DISCRETE NATURE OF THERMODYNAMIC PROPERTIES

Alhun Aydın* and Altuğ Şişman**

Istanbul Technical University, Energy Institute, 34469 Maslak, Istanbul, Turkey
*e-mail: alhunaydin@gmail.com
**e-mail: sismanal@itu.edu.tr

ABSTRACT

In this paper, we examined 0D and 1D Fermi gases (for example an electron gas in semiconductors or even atom gases like He_3) confined in certain dimensions. It has been shown that thermodynamic properties have a discrete nature in nanoscale. Also, they have certain physically meaningful values, which mean thermodynamic properties cannot take any continuous value, unlike classical thermodynamics in which they are considered as continuous quantities. We conclude that, as long as the confinement is strong enough, discrete nature of thermodynamic properties can be observed. Since quantum confinement in semiconductors is a well-established experimental research area, it is also possible to experimentally verify the results obtained here. Furthermore, the possibility of introducing new effects and developing new thermodynamic devices that depend on the discrete nature of thermodynamics in nanoscale will be discussed.

INTRODUCTION

Leap forwards in nanotechnologies in recent years, make it necessary to study thermodynamic behaviors of matter in nanoscale, which leads to a relatively new research area called as nano thermodynamics.[1-12] Numerous researches are going on in these areas recently. There are considerable deviations from classical thermodynamics and there have been proposed new effects based on the quantum nature of the systems. One of these new effects is examined under the name of Quantum Size Effects (QSE) in literature recently.

Thermodynamic properties such as number of particles, free energy, entropy, internal energy, chemical potential and heat capacity are represented with summations over quantum states, in their fundamental and exact forms. In macro scale, these summations in thermodynamic expressions may be replaced by integrals to make algebraic operations easy. However, when the sizes of the domain are comparable to the thermal de Broglie wavelength of particles, for instance in nanoscale; wave nature of particles become dominant, so we cannot use integrals instead of summations, since continuum approximation is no longer valid. Exact forms of thermodynamic properties must be considered in nanoscale thermodynamics. There are several ways to calculate exact sums in thermodynamics; one way is using Poisson summation formula. Evaluating partition function by Poisson summation formula expands the sum to three terms. Integral term is the conventional term that has been used in classical thermodynamics under continuum approximation. Zero correction term is a consequence of the fact that there are no zero-momentum states for particles in a system. Eventually, discrete term represents the discrete nature of momentum states and becomes dominant in nanoscale. Effects of zero correction term have been studied in literature as QSE. When the domain size is comparable to the thermal de Broglie wavelength of particles, contribution of zero correction term becomes recognizable. In addition to zero correction, in Fermi-Dirac statistics, discrete nature of thermodynamic properties, which depend on Pauli Exclusion Principle, starts to reveal itself. Intrinsic discrete nature has not seen in Maxwell-Boltzmann and Bose-Einstein statistics, since discretization is a consequence of Pauli Exclusion Principle, which is used fundamentally in the derivation of Fermi-Dirac statistics.

EXACT EXPRESSIONS OF THERMODYNAMIC PROPERTIES FOR A FERMI GAS CONFINED IN A RECTANGULAR DOMAIN

For a rectangular domain with dimensions L_1, L_2 and L_3, energy eigenvalues from Schrödinger equation are

$$\varepsilon = \frac{h^2}{8m}[(\frac{i_1}{L_1})^2 + (\frac{i_2}{L_2})^2 + (\frac{i_3}{L_3})^2], \quad \text{with } (i_1, i_2, i_3)=1,2,3,..., \tag{1}$$

where h is the Planck's constant and m is the mass of the fermion. Fermi-Dirac distribution function is

$$f = \frac{1}{e^{-\Lambda+(\alpha_1 i_1)^2+(\alpha_2 i_2)^2+(\alpha_3 i_3)^2}+1} \tag{2}$$

where $\Lambda = \mu/k_bT$ and α_n's are dimensionless scale factors defined as $\alpha_n = L_c(T)/L_n$ with $n = 1,2,3$ and $L_c(T) = h/\sqrt{8mk_bT} = \frac{\sqrt{\pi}}{2}\lambda_{th}$, where λ_{th} is the thermal de Broglie wavelength, k_b is the Boltzmann's constant and T is the temperature of the gas. Summations over all states of the distribution function will give the number of particles of a Fermi gas

$$N = \sum_{(i_1,i_2,i_3)=1}^{\infty} \frac{1}{e^{-\Lambda+(\alpha_1 i_1)^2+(\alpha_2 i_2)^2+(\alpha_3 i_3)^2}+1} \tag{3}$$

Now we can write the exact forms of thermodynamic properties such as internal energy U and heat capacity at constant volume C_V respectively as follows

$$U = k_b T \sum_{(i_1,i_2,i_3)=1}^{\infty} [(\alpha_1 i_1)^2 + (\alpha_2 i_2)^2 + (\alpha_3 i_3)^2] f \tag{4}$$

$$C_V = k_b \sum_{(i_1,i_2,i_3)=1}^{\infty} [(\alpha_1 i_1)^2 + (\alpha_2 i_2)^2 + (\alpha_3 i_3)^2]^2 f(1-f) - \frac{[\sum_{(i_1,i_2,i_3)=1}^{\infty} [(\alpha_1 i_1)^2 + (\alpha_2 i_2)^2 + (\alpha_3 i_3)^2] f(1-f)]^2}{\sum_{(i_1,i_2,i_3)=1}^{\infty} f(1-f)} \tag{5}$$

DISCRETE NATURE IN STRONGLY ANISOMETRIC QUANTUM DOTS

For $0D$, we examined two cases; strongly anisometric domain and isometric domain. In strongly anisometric domain, dimensionless scale factors are chosen as $\alpha_1 = 1$, $\alpha_2 = 40$ and $\alpha_3 = 40$, so that domain is confined in all three directions to make it a quantum dot, only 2 directions are confined much strongly than the other direction. Note that, $\alpha = 40$ is not a physically meaningless confinement, since it can be reached by using todays techniques in laboratories. For strongly anisometric domain, dimensionless chemical potential Λ against particle number N has been shown in Figure 1:

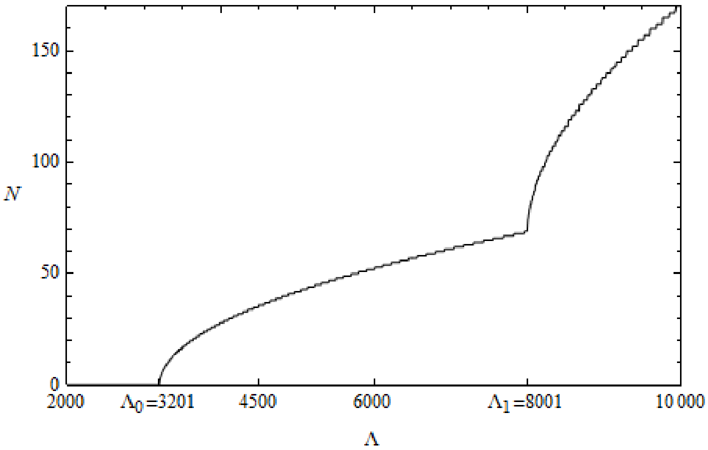

Figure 1. Strongly anisometric 0D domain (Quantum Dot), N vs Λ

Dimensionless chemical potential values between 0 and Λ_0 corresponds to zero particle. In other words, physically meaningful Λ values start from Λ_0. In Figure 1, critical Λ values are $\Lambda_0 = (\alpha_1)^2 + (\alpha_2)^2 + (\alpha_3)^2$ and $\Lambda_1 = (\alpha_1)^2 + (\alpha_2)^2 + (2\alpha_3)^2$. Beginning from $\Lambda_0 = (1)^2 + (40)^2 + (40)^2 = 3201$, states of the momentum component in direction-1, start to be occupied by particles since the discreteness of momentum in direction-1 is not as strong as in directions-2 and 3. That means, occupation of momentum states in direction-1 is possible, although the others are not. Hence, we can convert triple sum into a single sum, in a limited range of Λ.

$$N = \sum_{i_1=1}^{\infty} \frac{1}{e^{-\Lambda + (\alpha_1 i_1)^2 + (\alpha_2)^2 + (\alpha_3)^2} + 1} \tag{6}$$

Thereby, Eq. 6 gives exactly the same results of Eq. 3, for $\Lambda < \Lambda_1$. After $\Lambda_1 = (1)^2 + (40)^2 + (2 \times 40)^2 = 8001$ value, we have to consider excitations also in other directions. As it is shown in Figure 1, Λ changes with N in a stepwise manner. These steps can be seen in close-up more easily in Figure 2

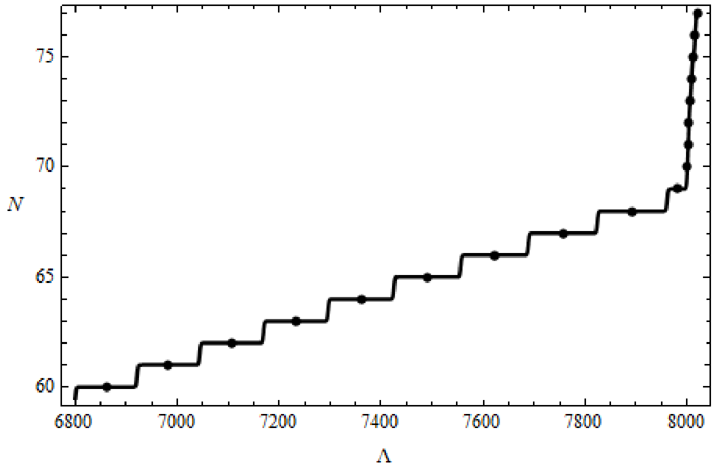

Figure 2. Strongly anisometric 0D domain (Quantum Dot) close-up, N vs Λ

Points on the middle of stepwise plateaus indicate Λ values corresponding to the integer particle numbers. As long as number of particles has integer values, continuous parts which do not contain points, are the forbidden region for Λ values. In other words, chemical potential can take only some certain discrete values which correspond to the integer number of particles. That is a very crucial deviation from classical thermodynamics. After Λ_1, the second modes of momentum components in direction-2 and 3 start to be occupied and the relation between N and Λ has a new character. Pay attention to that, horizontal steps are not completely flat, so the derivative of the function in any point is never zero. Similar stepwise behavior of particle number vs Λ, can be seen also in internal energy of Fermi gas. In Figure 3 and 4, dimensionless internal energy and specific heat at constant volume; $\widetilde{U} = \frac{U}{Nk_bT}$ and $\widetilde{C_V} = \frac{C_V}{Nk_b}$, versus Λ are shown respectively.

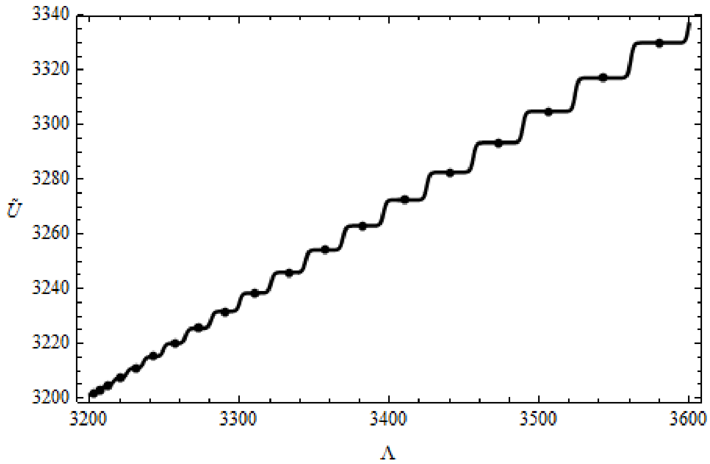

Figure 3. Strongly anisometric 0D domain (Quantum Dot), $\widetilde{U}$ vs Λ

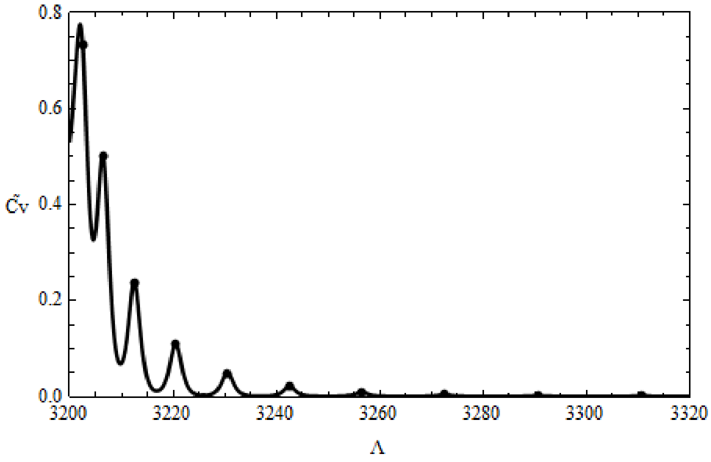

Figure 4. Strongly anisometric 0D domain (Quantum Dot), $\widetilde{C_V}$ vs Λ

Behavior of specific heat is as shown in Figure 4. Definite Λ values, marked with points, are determined from N vs Λ relationship and they are same in all figures. Besides, effects of particle addition to the system which is moderately confined in direction-1 and strongly confined in direction-2 and 3, can be shown in Figure 5.

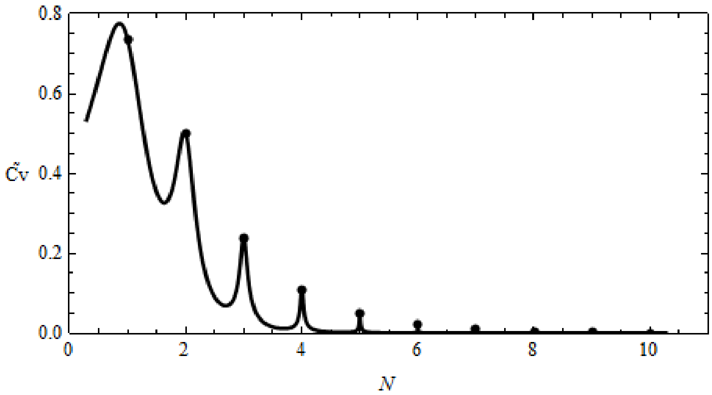

Figure 5. Strongly anisometric 0D domain (Quantum Dot), $\widetilde{C_V}$ vs N

DISCRETE NATURE IN ISOMETRIC QUANTUM DOTS

Now, let's consider isometric quantum dot. In isometric domain, dimensionless scale factors are chosen as $\alpha_1 = 3$, $\alpha_2 = 3$ and $\alpha_3 = 3$. So, confinement is not extremely strong, however it is strong enough to make the structure a quantum dot. Because of the contribution of the excited modes of momentum components, we have to do triple sum in order to express state functions and particle number, in all range.

For this case, N, U and C_V versus Λ are shown respectively in Figures 6, 7 and 8. Unlike the first case, for this case there are allowed values also in the steepnesses of the function, since excited modes in each direction start to be occupied from the very early $\Lambda = (3)^2 + (3)^2 + (3)^2 = 9$ value.

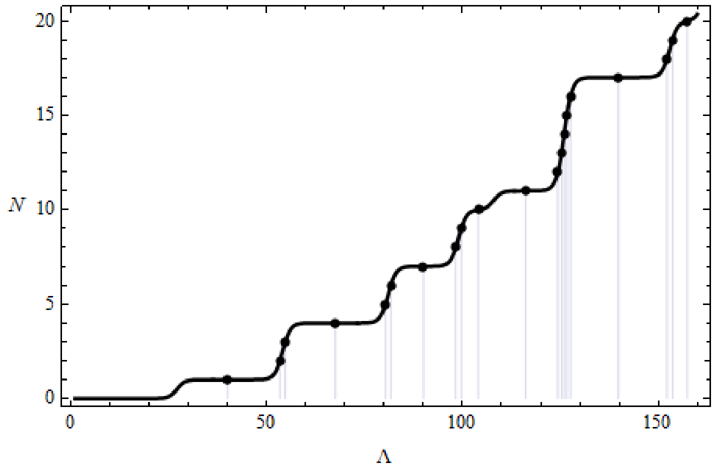

Figure 6. Isometric 0D domain (Quantum Dot), N vs Λ

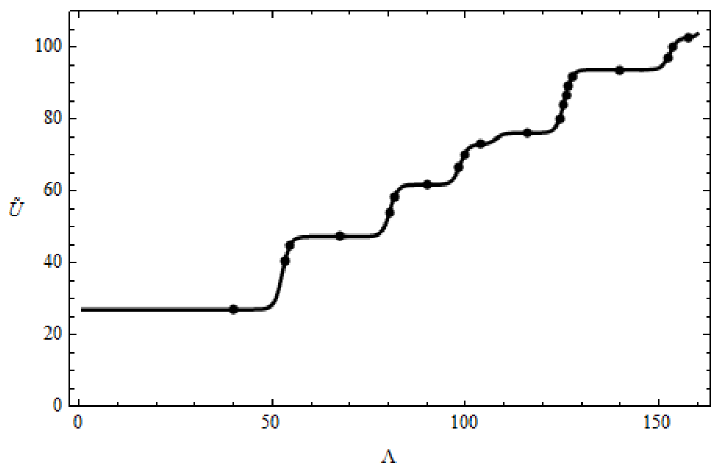

Figure 7. Isometric 0D domain (Quantum Dot), $\widetilde{U}$ vs Λ

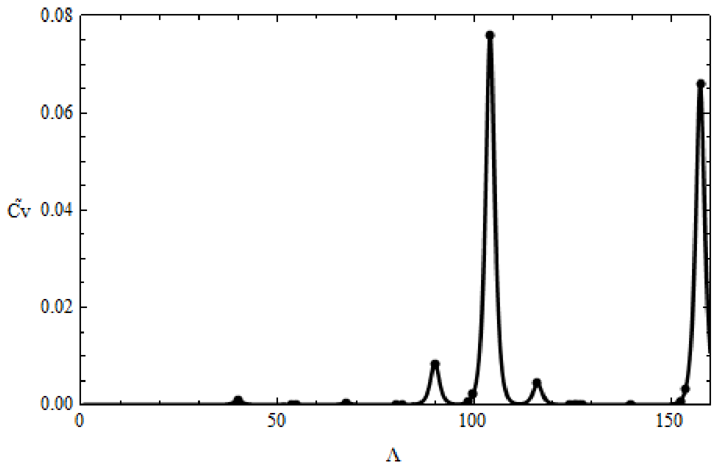

Figure 8. Isometric 0D domain (Quantum Dot), $\widetilde{C_V}$ vs Λ

Another interesting inference is that, unlike the first case we considered, adding particles does not affect thermodynamic properties equally in this case. Since occupation of momentum states in all directions are possible, particle addition causes sometimes to an increase, and sometimes to a decrease in specific heat C_V as in Figure 9. Particle number dependency of heat capacity is so severe that in some cases (high magnitude peaks on the Figure 9), changing number of particles in the domain causes to eight or more times radical changes in heat capacity of the system. Also, for a quantum dot with α values $\alpha_1 = 1$, $\alpha_2 = 1$ and $\alpha_3 = 1$, we can see oscillations in heat capacity, in Figure 10. Even for the large number of particles, oscillations are still observable.

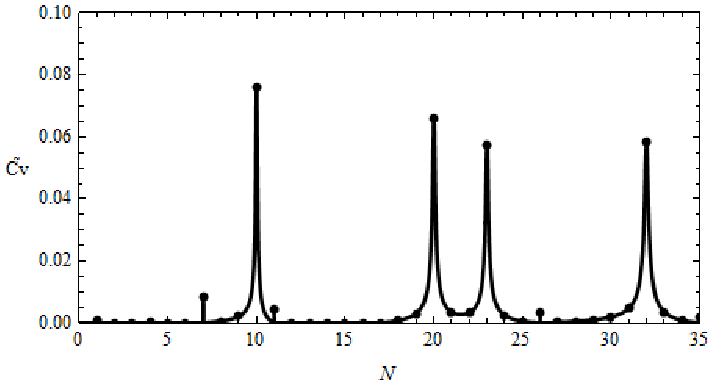

Figure 9. Isometric 0D domain (Quantum Dot), $\widetilde{C_V}$ vs N

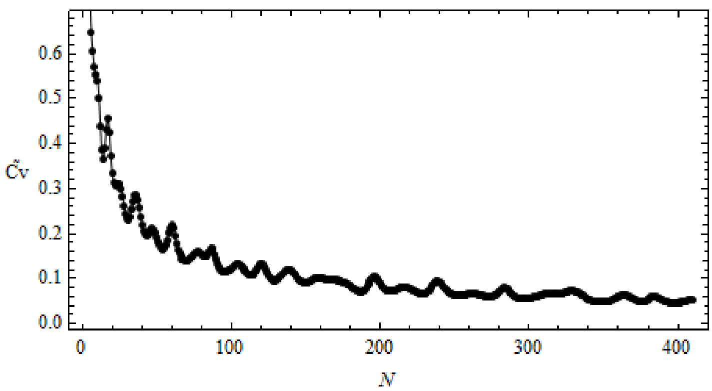

Figure 10. Isometric moderately ($\alpha_1 = \alpha_2 = \alpha_3 = 1$) confined 0D domain (Quantum Dot), $\widetilde{C_V}$ vs N

THE CASE OF QUANTUM WIRES

For 1D structures, it is shown in Figures 11 and 12, that stepwise behavior turns into kind of a quasi-continuous behavior. In spite of that, noticable peaks can still be observed in heat capacity, in Figure 13. Again changing number of particles in the system has different effects on the heat capacity, as it is shown in Figure 14. Change of particle number affects system drastically, so that C_V doubles and halves even for small changes in large number of particles. Such strong dependencies can be verified experimentally.

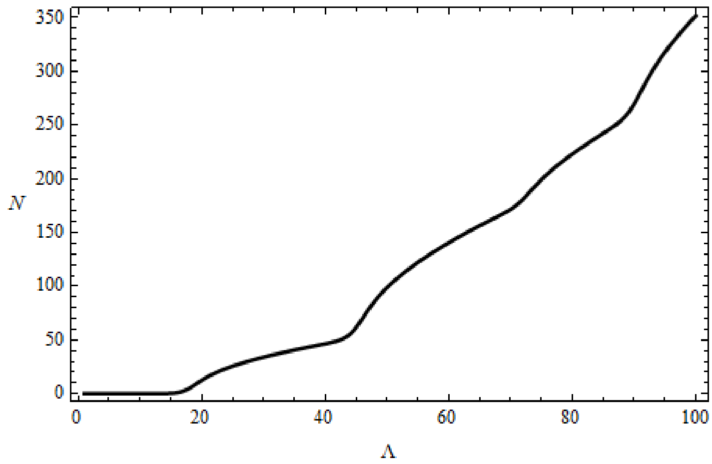

Figure 11. 1D domain (Quantum Wire), N vs Λ

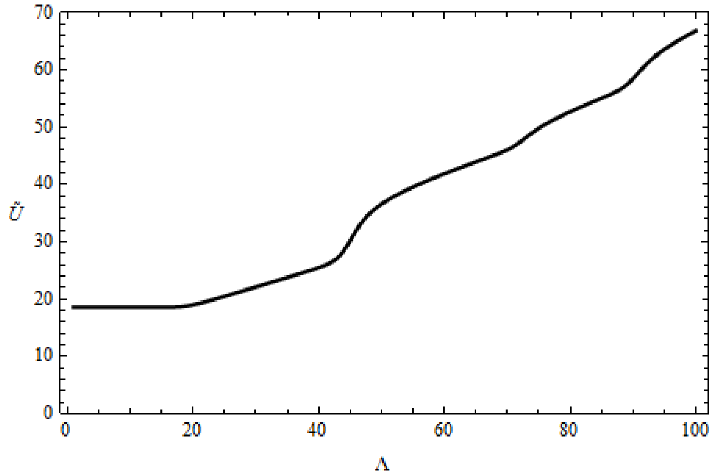

Figure 12. 1D domain (Quantum Wire), $\widetilde{U}$ vs Λ

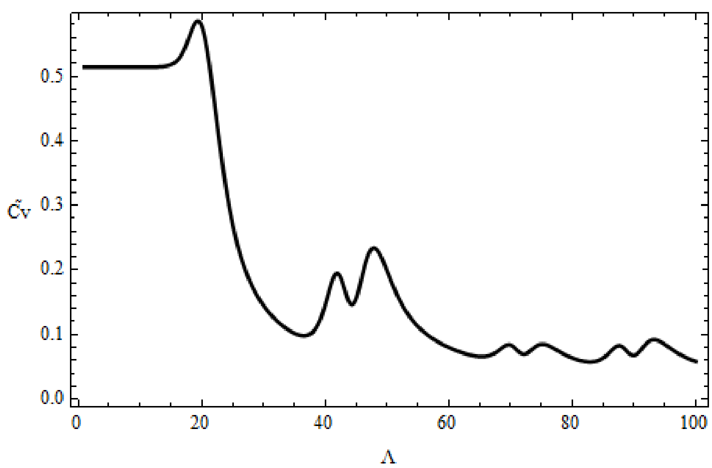

Figure 13. 1D domain (Quantum Wire), $\widetilde{C_V}$ vs Λ

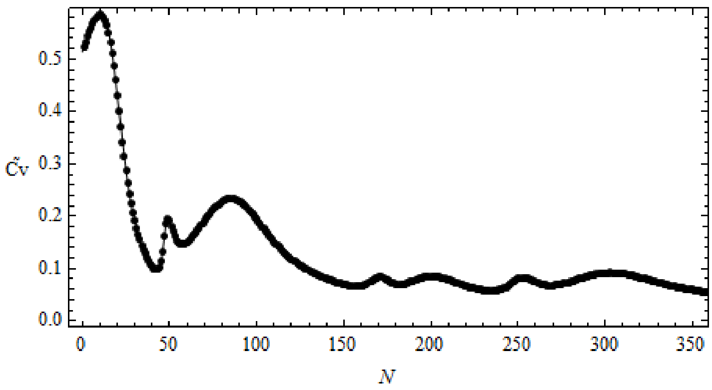

Figure 14. 1D domain (Quantum Wire), $\widetilde{C_V}$ vs N

As we expected, discrete nature of thermodynamics becomes slighter and slighter as we decrease the number of confined directions. For quantum wire (1D) and well (2D), discrete nature and peaks in heat capacity are still partially observable. Conversely, for the bulk (3D), discrete nature disappears almost completely.

DISCUSSION

In this study, we made numerical calculations on several thermodynamic quantities (N, U, C_V) by using exact summations. We showed that in nano scale, there is an intrinsic discrete nature in 0D and 1D Fermi gases (quantum dots and nanowires) and thermodynamic quantities can take only some certain values, if there is no applied external potential field to the system.

In case of the existence of electrical field, chemical potential becomes electrochemical potential. Therefore, it is possible to change Λ value by changing the strength of the field. In that case, intermediate values between certain Λ values, which correspond to the integer number of particles, correspond now to the non-integer number of particles. This means that, by applying and changing an electrical field, it is possible to create quasi-particles which have non-integer numbers. This also leads to a possibility of making quantum dot energy conversion and storage units. If the external electrical field is increased, quantum dot will store the energy and when the external field is disabled, system will turn back into its initial state, by releasing energy.

Considering the development rate of nanotechnology, it is very likely not only to verify the discrete nature of thermodynamic properties, but also to make efficient quantum energy storage devices which can easily be used later in new energy technologies. In addition to numerical results, evaluation of exact sums into analytical expressions is under consideration.

REFERENCES

[1] M. I. Molina, Ideal gas in a finite container, Am. J. Phys. **64 pp.** 503-505, 1996.

[2] R. K. Pathria, An ideal quantum gas in a finite-sized container, Am. J. Phys. **66 pp.**1080-1085, 1998.

[3] W. S. Dai and M. Xie, Quantum statistics of ideal gases in confined space, Phys. Lett. A **311 pp.** 340-346, 2003.

[4] W. S. Dai and M. Xie, Geometry effects in confined space, Phys. Rev. E **70** 016103, 2004.

[5] A. Sisman and I. Müller, The Casimir-like size effects in ideal gases, Phys. Lett. A **320 pp.** 360-366, 2004.

[6] A. Sisman, Surface dependency in thermodynamics of ideal gases, J. Phys. A- Math. Gen. **37 pp.** 11353-11361, 2004.

[7] H. Pang, W. S. Dai and M. Xie, The difference of boundary effects between Bose and Fermi systems, J. Phys. A-Math. Gen. **39 pp.** 2563-2571, 2006.

[8] A. Sisman, Z. F. Ozturk and C. Firat, Quantum boundary layer: a non-uniform density distribution of an ideal gas in thermodynamic equilibrium, Phys. Lett. A **362 pp.**16-20, 2007.

[9] C. Firat and A. Sisman, Universality of quantum boundary layer for a Maxwellian gas, Phys. Scripta **79** 065002, 2009.

[10] Z. F. Ozturk and A. Sisman, Quantum Size Effects on the Thermal and Potential Conductivities of Ideal Gases, Phys. Scripta **80** 065402, 2009.

[11] C. Firat, A. Sisman and Z. F. Ozturk, Thermodynamics of gases in nano cavities, Energy **35** Sp.Iss.SI: pp. 814-819, 2010.

[12] A. Sisman and G. Babac, Quantum Size Effects on Classical Thermosize Effects, J. Continuum Mechanics Thermodynamics **24**, pp.339-346, 2012.