
Exact Statistical Mechanics of Particle in a box using Canonical Ensemble

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Abstract

Statistical mechanics has been used for obtaining thermodynamics of systems mainly with classical energy and rarely for systems with quantum energy. For most of the situations with quantum energy, evaluation of the partition function which involves summation, is done by replacing the summation by integration. This replacement kills the basic effect of quantization like zero point energy and effects like the influence of size. Here we show that Euler-Maclaurin [EM] summation formula can be used to obtain the exact statistical mechanics of particles with discrete energy. We hope this method will help undergraduates for solving, similar problems in statistical mechanics using canonical ensemble.

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1 Introduction

Using Statistical Mechanics[SM] we can solve a large number of physical problems like magnetism, thermionic emission, photoelectric effect etc occurring in nature. For calculating the physical properties using SM we require energy of the system which may be classical(continuous in nature) or quantum energies(discrete in nature) depending upon their circumstances [1]. The classical energies possessed by particles under different situations may be equal to $\frac{p^2}{2m}$, pc , $\frac{p^2}{2m} + \frac{1}{2}kx^2$ etc and the particles may have corresponding quantum energies $\frac{n^2h^2}{8mL^2}$, $\frac{nhc}{2L}$, $(n + \frac{1}{2})\hbar\omega$ where m is the mass of the particle, p is the momentum, x is the displacement, c is the velocity of light, \hbar is the Dirac constant, ω is the angular frequency of the particle, L is the length of the box and n is the quantum number. One of the difficulties possessed by SM technicians is that, they are not able to solve the SM of systems with quantum energy because of the difficulty in evaluating the sum in the canonical ensemble. A quantized problem solved in SM text books completely is the case of nonrelativistic quantum harmonic oscillator[1]. In this case there is no difficulty in evaluating the partition function retaining the summation because of the availability of the Taylor series expansion method. But the simplest quantized system like Particle in a Box [PB] was not solved since the Taylor series method cannot be applied and alternate methods using Jacobian Theta function[2] and Abel-Plana formula[3]could not give complete solution. We show in com-

ing sections that Euler-Macularin[EM] summation formula[4] can be used effectively to sum the partition function.

This article concerns the calculation of the partition function in equilibrium statistical mechanics, without replacing the summations by integrations; in particular, by applying the EM summation formula. Section 2 reproduces well-known results, or presents straightforward analytic calculations, without additional insight into the physics of the examined case. Section 3 is devoted to an order of magnitude estimate of the spacing among the energy levels of a non-relativistic quantum particle in a box, as an argument for treating energy as a discrete quantity in the calculation of the partition function of this model. In section 4 thermodynamics of PB is evaluated and conspicuous difference in the internal energy between systems possessing continuous and discrete energy is depicted.

2 Statistical thermodynamics of non-relativistic PB

Particle in a box is the simplest physical model which has been solved quantum mechanically, but unsolved thermodynamically with quantum energy eigenvalue values, using statistical mechanics. Statistical mechanics has been earlier used for obtaining thermodynamics of PB[1,5], but the information we will have is that of a classical particle because of the conventional technique of replacing the summation by integration for evalu-

ating the partition function. Here, we respect the statistical thermodynamics of particle in a box initially using classical energy $\frac{p^2}{2m}$ and then by quantum energy $\frac{n^2 h^2}{8mL^2}$ by text book methods. The partition function of any classical system with energy ϵ_r is given by[1]

$$Q = \sum_r e^{-\beta \epsilon_r} \quad (1)$$

The partition function of any quantum system with energy ϵ_n is given by

$$Q = \sum_n g_I g_n e^{-\beta \epsilon_n} \quad (2)$$

where $\beta = \frac{1}{kT}$, g_I is the internal degrees of freedom, g_n is the degeneracy, k is the Boltzmann's constant, r and n represents the corresponding states and T is the absolute temperature.

2.1 Thermodynamics with classical energy

The partition function for a classical particle in 1D box is

$$Q = \int_0^\infty \frac{dp L e^{-\beta \epsilon_p}}{h}$$

where the energy of individual particle is $\epsilon_p = \frac{p^2}{2m}$. Using the standard integral

$$\int_0^\infty x^a e^{-\mu x} dx = a! \mu^{-a-1} \quad (3)$$

$$Q = \frac{L(2\pi mkT)^{\frac{1}{2}}}{h} \quad (4)$$

This can be written as

$$Q = \frac{\sqrt{\pi}}{2} \left(\frac{kT}{\epsilon_1} \right)^{\frac{1}{2}} \quad (5)$$

where ϵ_1 is equal to $\frac{h^2}{8mL^2}$.

2.2 Thermodynamics with continuous quantum energy

The partition function for particle in a box is

$$Q = \sum_{n=1}^\infty g_I g_n e^{-\beta \epsilon_n} \quad (6)$$

Here the energy of a particle is $\epsilon_n = \frac{n^2 h^2}{8mL^2}$. We take $g_I = 1$ and $g_n = 1$ for 1 D. Assumption of continuity in energy levels leads to the replacement of summation by integration and then the partition function becomes

$$Q = \int_{n=1}^\infty e^{-\beta \epsilon_n} dn$$

Using the approximation $\int_0^\infty \approx \int_1^\infty$

$$Q = \frac{\sqrt{\pi}}{2} \left(\frac{kT}{\epsilon_1} \right)^{\frac{1}{2}} \quad (7)$$

This is the same partition function we obtained for classical particle. Equations (5) and (7) show that both partition functions are identical and hence no new information regarding a quantum system is exhibited. This is due to the replacement of summation by integration evaluating the partition function. We can evaluate the the internal energy of PB using the relation given below .

$$U = -\frac{\partial(\ln Q)}{\partial \beta} = -\frac{1}{Q} \frac{\partial Q}{\partial \beta} \quad (8)$$

We get

$$U = \frac{1}{2}kT$$

This is the well known classical energy for a free particle. Here we have no information like zero point energy which is basically a quantum property.

3 Estimation of the spacing among the energy levels of a non-relativistic quantum PB

To justify our arguments for retaining the summation we make a simple calculation of the number of energy levels for systems with varying thickness. Our calculations once again demonstrate that thin or nano sized systems are basically of quantum origin.

Consider the case of a free particle confined in a box. The quantum energy

$$\epsilon_n = \frac{n^2 h^2}{8mL^2} \quad (9)$$

where $n = 1, 2, 3, \dots$, h is the Planck's constant, m is the mass of the confined particle and L is the length of the box. For n and $(n + 1)^{th}$ levels the difference in energy is

$$\Delta E = E_{n+1} - E_n$$

$$\Delta E = ((n + 1)^2 - n^2) \frac{h^2}{8mL^2}$$

$$\Delta E = (2n + 1) \frac{h^2}{8mL^2}$$

Thus when L is large ΔE is small or the energy levels are closely spaced.

For one degree of freedom the average thermal energy is

$$\epsilon_{nx} = \frac{1}{2}kT$$

For a bulk material of size 10 cm, assuming room temperature as 300 K

$$\epsilon_{nx} = 2.1 \times 10^{-21} J$$

Using Eq(9) and taking mass of electron

$$m = 9.1 \times 10^{-31} kg$$

and Planck's constant $h = 6.6 \times 10^{-34} Js$ we get

$$n_x \approx 10^9$$

Similar calculation for a micro material with thickness $10^{-6}m$ gives n nearly equal to 15 and for a nano material gives n nearly equal to .015. With the above n when ΔE is found we get

$$\Delta E \approx 10^{-26} J$$

for bulk material

$$\Delta E \approx 10^{-25} J$$

for micro material and

$$\Delta E \approx 10^{-18} J$$

for nano material. Thus when a substance becomes nano sized the energy levels becomes 10^8 times separated.

Besides the expression for energy also shows that the difference in energy eigenvalue values increases as 'n' increases which will never lead to continuum. Hence we are forced to retain the summation while evaluating the partition function. But no simple series expansion is available to evaluate the sum. Thus we go for EM method in the following section.

4 Statistical Thermodynamics of non relativistic PB using EM method

Euler- Maclaurin formula for evaluating a sum is given by

$$\sum_{n=i}^f f(n) = \frac{1}{2}f(i) + \int_i^f f(x)dx - \sum_{p=1}^{\infty} \frac{B_{2p}}{2p!} f^{2p-1}(i)$$

where B_{2p} are the Bernoulli numbers with $B_2 = \frac{1}{6}$, $B_4 = \frac{-1}{30}$ and $B_6 = \frac{1}{42}$ where i and f are the initial and final values of n. For PB this formula modifies to

$$\sum_{n=1}^{\infty} f(n) = \frac{1}{2}f(1) + \int_1^{\infty} f(x)dx - \sum_{p=1}^{\infty} \frac{B_{2p}}{2p!} f^{2p-1}(1)$$

We plotted $\frac{U}{\epsilon_1}$ and $\frac{kT}{\epsilon_1}$ numerically using Mathematica. The plots given below show that there is clear distinction between energies without replacing summation and with summation.

Numerically we found the summation for $p = \infty$ and it is observed that for $p = 2$ onwards the plot does not vary prominently. Since obtaining an analytic expression for partition function for large values of p is difficult we evaluate below the partition function for $p = 2$. EM formula becomes

$$\sum_{n=1}^{\infty} f(n) = \frac{1}{2}f(1) + \int_1^{\infty} f(x)dx - \frac{B_2}{2!}f'(1) - \frac{B_4}{4!}f'''(1)$$

we have

$$\begin{aligned} f(x) &= e^{-\frac{\epsilon_1}{kT}x^2} \\ f'(1) &= -2 \left[\frac{\epsilon_1}{kT} \right] e^{-\frac{\epsilon_1}{kT}} \\ f'''(1) &= \left[-8 \left(\frac{\epsilon_1}{kT} \right)^3 + 12 \left(\frac{\epsilon_1}{kT} \right)^2 \right] e^{-\frac{\epsilon_1}{kT}} \end{aligned}$$

Substituting, the partition function becomes

$$Q = \frac{\sqrt{\pi}}{2} \left(\frac{kT}{\epsilon_1} \right)^{\frac{1}{2}} + \left[-\frac{1}{90} \left(\frac{\epsilon_1}{kT} \right)^3 + \frac{1}{60} \left(\frac{\epsilon_1}{kT} \right)^2 + \frac{1}{6} \left(\frac{\epsilon_1}{kT} \right) + \frac{1}{2} \right] e^{\frac{-\epsilon_1}{kT}}$$

Using the above Q we get

$$\frac{U}{\epsilon_1} = \frac{\frac{\sqrt{\pi}}{4} \left(\frac{kT}{\epsilon_1} \right)^{\frac{3}{2}} + \left[\frac{1}{3} + \frac{2\epsilon_1}{15kT} + \frac{1}{20} \left(\frac{\epsilon_1}{kT} \right)^2 - \frac{1}{90} \left(\frac{\epsilon_1}{kT} \right)^3 \right] e^{\frac{-\epsilon_1}{kT}}}{\frac{\sqrt{\pi}}{2} \left(\frac{kT}{\epsilon_1} \right)^{\frac{1}{2}} + \left[\frac{1}{2} + \frac{\epsilon_1}{6kT} + 15 \left(\frac{\epsilon_1}{kT} \right)^2 - \frac{1}{90} \left(\frac{\epsilon_1}{kT} \right)^3 \right] e^{\frac{-\epsilon_1}{kT}}}$$

A plot of $\frac{kT}{\epsilon_1}$ with $\frac{U}{\epsilon_1}$ is shown in Figure(1). The plot depends on ϵ_1 where ϵ_1 is equal to $\frac{h^2}{8mL^2}$ which is a function of L. Thus thermodynamics of particle in a box is size dependent which is contradicting our earlier result that internal energy of the particle in a box is only a function of temperature.

5 Conclusions

In this paper we showed that EM summation formula can be successfully used to find the thermodynamics of a system with quantized energy. In the case of particle in a box there are differences in energies at different temperatures similar to a harmonic oscillator[1]. The two curves show that there is a clear separation which is due to the zero point energy. Besides at the beginning, which is low temperature region, there is conspicuous difference.

We are familiar with different applications of quantum harmonic oscillators in SM and hence we hope that the exact thermodynamics of PB also will play some key roles in SM of nanosized systems.

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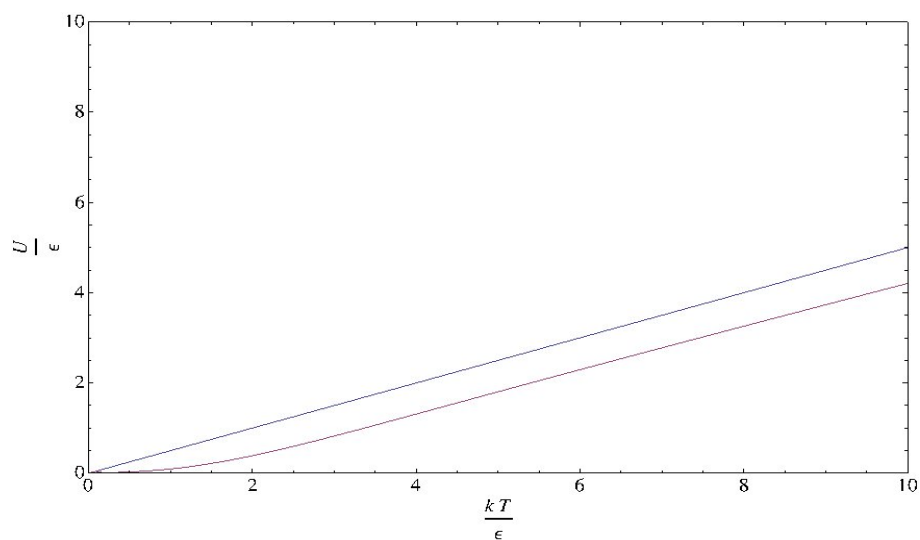


Figure 1: $\frac{kT}{\epsilon_1}$ versus $\frac{U}{\epsilon_1}$ curve for particle in a box using E M series expansion. The upper curve is for classical energy and lower curve is for quantum energy