For the translational ground state ($n = 1$) the particle is most probably found exactly in the middle of the box. For the second quantum state available, there are two points with maximum probability. In general, the number of maxima in the probability density function matches the quantum number of the respective energy level. Furthermore, for $n > 1$ there are also points within the box where there is zero probability of finding the particle. These are called the nodes of the wavefunction. The number of nodes per energy level is $n - 1$. Maxima and nodes are all equidistant.

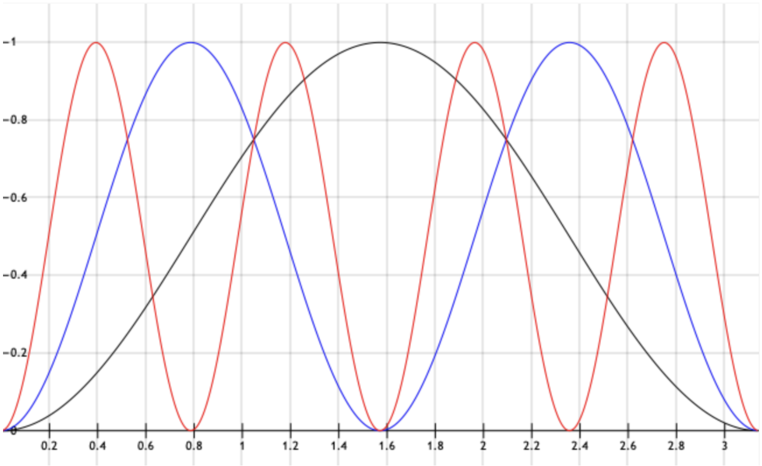

Figure 2: Representation of the probability density function for the quantum levels $n = 1$ (black), $n = 2$ (blue) and $n = 4$ (red) for a box with $L = \pi$.

Integrating this function over some given positions allows us to calculate the probability of finding the particle in a specific part of the box (in a given hypervolume for the N_{dim}-dimensional case). This probability is given thus by

$$P(a,b) = \int_a^b D(x)dx = \frac{1}{2n\pi}[x]|_{\frac{2n\pi a}{L}}^{\frac{2n\pi b}{L}} - \frac{1}{4n\pi}[sin(2x)]|_{\frac{2n\pi a}{L}}^{\frac{2n\pi b}{L}} \tag{10}$$

Applications

The particle in a box is a quantum mechanical description of the translational movement of a quantum particle in an environment free of interactions. The most common use of the model is to estimate translational energies of an ideal gas. Using (only) the particle in a box to describe inert monoatomic gases provides a relatively accurate model.

The other known use for the model is to calculate excitation energies on highly conjugated polyenes. In this case, the electron is considered to be trapped in a box, which is the molecule's π system.

The Partition Function for a Particle in a Box

The largest use of the particle in a box model is to estimate the translational energy levels of a molecule in a closed box. These energies, calculated using quantum mechanics, can be used directly to obtain the partition function for the system:

$$q_{trans} = \sum_{j}^{trans} exp[-\frac{\varepsilon_j^{trans}}{k_B T}] \tag{11}$$

Using the equation above for the energies of the particle in a box, *i.e.*

$$E_{n_x,n_y,n_z,\dots} = \varepsilon_j^{trans} \tag{12}$$

we get

$$q_{trans} = \sum_{j} exp[-\frac{\hbar^2 k_j^2}{2mk_B T}] \tag{13}$$

However, the calculation of thermodynamical quantities does not involve directly the partition function, it requires derivatives of the logarithm of the partition function. By direct substitution we obtain:

$$log(q_{trans}) = log(\sum_{j} exp[-\frac{\hbar^2 k_j^2}{2mk_B T}]) \tag{14}$$

In the three-dimensional case,

$$k_j^2 = k_{n_x,n_y,n_z}^2 = \frac{(n_x^2 L_y^2 L_z^2 + n_y^2 L_x^2 L_z^2 + n_z^2 L_x^2 L_y^2)}{V^2} \pi^2 \tag{15}$$

We can thus make

$$A(n_x, n_y, n_z) = \frac{\hbar^2 \pi^2 (n_x^2 L_y^2 L_z^2 + n_y^2 L_x^2 L_z^2 + n_z^2 L_x^2 L_y^2)}{2mk_B} \tag{16}$$

so that

$$log(q_{trans}) = log(\sum_{n_x} \sum_{n_y} \sum_{n_z} exp[-\frac{A(n_x, n_y, n_z)}{TV^2}]) \tag{17}$$

The first derivative we need to calculate is

$$\frac{\partial}{\partial T} log(q_{trans}) = \frac{1}{\sum_{n_x} \sum_{n_y} \sum_{n_z} exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]} \frac{\partial}{\partial T} \sum_{n_x} \sum_{n_y} \sum_{n_z} exp[-\frac{A(n_x, n_y, n_z)}{TV^2}] \tag{18}$$

$$=\frac{1}{\sum_{n_x}\sum_{n_y}\sum_{n_z} exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]}\sum_{n_x}\sum_{n_y}\sum_{n_z}\frac{\partial}{\partial T}exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]$$

$$=\frac{1}{(TV)^2}\frac{\sum_{n_x}\sum_{n_y}\sum_{n_z} A(n_x,n_y,n_z)exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]}{\sum_{n_x}\sum_{n_y}\sum_{n_z} exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]}$$

For the heat capacity at constant volume we also need the second derivative of $log(q_{trans})$ with respect to the temperature. We must thus differentiate the above expression once more to obtain:

$$\begin{aligned}\frac{\partial^2}{\partial T^2}log(q_{trans})=&\frac{\partial}{\partial T}(\frac{\partial}{\partial T}log(q_{trans}))\\
=&\frac{\partial}{\partial T}(\frac{1}{(TV)^2}\frac{\sum_{n_x}\sum_{n_y}\sum_{n_z} A(n_x,n_y,n_z)exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]}{\sum_{n_x}\sum_{n_y}\sum_{n_z} exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]})\\
=&\frac{\sum_{n_x}\sum_{n_y}\sum_{n_z} A(n_x,n_y,n_z)exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]}{\sum_{n_x}\sum_{n_y}\sum_{n_z} exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]}\frac{\partial}{\partial T}(\frac{1}{(TV)^2})\\
&+\frac{1}{(TV)^2}\frac{\partial}{\partial T}(\frac{\sum_{n_x}\sum_{n_y}\sum_{n_z} A(n_x,n_y,n_z)exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]}{\sum_{n_x}\sum_{n_y}\sum_{n_z} exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]})\\
=&-\frac{2}{V^2T^3}\frac{\sum_{n_x}\sum_{n_y}\sum_{n_z} A(n_x,n_y,n_z)exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]}{\sum_{n_x}\sum_{n_y}\sum_{n_z} exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]}\\
&+\frac{1}{(TV)^4}\frac{\sum_{n_x}\sum_{n_y}\sum_{n_z} [A(n_x,n_y,n_z)]^2exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]}{\sum_{n_x}\sum_{n_y}\sum_{n_z} exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]}\\
&-\frac{1}{(TV)^4}(\frac{\sum_{n_x}\sum_{n_y}\sum_{n_z} A(n_x,n_y,n_z)exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]}{\sum_{n_x}\sum_{n_y}\sum_{n_z} exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]})^2\end{aligned}\tag{19}$$

Another derivative we require is

$$\frac{\partial}{\partial V}log(q_{trans})=\frac{1}{\sum_{n_x}\sum_{n_y}\sum_{n_z} exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]}\frac{\partial}{\partial V}\sum_{n_x}\sum_{n_y}\sum_{n_z} exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]\tag{20}$$

$$=\frac{2}{TV^3}\frac{\sum_{n_x}\sum_{n_y}\sum_{n_z} A(n_x,n_y,n_z)exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]}{\sum_{n_x}\sum_{n_y}\sum_{n_z} exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]}$$

The last two derivatives we require are with respect to the logarithm of the variables of state:

$$\frac{\partial log(q_{trans})}{\partial log(T)}=\frac{1}{\sum_{n_x}\sum_{n_y}\sum_{n_z} exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]}\frac{\partial}{\partial log(T)}\sum_{n_x}\sum_{n_y}\sum_{n_z} exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]\tag{21}$$

$$=\frac{1}{TV^2}\frac{\sum_{n_x}\sum_{n_y}\sum_{n_z}A(n_x,n_y,n_z)exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]}{\sum_{n_x}\sum_{n_y}\sum_{n_z}exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]}$$

and finally

$$\frac{\partial log(q_{trans})}{\partial log(V)}=\frac{1}{\sum_{n_x}\sum_{n_y}\sum_{n_z}exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]}\frac{\partial}{\partial log(V)}\sum_{n_x}\sum_{n_y}\sum_{n_z}exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]$$

$$=\frac{2}{TV^2}\frac{\sum_{n_x}\sum_{n_y}\sum_{n_z}A(n_x,n_y,n_z)exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]}{\sum_{n_x}\sum_{n_y}\sum_{n_z}exp[-\frac{A(n_x,n_y,n_z)}{TV^2}]} \tag{22}$$

With all these derivatives the whole system is defined and all state variables can be calculated.

Particle in a Box in the Classical Limit

The problem of describing the translational energy is that the gap between consecutive energy levels is very small. This gap can be so small that to reach thermal equilibrium with the environment, extremely large sets of quantum numbers have to be considered in the calculation of the partition function. In other words, there is a quasi continuum in the energy as a function of the quantum numbers (*4*).

We can take as example a molecule of N_2 inside a cubical box. If we assume the system is in thermal equilibrium, we can estimate the quantum number of the highest energy level occupied at a given temperature. Using the energy expression (equation 5) and substituting all constants and the mass for one N_2 molecule ($[MW]_{N_2}=\frac{28.01\times10^{-3}}{6.022\times10^{22}}=4.65\times10^{-26}$) we get that

$$n_x^2+n_y^2+n_z^2=1.170\times10^{19}TL^2 \tag{23}$$

For a box of dimensions 1 nm^3, the sum of the square of the quantum numbers is around ten times the temperature of the system. Even though there are many combinations possible, the problem should still be easily tractable with the aid of a computer, if the temperature is low enough. For a box with dimensions 1 μm^3 there is already a sum of the square of quantum numbers of around ten billion (10^7) times larger than the system's temperature, and for a 1 mL box there is a sum of the square of the quantum numbers around 10^{15} times larger than that same temperature. The amount of energy levels required for the calculation of the partition function becomes absurdly high and storing of all those numbers is no longer affordable. Furthermore, the energy gap between consecutive energy levels is ridiculously small (simply put in the values above in equation 5 and see for yourself).

In the classical limit, the energy of the particle becomes a continuous function of the quantum numbers. This means that the energy is no longer quantised and the n_i are no longer considered natural but rather real numbers instead. The sum over the quantum numbers in the partition function becomes an integral in $\mathbb{R}^+$:

$$q_{trans}{=}\sum_j^{trans} exp[-\frac{\varepsilon_j^{trans}}{k_B T}]{=}\sum_j^{trans} exp[-\frac{\hbar^2}{2mk_BT}(\frac{b_x n_x^2\pi}{V^2}+\frac{b_y n_y^2\pi}{V^2}+\frac{b_z n_z^2\pi}{V^2})] \tag{24}$$

$$\begin{aligned} q_{trans}^{classical}&{=}\int_0^{+\infty} exp[-\frac{\hbar^2 b_x\pi}{2mk_BTV^2}x^2]dx\int_0^{+\infty} exp[-\frac{\hbar^2 b_y\pi}{2mk_BTV^2}y^2]dy\int_0^{+\infty} exp[-\frac{\hbar^2 b_z\pi}{2mk_BTV^2}z^2]dz \\ &{=}\frac{1}{2}\sqrt{\frac{2mk_BTV^2}{\hbar^2 b_x\pi}}\frac{1}{2}\sqrt{\frac{2mk_BTV^2}{\hbar^2 b_y\pi}}\frac{1}{2}\sqrt{\frac{2mk_BTV^2}{\hbar^2 b_z\pi}} \\ &{=}\frac{1}{2^{\frac{6}{2}}}\frac{(2mk_BTV^2)^{\frac{3}{2}}}{\pi^{\frac{3}{2}}\hbar^{\frac{6}{2}}}\times(b_xb_yb_z)^{-\frac{1}{2}}{=}\frac{1}{2^{\frac{6}{2}}}\frac{(2mk_BTV^2)^{\frac{3}{2}}}{\pi^{\frac{3}{2}}\hbar^{\frac{6}{2}}}\times(L_x^4L_y^4L_z^4)^{-\frac{1}{2}} \\ &{=}(\frac{mk_BTV^2}{2\pi\hbar^2})^{\frac{3}{2}}V^{-2}{=}V(\frac{mk_BT}{2\pi\hbar^2})^{\frac{3}{2}} \end{aligned} \tag{25}$$

Note that unlike the partition function given to the "quantum" particle in a box, the partition function for the "classical" particle in a box is only dependent on the volume and no longer on the shape of the recipient. It can indeed be proved that this result is independent from the shape of the box (*4*).

In order to calculate the thermodynamic quantities we require derivatives of the function $log(q_{trans}^{classical})$, as well as that function itself.

$$log(q_{trans}^{classical}){=}log(V)+\frac{3}{2}log(\frac{mk_BT}{2\pi\hbar^2}) \tag{26}$$

$$\frac{\partial}{\partial T}log(q_{trans}^{classical}){=}\frac{3}{2T} \tag{27}$$

$$\frac{\partial^2}{\partial T^2}log(q_{trans}^{classical}){=}-\frac{3}{2T^2} \tag{28}$$

$$\frac{\partial}{\partial V}log(q_{trans}^{classical}){=}\frac{1}{V} \tag{29}$$

$$\frac{\partial}{\partial log(T)}log(q_{trans}^{classical}){=}\frac{3}{2} \tag{30}$$

$$\frac{\partial}{\partial log(V)}log(q_{trans}^{classical}){=}1 \tag{31}$$

Using these we can now calculate the pressure in the system:

$$P{=}k_BT\frac{\partial}{\partial V}log(q_{trans}^{classical}){=}\frac{k_BT}{V}{=}\frac{RT}{N_AV} \tag{32}$$

which for N particles yields

$$P{=}\frac{NRT}{N_AV}{=}\frac{nRT}{V} \tag{33}$$

The heat capacity at constant volume is given by:

$$C_V{=}2k_BT\frac{\partial}{\partial T}log(q_{trans}^{classical})+k_BT^2\frac{\partial^2}{\partial T^2}log(q_{trans}^{classical}){=}\frac{3R}{2N_A} \tag{34}$$

which for N molecules yields

$$C_V{=}\frac{3}{2}nR \tag{35}$$

The absolute internal energy,

$$U{=}k_BT^2\frac{\partial}{\partial T}log(q_{trans}^{classical}){=}\frac{3RT}{2N_A} \tag{36}$$

which, similarly, for N particles,

$$U{=}\frac{3}{2}nRT \tag{37}$$

The absolute entropy for this system is given by,

$$S{=}k_BT\frac{\partial}{\partial T}log(q_{trans}^{classical})+k_Blog(q_{trans}^{classical}){=}\frac{3R}{2N_A}+\frac{R}{N_A}log(V)+\frac{3R}{2N_A}log(\frac{mk_BT}{2\pi\hbar^2}) \tag{38}$$

for N molecules we obtain,

$$S{=}\frac{3nR}{2}+nRlog(V)+\frac{3nR}{2}log(\frac{mk_BT}{2\pi\hbar^2}) \tag{39}$$

Finally, we still have the enthalpy and the Gibbs free energy of a single particle,

$$H{=}k_BT^2\frac{\partial}{\partial T}log(q_{trans}^{classical})+k_BTV\frac{\partial}{\partial V}log(q_{trans}^{classical}){=}\frac{5RT}{2N_A} \tag{40}$$

$$G{=}k_BTV\frac{\partial}{\partial V}log(q_{trans}^{classical})-k_BTlog(q_{trans}^{classical}){=}\frac{RT}{N_A}{-}\frac{RT}{N_A}log(V){+}\frac{3RT}{2N_A}log(\frac{mk_BT}{2\pi\hbar^2}) \tag{41}$$

and the respective N molecule cases:

$$H{=}\frac{5}{2}nRT \tag{42}$$

$$G{=}nRT(1-log(V))+\frac{3}{2}nRTlog(\frac{mk_BT}{2\pi\hbar^2}) \tag{43}$$

These same results for N molecules can be obtained if we calculate the partition function for N distinguishable particles and then calculate the respective derivatives. In this case, the total partition function is given by

$$Z{=}(q_{trans}^{classical})^N \tag{44}$$

However, if we want to consider N indistinguishable particles the partition function is rather given by

$$Z=\frac{(q_{trans}^{classical})^N}{N!} \tag{45}$$

Because of the denominator in the latter partition function, for N indistinguishable particles we need to subtract $log(N!)=Nlog(N)$ to the entropy and to the Gibbs free energy. All other results remain the same.

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