

Where are the particles when the box is hot?

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Abstract

We consider the known problem of a particle in a one-dimensional box, i.e. in an infinite potential well. Specifically, we evaluate the probability density for finding a particle in a certain position when the system is in contact with a reservoir at a temperature $T \neq 0$. We observe that, when the T is increased, the density tends to become uniform in the box, except in a ‘boundary layer’ close to the walls. Then, we consider two particles in the box, discriminating between bosons and fermions. The particles are first analyzed without accounting for the spin. Evaluating the thermalized probability density in this way, results in a clear difference between bosons and spinless fermions. Next, we consider the complete wave function for spin- $1/2$ fermions, and the probability density changes significantly with respect to the spinless case. This shows that disregarding the electron spin for the sake of simplicity may lead to misleading results.

Keywords: particle in a box, thermalized probability, fermions and bosons

(Some figures may appear in colour only in the online journal)

1. Introduction

The quantum particle in a box is an inescapable exercise for students taking a course on modern physics [1] or quantum mechanics [2, 3]. And there is good reason for this, since the problem allows applying quantum concepts to a system that admits of a simple mathematical treatment. Therefore, there is abundant bibliography [4–18] on the topic, where the original problem is modified and analyzed from different perspectives. Honoring that tradition, and in general terms, the question we want to answer in this article is: **where are the particles when the box is at temperature T ?** To be more precise, in this work we will study the behavior of the probability density for finding a particle at a given position when the infinite potential well is in contact with a thermal reservoir.

Primero

We will first study the case of a particle in an infinite potential well, recall some well-known results, and evaluate the probability density for finding that particle in a given position. Next, the system will be put in contact with a reservoir at temperature T and we will observe how that probability density changes. The following step will be to consider two quantum particles in the well, and it will be necessary to distinguish between fermions and bosons. Since this article is meant to be educational, we will first analyze the system omitting the spin, i.e. focusing on the spatial aspect of the wave function. And we will repeat the same steps, as in the case of a single particle: evaluating the probability density for finding the particles in certain spatial positions, and then observing what happens when the system is at a temperature different to zero. Finally, we will analyze the problem of two fermions including their spin, and we will show that it introduces an interesting change to the results obtained previously.

2. Particle in a box

Any course on quantum mechanics explains that the probability for finding a particle at a position X and at a time t is proportional to the square of the wave function Ψ at that point. If $P(X, t)$ represents the probability density, quantum mechanics states that $P(X, t) = |\Psi(X, t)|^2$. Considering a particle of mass m in an infinite potential well of width L , Schrödinger's equation has an exact solution and it turns out to be $\Psi_n(X, t) = \varphi_n(x) \exp(-i2\pi E_n t/h)$, where subscript n indicates the current auto-state of the system. This auto-state is characterized by an energy E_n and a spatial wave function $\varphi_n(x)$ given by

$$E_n = \frac{h^2 n^2}{8mL^2}, \quad (1)$$

$$\varphi_n(X) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}X\right). \quad (2)$$

Then, as the quantum mechanics textbooks explain [2, 3], to evaluate the probability density we have to calculate: $P(X, t) = \Psi^*(X, t) \Psi(X, t)$. In the case at hand, as the system is in an auto-state, the time dependence is canceled and we get

$$P_n(X) = \frac{2}{L} \left(\sin\left(\frac{n\pi}{L}X\right) \right)^2. \quad (3)$$

To this point, these are known results. But now, we wonder what happens when this system is in contact with a thermal reservoir at temperature T . This condition corresponds to the canonical ensemble of statistical mechanics [19, 20]. Therefore, to obtain the thermal average of the probability density, we need to multiply the value of that quantity when the system is in a state n , by the Boltzmann's factor corresponding to the energy of that state $\exp(-E_n/k_B T)$, then add on all the states and normalize. As usual, k_B denotes Boltzmann's constant. The thermalized probability density will be designated by P_{th} .

In mathematical terms, the corresponding formula is

$$P_{th}(X, T) = \frac{\sum_{n=1}^{\infty} P_n(X) \exp\left[-\frac{E_n}{k_B T}\right]}{\sum_{n=1}^{\infty} \exp[-E_n/k_B T]}, \quad (4a)$$

$$Pth(X, T) = \frac{\sum_{n=1}^{\infty} \left(\frac{2}{L} \left(\sin \left(\frac{n\pi}{L} X \right) \right)^2 \exp \left[-\frac{h^2 n^2}{k_B T 8 m L^2} \right] \right)}{\sum_{n=1}^{\infty} \left(\exp \left[-\frac{h^2 n^2}{k_B T 8 m L^2} \right] \right)}. \quad (4b)$$

To simplify the notation, we will introduce an adimensional spatial coordinate x and an adimensional temperature t given by

$$T = t^* \frac{h^2}{8mL^2 k_B}, \quad (5a)$$

$$X = x^* \frac{L}{\pi}, \quad (5b)$$

$$\varphi_n(x) = \sqrt{\frac{2}{\pi}} \sin(n x). \quad (5c)$$

Note that now the spatial variable is limited to the interval $(0, \pi)$. The change in the amplitude of the wave function in (5c) is necessary so that the probability density integrated in this interval continues to be 1.

With these new variables, (4b) can be rewritten as

$$Pth(x, t) = \frac{2}{\pi} \frac{\sum_{n=1}^{\infty} \exp \left[-\frac{n^2}{t} \right] (\sin(n x))^2}{\sum_{n=1}^{\infty} \exp \left[-\frac{n^2}{t} \right]}. \quad (6)$$

Let us observe the influence of temperature on the probability density. First, though, we need to decide what to do with the infinite terms that appear in the summations of (6). For this, expression (6) is evaluated numerically, taking a number n_{\max} of terms in the summation. It turns out that for $t \leq 10$ the value of Pth is stabilized with $n_{\max} \approx 25$ and does not change when this number is increased. Thus, that is the number of terms that can be taken in the summations. Naturally, at higher temperatures, it would be necessary to consider more terms in the summations; for example, for $t = 100$ it is necessary to take $n_{\max} = 50$.

Figure 1(a) shows the probability density in relation to the position of the particle for three temperatures. For low temperature ($t = 1$), the particle tends to be in the central part of the box, while at a higher temperature the probability density tends to become uniform ($t = 10$). It is interesting to note the occurrence of a ‘boundary layer’ type phenomenon; there is an area very close to the walls of the box where the particle is extremely unlikely to be found. This is clearly evident for the high temperature ($t = 100$) represented by the solid line in the graph. A width d of the boundary layer can be defined by $Pth(d, t) = 0.1$. Of course, one could choose another value of the probability density, but 0.1 seems to be a reasonable one. Figure 1(b) shows d as a function of t . It is clear that for high temperatures there is a sort of boundary layer for the probability distribution.

It can be instructive to estimate, for a particular system, the real values of those temperatures. As known [11], it is possible to build semiconducting nanostructures that, under certain circumstances, can be modeled as an infinite potential well. Let us suppose that we have an electron confined in one such nanostructure with $L = 10$ nm. From (5a), we see that the unit to measure the temperature is 43 K and, therefore, the lines shown in figure 1 correspond to 43, 430 and 4300 K. It should be highlighted that the temperature unit depends heavily on the size of the system. If the nanostructure has a width of 2 nm, then the unit is valued as 1080 K and the only line that makes some sense is the one corresponding to $t = 1$.

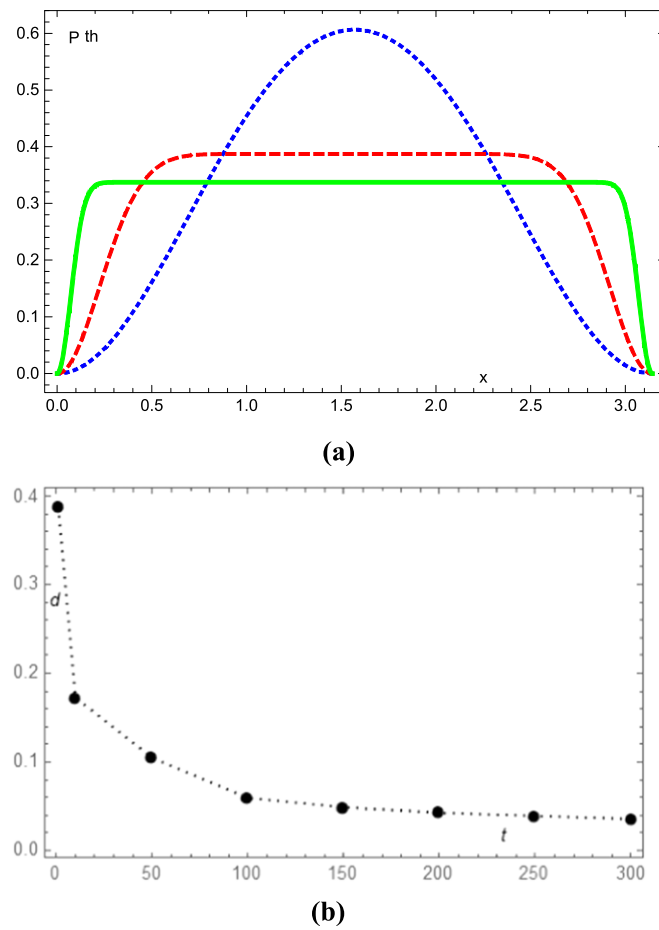


Figure 1. (a) Graph shows the thermalized probability density P_{th} for finding the particle in a position x for different temperatures: (I) $t = 1$ –dotted line, (II) $t = 10$ –dashed line, (III) $t = 100$ –solid line. Note the ‘boundary layer’ effect; in the area near the walls of the box, the probability density plummets to zero. This is especially clear for the case of the highest temperature –solid line. (b) Width d of the ‘boundary layer’ as a function of the temperature t . Width d is defined by $P_{th}(d, t) = 0.1$.

On the other hand, if $L = 15$ nm, then the temperature unit is 19 K, and the curves shown correspond to 19, 190 and 1900 K.

3. Two spinless particles

Now, we propose the same problem of the previous section, but with two particles in the box. Since in quantum mechanics it is necessary to distinguish between fermions and bosons, we will identify the wave functions and physical quantities of fermions with superscript ‘ f ’ and those of bosons with superscript ‘ b ’. For teaching purposes, in this section we will omit the spin in order to concentrate on the spatial aspect of the wave function. In section 4, the complete wave function will be considered.

For fermions, it is known that the total wave function must be antisymmetric under particle interchange, which implies that the two particles cannot occupy the same energy level ($n_1 \neq n_2$) if there is no spin. Consequently, the wave function ψ^f will be as follows:

$$\psi_{n_1, n_2}^f(x_1, x_2) = \frac{1}{\sqrt{2}}(\varphi_{n_1}(x_1)\varphi_{n_2}(x_2) - \varphi_{n_1}(x_2)\varphi_{n_2}(x_1)), \quad (7a)$$

$n_1 \neq n_2$.

For bosons, the wave function must be symmetrical in relation to particle interchange, and there is no restriction regarding their occupying the same energy level, so that

$$\psi_{n_1, n_2}^b(x_1, x_2) = \frac{1}{\sqrt{2}}(\varphi_{n_1}(x_1)\varphi_{n_2}(x_2) + \varphi_{n_1}(x_2)\varphi_{n_2}(x_1)). \quad (7b)$$

After replacing in (7) the wave function of the particles as expressed in (5c), the probability density for finding one particle in x_1 and the other in x_2 will be given by

$$P_{n_1, n_2}^f(x_1, x_2) = \frac{2}{\pi^2}(\sin(n_1 x_1) \sin(n_2 x_2) - \sin(n_1 x_2) \sin(n_2 x_1))^2, \quad (8a)$$

$$P_{n_1, n_2}^b(x_1, x_2) = \frac{2}{\pi^2}(\sin(n_1 x_1) \sin(n_2 x_2) + \sin(n_1 x_2) \sin(n_2 x_1))^2. \quad (8b)$$

Note that the wave functions are expressed in terms of the adimensional variable x defined in (5b).

At this point, it can be instructive to plot these probabilities for different n_1 and n_2 values. This is done in figure 2 for bosons and in figure 3 for fermions.

The plots for bosons can be seen in figure 2. Figure 2(a) corresponds to the case where both particles are in the ground state ($n_1 = n_2 = 1$) and we can see that the probability for finding a particle is at its maximum in the middle of the box when both bosons occupy the same spatial position. Figure 2(b) shows the probability when a particle is in the ground state and the other in an excited state ($n_1 = 1, n_2 = 5$). Again, we observe that the maxima appear along the diagonal, i.e. when $x_1 = x_2$.

Figure 3 shows the plots for two fermions. Figure 3(a) represents the ground state of the system, when one fermion is in the ground state and the other in the first excited state ($n_1 = 1, n_2 = 2$). Figure 3(b) plots the case where $n_1 = 1$ and $n_2 = 5$. As one of the quantum numbers increases, the plot becomes more complicated but visually attractive. We will see that the temperature erases all that complexity. It should be highlighted that the probability for finding the fermions in the same spatial position, i.e. along the diagonal of the plot, is strictly zero.

To calculate the effect of temperature we will need to multiply the probability obtained for each pair (n_1, n_2) by Boltzmann's factor and then normalize. Naively, this could be written

$$Pth(x_1, x_2, t) = \frac{\sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} P_{n_1, n_2}(x_1, x_2) \exp\left[-\frac{E_{n_1, n_2}}{t}\right]}{\sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \exp\left[-\frac{E_{n_1, n_2}}{t}\right]}. \quad (9a)$$

However, we must be careful when evaluating the thermalized probability Pth . On the one hand, the numeric calculation requires that we replace the upper limit of the summations with a parameter n_{\max} to be determined. On the other hand, it is necessary to avoid adding the same term twice. Finally, we need to remember that two fermions cannot occupy the same level. With these considerations in mind, expression (9a) assumes the following form for fermions or bosons:

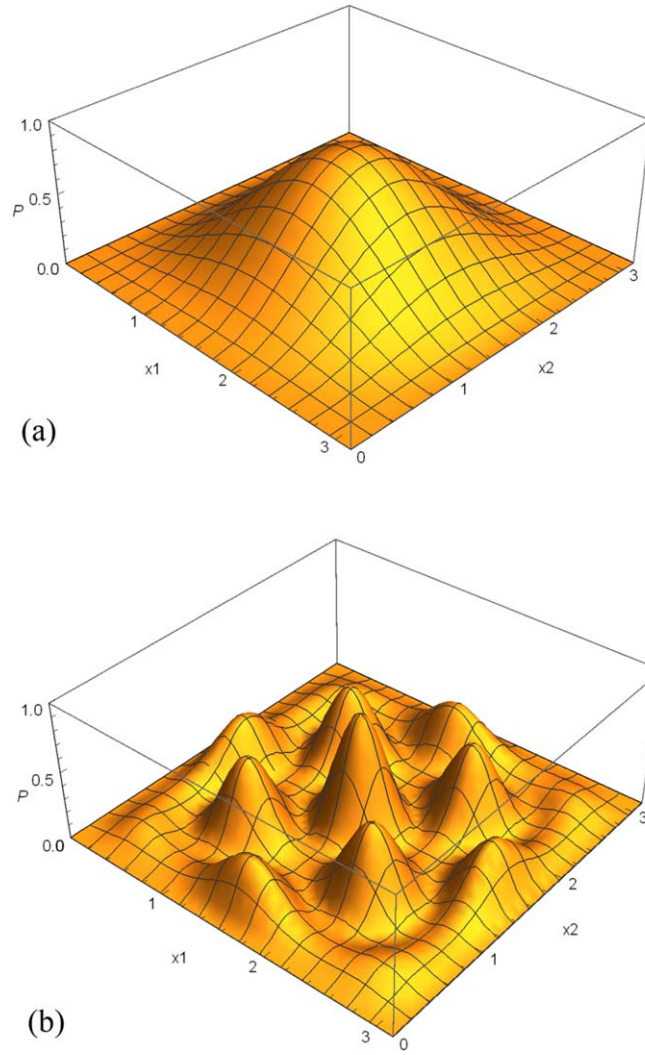


Figure 2. Plots of the probability P (vertical axis) for finding one particle in x_1 and the other in x_2 (horizontal axes). Since we are dealing with bosons, there is no restriction regarding the energy level that each occupies. Figure 2(a): both particles are in the ground state ($n_1 = n_2 = 1$). Figure 2(b): One particle is in the ground state ($n_1 = 1$), while the other is in an excited state ($n_2 = 5$). Note that the relative maxima occur along the diagonal, which means that the probability reaches its maximum in situations where $x_1 = x_2$.

$$Pth^f(x_1, x_2, t) = \frac{\sum_{n_1=1}^{n_{\max}-1} \sum_{n_2=n_1+1}^{n_{\max}} P_{n_1, n_2}^f(x_1, x_2) \exp\left[-\frac{E_{n_1, n_2}}{t}\right]}{\sum_{n_1=1}^{n_{\max}-1} \sum_{n_2=n_1+1}^{n_{\max}} \exp\left[-\frac{E_{n_1, n_2}}{t}\right]}, \quad (9b)$$

$$Pth^b(x_1, x_2, t) = \frac{\sum_{n_1=1}^{n_{\max}} \sum_{n_2=n_1}^{n_{\max}} P_{n_1, n_2}^b(x_1, x_2) \exp\left[-\frac{E_{n_1, n_2}}{t}\right]}{\sum_{n_1=1}^{n_{\max}} \sum_{n_2=n_1}^{n_{\max}} \exp\left[-\frac{E_{n_1, n_2}}{t}\right]}. \quad (9c)$$

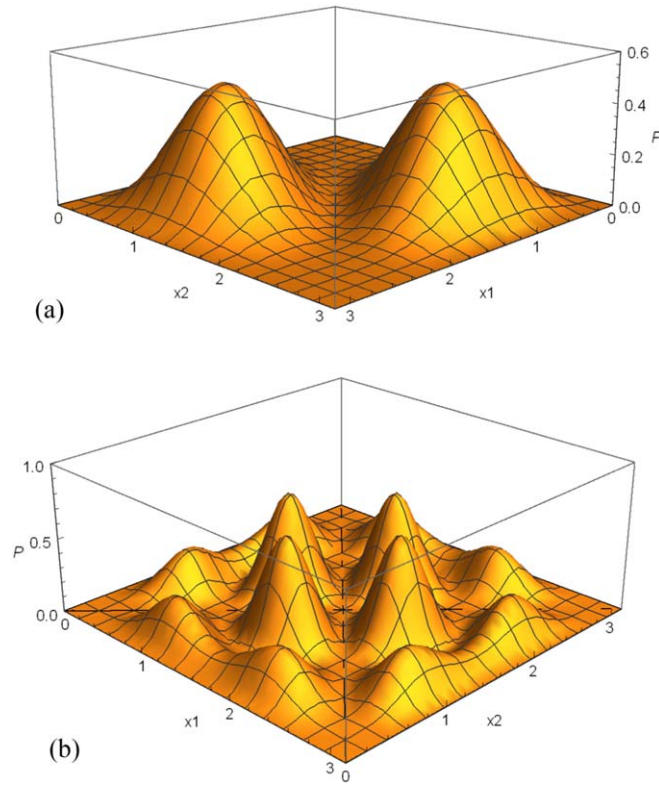


Figure 3. Plots of the probability density P (vertical axis) for finding one fermion in position x_1 and the other in position x_2 (horizontal axes). Remember that due to the change of variables we introduced, the positions vary in the interval $(0, \pi)$. (a): One fermion is in the ground state ($n = 1$), while the other is in the first excited state with $n = 2$. Note that the probability is strictly zero along the diagonal $x_1 = x_2$. (b): For the case where one fermion is in the ground state ($n = 1$) and the other in a higher excited state ($n = 5$), again the probability is strictly zero along the diagonal.

Note that the limits of the summations are different for fermions and bosons. For fermions, the limits are $1 \leq n_1 \leq n_{\max}-1$ and $n_1 + 1 \leq n_2 \leq n_{\max}$. For bosons, as there is no impediment for them to occupy the same energy level, the limits are $1 \leq n_1 \leq n_{\max}$ and $n_1 \leq n_2 \leq n_{\max}$. Now, all we need to do is replace expressions (8) in (9) to calculate the probability density for finding one particle in x_1 and the other in x_2 when the entire system is in contact with a reservoir at temperature t . The parameter n_{\max} is determined by trial and error; it needs to be increased until the probability values obtained for a given temperature become stable. As for the energy, it is considered that there is no interaction between the particles, therefore

$$E_{n_1, n_2} = n_1^2 + n_2^2. \quad (10)$$

Figure 4 shows the thermalized probability density at $t = 10$ for bosons (figure 4(a)) and for fermions (figure 4(b)). The value used is $n_{\max} = 25$.

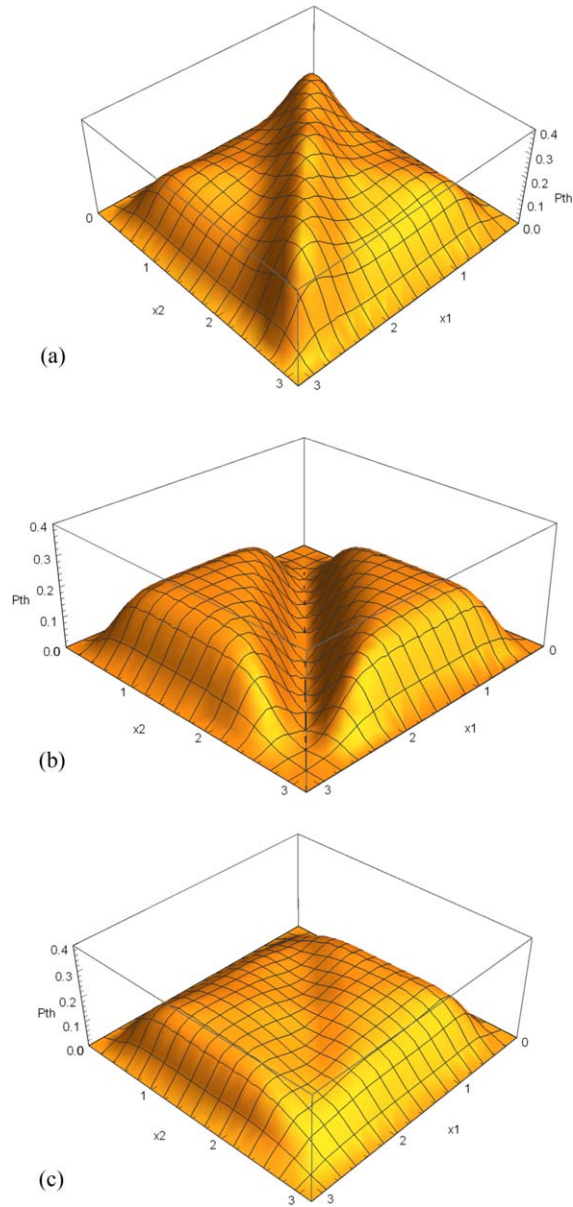


Figure 4. Plots of the thermalized probability density P_{th} (vertical axis) for finding one particle in x_1 and the other in x_2 (horizontal axes) when the system is in contact with a reservoir at $t = 10$: (a) bosons, (b) spinless fermions and (c) fermions with spin $1/2$. In the first case, the probability for two bosons to have the same spatial coordinate is at its maximum, while for spinless fermions, that probability is null. These results are obtained using only the spatial part of the wave function. However, in (c) the complete wave function of fermions is used, including the spin, which changes the result significantly, as will be explained in section 4.

4. Fermions with spin

So far, the most significant contribution was to show how the probability density differs when distinguishing bosons from fermions. To do this, however, the spin was deliberately omitted to concentrate on the spatial aspect of the wave function. Now, we will move on to carry out the complete analysis, i.e. assuming that fermions have spin $\frac{1}{2}$. We focus on fermions because the introduction of the spin implies qualitative changes in their behavior. The total wave function of fermions must be antisymmetric and have two components, one referred to the spatial variables and the other to the spins. If we use $\chi_+(1)$ to indicate that the first is a spin-up particle, while the second is a spin-down particle denoted by $\chi_-(2)$, then we have the following possible cases when one particle is in level n_1 and the other in level n_2 :

(a) Symmetric spatial wave function:

$$\Psi_{n_1, n_2}^f = \frac{1}{\sqrt{2}} [\varphi_{n_1}(x_1) \varphi_{n_2}(x_2) + \varphi_{n_1}(x_2) \varphi_{n_2}(x_1)] \frac{1}{\sqrt{2}} [\chi_+(1) \chi_-(2) - \chi_+(2) \chi_-(1)], \quad (11a)$$

(b) Antisymmetric spatial wave function:

$$\Psi_{n_1, n_2}^f = \frac{1}{\sqrt{2}} [\varphi_{n_1}(x_1) \varphi_{n_2}(x_2) - \varphi_{n_1}(x_2) \varphi_{n_2}(x_1)] \frac{1}{\sqrt{2}} [\chi_+(1) \chi_-(2) + \chi_+(2) \chi_-(1)], \quad (11b)$$

$$\Psi_{n_1, n_2}^f = \frac{1}{\sqrt{2}} [\varphi_{n_1}(x_1) \varphi_{n_2}(x_2) - \varphi_{n_1}(x_2) \varphi_{n_2}(x_1)] [\chi_+(1) \chi_+(2)], \quad (11c)$$

$$\Psi_{n_1, n_2}^f = \frac{1}{\sqrt{2}} [\varphi_{n_1}(x_1) \varphi_{n_2}(x_2) - \varphi_{n_1}(x_2) \varphi_{n_2}(x_1)] [\chi_-(1) \chi_-(2)]. \quad (11d)$$

It is important to emphasize the qualitative difference between both cases. If the spatial wave function is symmetric, then the part of the wave function associated with the spin must be antisymmetric, and there is only one way of doing that. This state is said to be a spin singlet. But if the spatial wave function is antisymmetric, then there are three different ways to express the part owing to the spin, and the three are symmetric under particle interchange. The antisymmetric spatial wave function is said to be associated with a spin triplet. Now, how do we calculate the probability for finding one particle in x_1 and the other in x_2 , independently of their spin? It will be necessary to keep in mind the four possible wave functions and to remember that three of them are associated with the antisymmetric spatial wave function and one with the symmetric spatial wave function. Then,

$$P_{n_1, n_2}(x_1, x_2) = \frac{1}{4} \left(\frac{1}{2} [\varphi_{n_1}(x_1) \varphi_{n_2}(x_2) + \varphi_{n_1}(x_2) \varphi_{n_2}(x_1)]^2 \right) + \frac{3}{4} \left(\frac{1}{2} [\varphi_{n_1}(x_1) \varphi_{n_2}(x_2) - \varphi_{n_1}(x_2) \varphi_{n_2}(x_1)]^2 \right). \quad (12)$$

It should be highlighted that when the spin was *not* taken into account, the case of $n_1 = n_2$ was forbidden by the Pauli exclusion principle. Now that the spin is being considered, it is possible for both fermions to have the same quantum number n but opposing spins. Figure 5 shows: (a) the case for $n_1 = 1$ and $n_2 = 2$ and (b) the case for $n_1 = 1$ and $n_2 = 5$. Figure 5 should be compared with figure 3.

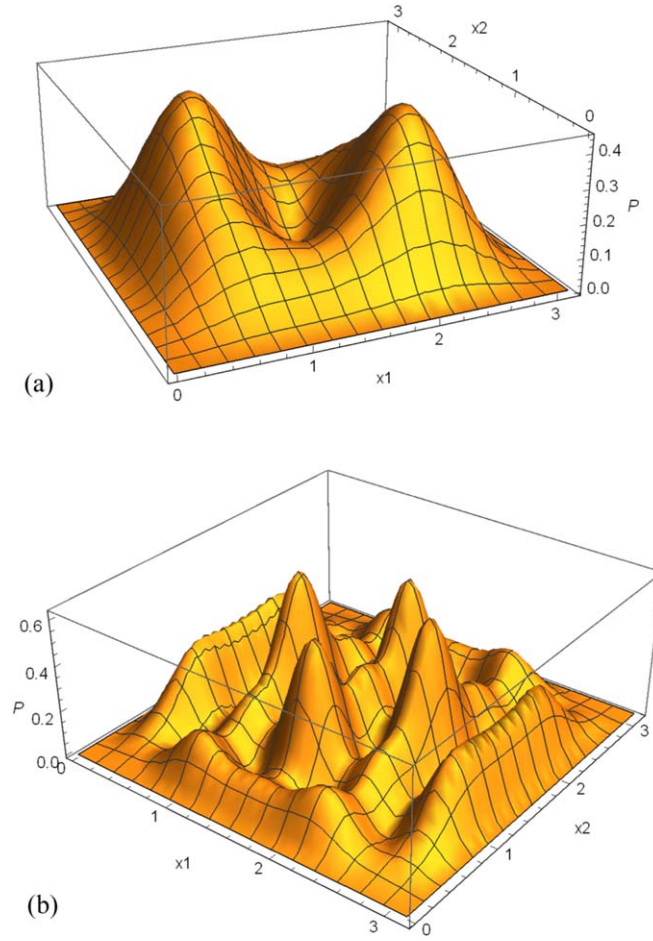


Figure 5. Plots of the probability density P for finding one fermion in x_1 and the other in x_2 when the complete wave function is considered, i.e. the spin is included. Two cases are analyzed: (a) $n_1 = 1$ and $n_2 = 2$ and (b) $n_1 = 1$ and $n_2 = 5$. Comparison of these plots with figure 3 shows that including the spin has a great impact in the shape of P .

Finally, all that remains is to evaluate the effect of temperature, when we put the potential well in contact with a thermal reservoir at temperature t . For this, we should take the probability density $P_{n1,n2}$ given by (12), multiply it by the corresponding Boltzmann's factor and normalize. This gives

$$Pth(x_1, x_2, t) = \frac{\sum_{n1=1}^{n \max} \sum_{n2=n1}^{n \max} P_{n1,n2}(x_1, x_2) e^{-\frac{(n1^2+n2^2)}{t}}}{\left(\sum_{n1=1}^{n \max} \sum_{n2=n1}^{n \max} e^{-\frac{(n1^2+n2^2)}{t}} \right)}. \quad (13)$$

Now, refer to figure 4(c), which shows the Pth for fermions with spin at temperature $t = 10$. It is clear that the new result is interpolated, in a way, between what was found for bosons and spinless fermions. Also, we can see the importance of taking into account the spin

when considering fermions; if the spin is omitted, the values obtained stray very far from the correct result (compare figures 4(b) and (c)).

The case of bosons with spin is not of interest. We could consider a neutral atom in a potential well, but such an object has a spin 0. Consequently, there is only one possible wave function, which is the symmetric spatial wave function, already considered, multiplied by an also symmetric function that accounts for the spin part. The spatial probability density would yield the same result as shown in section 3 for bosons with 0 spin.

5. Conclusions

Some interesting remarks can be made after completing this exercise. First, it is clear that when the temperature of the box increases, the probability density tends to become uniform in the box, except for the ‘boundary layer’ effect observed in figure 1. When we think about it, we see that this is expected. All the wave functions of this model are strictly zero in the walls, so that the thermalized probability density is also zero, and we get this area where the probability necessarily falls abruptly to zero. If we worked with a finite potential well, where the wave functions in the walls are different to zero, this boundary layer phenomenon would not occur, but rather the thermalized probability density would decrease smoothly towards zero. This means that the boundary layer phenomenon is, in fact, an artifact caused by the excessive simplification involved in using the infinite potential well as a model.

Although it is a well-known fact, it is worth emphasizing once again the attraction (repulsion) of strictly quantum origin that occurs between bosons (fermions), which can be observed in figure 2 (3). That attraction (repulsion) becomes even clearer when the thermalized probability density is analyzed (figure 4). The probability density for finding a particle is maximum along the diagonal (i.e. when $x_1 = x_2$) for bosons (figure 4(a)) and is strictly zero for fermions (figure 4(b)).

Perhaps the most interesting point made in this work has been to show the effect of the spin in the probability density. It is very common to omit the spin in the development of models that include electrons, even though this changes the physics of the system. A comparison of figures 3 and 5, or of figures 4(b) and (c), shows great difference in the probability density. And since the probability density is necessary to evaluate the mean value of any observable, it can be concluded that omitting the spin leads to the prediction of erroneous values of experimentally observable magnitudes. Naturally, the right approach is to include the spin in the wave function. However, it is not uncommon to omit it for the sake of simplicity, but this leads to the wrong results.

To sum up, this article has dealt with a topic of clear educational interest. It integrates knowledge from two different subjects (quantum mechanics and statistical physics) and the concepts presented here can be grasped by advanced undergraduate students. Sections 2 and 3 can even be used in a Modern Physics course that does not deal with the topic of identical particles. In addition, the first part of section 4 can be used to show the difference between singlet and triplet states in a two-electron system, which is usually a difficult topic for students.

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