THERMODYNAMICS UNDER QUANTUM SIZE EFFECTS

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ABSTRACT

Thermodynamics of nanoscale systems is considerably different than that of macro ones. Wave nature of particles cause quantum size effects (QSE) which change the thermodynamic behaviors of nano systems considerably. QSE become important when thermal de Broglie wavelength of particles is not negligible in comparison with the characteristic size of the system. In such a case, QSE make thermodynamic state functions depend on size and shape of the system and cause some new and interesting behaviors which cannot be observed at macro scale. The subject of QSE on thermodynamics of nano systems is a relatively new research subject and it has many potential applications for nano technology. New effects caused by the wave nature of particles can be used to design and produce completely new nano devices and even new thermodynamic cycles. In this study; after the brief introduction of QSE and the methodology used for the calculation of thermodynamic properties under QSE, corollaries of QSE on thermodynamics are summarized and discussed by considering some novel results.

INTRODUCTION

Wave nature of particles modifies the probability density at thermodynamic equilibrium from a constant quantity to a space and momentum dependent quantity and also particle’s momentum spectrum from continuous quantity to a discrete one. These modifications cause quantum size effects (QSE) which change the thermodynamic behaviors of nano systems. Therefore the following questions emerge: how thermodynamic behaviors change at nanoscale, how it can be modeled, how one can make use of these different behaviors, how new devices and technologies can be developed based on the effects appearing at this scale. The subject of QSE on thermodynamics of nano systems is a relatively new research topic [1-13] and it has many potential applications for nano technology. New effects caused by the wave nature of particles can be used to design and produce completely new nano devices and even new thermodynamic cycles [14-19].

QSE become important when thermal de Broglie wavelength of particles is not negligible in comparison with the system’s characteristic size (L_q = V/A , V is volume and A is surface area of the domain). Therefore, they are mainly the nonscale effects. Due to QSE, thermodynamic state functions become dependent on size and shape of the system and some new and interesting behaviors appear at nano scale [1-13]. It has been shown that due to wave character of particles, density distribution of a gas in a finite domain is not homogenous even at thermodynamic equilibrium. There is a layer near to the boundaries of the domain and gas density goes to zero within this layer, which has been called as quantum boundary layer (QBL) since it disappears when the Planck’s constant goes to zero [8, 9, 11]. Another unusual behavior appearing at nano scale is the anisotropic pressure of a gas confined in an anisometric domain.

The aim of this study is to give a brief review of some recent published results besides some very recent and unpublished ones yet. After the brief introduction of QSE and the methodology used for the calculation of thermodynamic properties under QSE, some novel results are summarized and discussed. These are quantum surface energy, loss of additivity rule for extensive quantities, anisotropic gas pressure, diffusion driven by size and shape differences, thermosize effects (similar to thermoelectric effects), quantum boundary layer, quantum forces as a macroscopic manifestation of quantum boundary layer, discrete nature of thermodynamic properties of a Fermi gas and multi-step Bose-Einstein condensation.

QUANTUM SIZE EFFECTS ON THERMODYNAMIC QUANTITIES

In general, size effects are the changes in material behaviors due to change in material sizes. They appear when the characteristic size of a material is not sufficiently larger than the characteristic lengths of physical processes. Characteristic size of a material (a domain) can simply be represented by L_q = V/A . On the other hand, there are many characteristic lengths for physical processes and they are classified into two groups, namely classical and quantum. Classical ones are mean free path, mean distance between particles, characteristic length for a driving force, like L_f = T/|V T|, etc. Quantum characteristic lengths are thermal de Broglie wave length λ_{th}, quantum coherence length, etc. Quantum size effects appear if λ_{th} is not negligible in comparison with L_q , (L_q ∝ λ_{th}). In that case, wave nature of particles become important and causes some fundamental assumptions and approximations to change: Momentum values of a particle become a discrete set although it is assumed to be a continuous quantity during the classical
treatments of macro systems. Besides the discrete nature of momentum, its minimum value is not zero in a finite-size system and this value is inversely proportional with the system size. Another quantity which has to be modified is the probability density. When the wave nature of particles is negligible, it is a homogenous quantity and equal to the classical probability density given by $1/V$ for a system of volume $V$. On the other hand, when the wave nature of particles becomes important, it is equal to the quantum probability density $|\Psi(x,p)|^2$ where $\Psi$ is the wave function obtained by the solution of the Schrödinger equation. The classical probability density predicts a homogenous density distribution at thermodynamic equilibrium whereas quantum one predicts a non-homogenous density distribution [8].

An ideal Maxwell gas confined in a rectangular finite domain: the simplest case

To understand the appearance of QSE on thermodynamic quantities, the simplest way is to consider an ideal Maxwell gas of mono particles (like monatomic gas, free electron gas etc.) confined in a non-penetrable rectangular domain with sizes of $L_1, L_2$ and $L_3$. Free energy expression of gas is

$$ F = N(\mu - k_B T) \tag{1} $$

where $k_B$ is the Boltzmann’s constant, $T$ is temperature, $N$ is number of particles in the domain and $\mu$ is chemical potential determined by

$$ \mu = -k_B T \ln \left( \frac{\zeta}{N} \right) \tag{2} $$

where $\zeta$ is the single particle partition function defined by

$$ \zeta = \sum_r \exp(-\varepsilon_r / k_B T). \tag{3} $$

Here the summation is over the quantum states $r$, $\varepsilon_r$ is the energy eigenvalue of particles corresponding to quantum state $r$. Energy eigenvalues of a single particle confined in a rectangular box are well known and they are given as follows,

$$ \varepsilon_r = \varepsilon_{ijk} = \frac{\hbar^2}{8m} \left[ \frac{i_1^2}{L_1^2} + \frac{i_2^2}{L_2^2} + \frac{i_3^2}{L_3^2} \right] \quad \text{where } i_1, i_2, i_3 \text{ are integer numbers running from one to infinity. By using Eq.(4), Eq.(3) can be expressed as}
$$

$$ \zeta = \sum_{i,j,k} \exp \left[ - \left( \frac{\alpha_1 i_1^2}{L_1^2} + \frac{\alpha_2 i_2^2}{L_2^2} + \frac{\alpha_3 i_3^2}{L_3^2} \right) \right] \tag{5} $$

where $\alpha_1 = L_1/L_4$, $\alpha_2 = L_2/L_4$, $\alpha_3 = L_3/L_4$ and the length $L_q = h/\sqrt{8\pi m k_B T} = \sqrt{\pi} \lambda_{\text{ph}}/2$ is one half of the most probable de Broglie wavelength of the particles.

In macro system: $L_1, L_2, L_3 > L_q$ and $\alpha_1, \alpha_2, \alpha_3 << 1$. In that case; discrete nature of momentum values of particles (and so the energy values) is negligible and they are assumed to be continuous quantities. Therefore, infinite summations can be replaced by infinite integrals and the trivial thermodynamic expressions, which are independent of the system size and shape, are obtained. In nano systems, however, at least one of the domain sizes is near to the order of $L_q$. Therefore wave nature of particles becomes important.

In this case, discrete nature of momentum values is noticeable and their discrete values are running from a non-zero value to infinity. Therefore, integral representations of summations give the incorrect results and more precise methods, like Poisson, Abel-Plana or Euler-Mac Lauren summation formula, should be used for the calculations of summations. Poisson summation formula is given for an even function $f(i)$ as

$$ \sum_{i=1}^{\infty} f(i) = \frac{f(0)}{2} + 2 \sum_{i=1}^{\infty} f(i) \cos(2\pi si) di \tag{6} $$

The first term on the right hand side is the dominant and conventional integral term. The second one is the zero correction term, which excludes the false contribution of the zero value of $i$ to the integral term. The third one is the discreteness correction due to discrete values of $i$ instead of continuous ones. It is possible to show numerically that the contribution of discreteness correction is much smaller than that of the zero correction as long as the system size is bigger than $L_q$ ($\alpha < 1$). As an example, the ratio of the discreteness correction to the zero correction for the summation in Eq.(5) is less than $10^{-4}$ even for $\alpha=1$. Therefore, the main correction to the integral approximation comes from the second term in Eq.(6) for $\alpha \leq 1$.

By using the first two terms of Eq.(6), partition function in Eq.(5) is determined as

$$ \zeta = \frac{\pi^{3/2}}{8\alpha_1 \alpha_2 \alpha_3} \left( 1 - \frac{\alpha_1}{\sqrt{\pi}} \right) \left( 1 - \frac{\alpha_2}{\sqrt{\pi}} \right) \left( 1 - \frac{\alpha_3}{\sqrt{\pi}} \right) \tag{7} $$

If the values of alphas are smaller than unity but greater enough than zero, then the second and third order terms in alphas can be neglected. In that case, Eq.(7) is simplified as [5]

$$ \zeta = n_q V \left[ 1 - \frac{1}{\sqrt{\pi}} (\alpha_1 + \alpha_2 + \alpha_3) \right] \tag{8} $$

where $n_q = 1/\lambda_{\text{ph}}^3$ is the quantum density and $V = L_1 L_2 L_3$ is the domain volume. Thus free energy expression is obtained by using Eq.(8) in Eqs.(2) and (1) as follows

$$ F = -nk_B T \left[ \ln \left( \frac{n_q}{n} \right) + 1 \right] V + nk_B T \frac{\lambda_{\text{ph}}^3}{4} A \tag{9} $$

The first term in Eq.(9) is the classical bulk free energy while the second term is the quantum surface energy [5, 6, 8, 9, 11]. It is seen that free energy is proportional to both volume and surface area of the domain. This means that free energy of a simple system does not depend on only two variables like temperature and density but also depend on surface over volume ratio which is the quantity sensitive to size and shape of the domain. In other words, thermodynamic state functions of nano systems are size and shape dependent. It should be noted that quantum surface energy disappears when the system size becomes macroscopic since $\lambda_{\text{ph}} A/V$ goes to zero.
Furthermore, it also disappears when the Planck’s constant goes to zero. Therefore, the second term is a pure quantum term which is noticeable only in nano systems.

Instead of using the summations over quantum states, it is also possible to use summations over energy states by considering the density of states. In that case, the same free energy expression can be obtained by using the Weyl’s conjecture, which gives a precise formula for density of states depending on not only the domain volume but also the surface area, periphery and even the corners or end points of the domain [2-4, 7]. The advantage of using the Weyl’s conjecture is that there is no need to solve the Schrödinger equation for each different domain shape. It is the general expression for any domain shape. In other words, in addition to the rectangular domain, Eq.(9) is valid also for cylindrical, spherical or other shapes of domain [6, 11].

**COROLLARIES OF QSE ON THERMODYNAMICS**

By using Eq.(9), internal energy, pressures in each direction, entropy and chemical potential are obtained as follows respectively,

\[ U = \frac{3}{2} N k_b T + N k_b T \frac{\lambda_{th}}{8} A \]  
\[ p_1 = n k_b T \left(1 + \frac{\lambda_{th}}{2L_i}\right) \]  
\[ p_2 = n k_b T \left(1 + \frac{\lambda_{th}}{2L_2}\right) \]  
\[ p_3 = n k_b T \left(1 + \frac{\lambda_{th}}{2L_3}\right) \]  
\[ S = N k_b \left[ \ln \left(\frac{n \alpha}{n}\right) + \frac{5}{2} - N k_b \frac{\lambda_{th}}{8} A \right] \]  
\[ \mu = -k_b T \ln \left(\frac{n \alpha}{n}\right) + k_b T \frac{\lambda_{th}}{4} A \]  

**Non-extensivity:** Due to the second terms of Eqs.(9), (10), (12) and (13), additivity rule of extensive quantities is not valid in nano systems [5].

**Pressure anisotropy:** Eqs.(11a-11c) shows that pressure becomes an anisotropic quantity in an anisometric nano domain since it is different in each directions. In other words, pressure of even an ideal gas is not a scalar quantity and it becomes a tensorial quantity generally in nano systems [5, 6].

**Size and shape difference driven diffusion:** As a result of the second term in Eq.(13), a chemical potential difference can be created by size or shape differences even if density and temperature are kept constant. This causes a diffusion driven by size and shape differences [5].

**Thermosize effects:** Another interesting behaviour appearing due to QSE is thermosize effects. They are very similar to thermoelectric effects which arise when two different conductors or semi-conductors are under the same temperature gradient. The temperature gradient induces an electrochemical potential gradient in each conductor and it is known as Seebeck effect. As long as the conductors are made by the different materials, the same temperature gradient causes different electrochemical potential gradients in each conductor. Therefore, a net electrochemical potential difference is obtained at hot or cold side when the conductors are connected to each other at the other side. This potential difference can drive an electrical current on an external load.

During the isothermal flow of electrical current from one material to the other, a heat exchange between the charge carriers and their environment at interface is observed which is known as Peltier effect. Therefore, two different types of conductors having different electrical properties should be used to observe the thermoelectric effects. Consequently, differences in both temperature and electrical properties are necessary to get the thermoelectric effects. If the conductors are made by the same material, then the thermoelectric effects disappear. On the other hand, since the size itself becomes a control variable on thermodynamic state functions at nano scale, instead of using two different materials, it becomes possible to get a net potential difference by using the two different sized (macro and nano) structures made by the same material under the same temperature gradient. In that case, differences in both temperature and size cause some new effects so called “thermosize effects” [5, 13]. After the proposition of thermosize effects, some recent works have been done to analyze the thermodynamic cycles based on thermosize effects [14-19].

**Quantum boundary layer:** For an ideal Maxwellian gas confined in a domain with finite size, the local density is given by [8]

\[ n(x) = \frac{1}{V} \sum_r \exp(-\epsilon_r/k_b T) \]  
\[ n(x) = \frac{1}{V} \sum_r \exp(-\epsilon_r/k_b T) \]  

where \( n_{cl} \) is the classical density defined by \( n_{cl} = N/V \), \( N \) is the total number of particles in the whole confinement volume \( V \) and \( \psi_r(x) \) is the eigenfunction corresponding to quantum state \( r \). For an ideal Maxwell gas confined in a rectangular box, dimensionless density distribution in one direction is

\[ \tilde{n}(\tilde{x}) = \frac{2 \sum_{i=1}^{\infty} \exp\left[-(\alpha \tilde{x})^2\right] \sin^2\left(\frac{\alpha \tilde{x}}{L_x}\right)}{\sum_{i=1}^{\infty} \exp\left[-(\alpha \tilde{x})^2\right]} \]  

where \( \tilde{n} = n(\tilde{x})/n_{cl} \), \( \tilde{x} = x/L_x \) and \( L_x \) is the size of the domain in chosen direction [8]. Figure 1 shows the density distribution for \( \alpha = 0.2 \). It is seen that density distribution is not homogenous and there is a boundary layer where the density goes to zero. As a result of the wave character of particles, particles tend to accumulate in the inner parts of the domain and this tendency causes higher local gas density than the classical one, \( \tilde{n} > 1 \), for the interior region. Thickness of quantum boundary layer is given as [8]

\[ \delta = \frac{L_x}{2\sqrt{\pi}} \frac{\lambda_{th}}{4} \]  

\[ \delta = \frac{L_x}{2\sqrt{\pi}} \frac{\lambda_{th}}{4} \]
Since the thickness of boundary layer depends on thermal de Broglie wavelength of particles, it has been called as quantum boundary layer, QBL.

**Effective volume and effective density:** By using the concept of QBL, it is possible to define an effective volume and effective density respectively as

\[
V_{\text{eff}} = V - A\delta \\
n_{\text{eff}} = \frac{N}{V_{\text{eff}}} = \frac{N}{V - A\delta} = \frac{n_{ij}}{1 - \frac{A\delta}{V}}
\]

(17)

(18)

Therefore, if the effective density is used instead of classical density in trivial free energy expression of an ideal Maxwell gas, Eq. (9) is directly obtained without following its relatively complicated calculation procedure. Application of effective density in trivial free energy expression gives

\[
F = -Nk_B T \left[ \ln \left( \frac{n_y}{n_{ij}} \right) + 1 \right]
\]

\[
= -Nk_B T \left[ \ln \left( \frac{n_y}{n_{ij}} \right) + 1 \right] - Nk_B T \ln \left( 1 - \frac{A\delta}{V} \right)
\]

(19)

In case of \(A\delta << V\), by use of the approximation \(\ln(1-x) = -x\) for \(x << 1\) and considering \(\delta = \lambda_{bh}/4\), Eq. (19) is expressed as

\[
F = -nk_B T \left[ \ln \left( \frac{n_y}{n} \right) + 1 \right] V + nk_B T \frac{\lambda_{bh}}{4} A
\]

(20)

Eq. (20) is exactly equal to Eq. (9). Thus the concepts of effective volume and density give an opportunity to derive the thermodynamic quantities under QSE in a simple way. Furthermore, the second term can physically be explained as a compression work against the normal gas pressure to push the gas particles into the inner parts of the domain from the boundaries for a distance of \(\delta = \lambda_{bh}/4\). This work simply results from the wave nature of particles. Collisions between particles and the boundary are switched on when the distance is less than \(2\delta = \lambda_{bh}/2\) as it can be seen from Figure 1.

**Density distributions in quantum gases:** For ideal Fermi and Bose gases, dimensionless density distribution is expressed as [10]

\[
\tilde{n}(\tilde{x}) = \frac{1}{V} \sum_{w} \frac{\exp[-\Lambda + \epsilon_w/k_B T + \Lambda]}{\exp[-\Lambda + \epsilon_w/k_B T + \Lambda T^+1} - \frac{\exp[-\Lambda + \epsilon_w/k_B T - \Lambda]}{\exp[-\Lambda + \epsilon_w/k_B T - \Lambda T^+1}
\]

(21)

where \(\Lambda\) is dimensionless chemical potential defined as \(\Lambda = \mu/k_B T\). Density distributions are shown in comparison with that of a Maxwell gas in Figure 2. \(\alpha\) is chosen as \(\alpha = 0.2\) while the values of \(\Lambda\) are \(\Lambda = 10\) and \(\Lambda = -0.05\) for Fermi and Bose gases respectively.

Figure 2: Dimensionless density distributions of ideal monatomic Maxwell, Fermi and Bose gases in one direction.

It is seen that in a degenerate Fermi gas, there is also density oscillation, which is called Friedel oscillation in literature for the electron gas. In a degenerate Bose gas, inhomogeneous region expands and covers the whole domain.

**Quantum surface tension and quantum forces:** A hypothetical experimental setup is shown in figure 1. A rectangular box is filled by a Maxwellian gas and separated into two parts by a movable and infinitesimally thin wall.

Figure 3: A schematic view of a quantum force, \(\mathbf{F}\), acting on a moving wall.

The change in total surface area of the domain is only due to the change in lateral area of the interior part of the moving wall \((\Delta = 2L_y L_z)\). By making use of Eq. (20), quantum surface tension of a Maxwellian gas can be determined as [12].

\[
\sigma = \left( \frac{\partial F}{\partial A} \right)_{N,Y,T} = \frac{1}{2L_y L_z} \left( \frac{\partial F}{\partial L_y} \right)_{N,Y,T} = n_T k_B T \frac{\lambda_{bh}}{4} P
\]

(22)
Surface tension is an unexpected behavior for an ideal gas in a classical manner. On the other hand, even an ideal gas has surface tension due to the existence of QBL. Since the thickness of QBL goes to zero in classical limit ($\hbar \to 0$), it has been called as quantum surface tension (QST) [12]. QST is approximately $10^6 \text{Nm}^{-1}$ for He-4 gas under the standard conditions (300 K and 10$^5$ Pa). As shown in Figure 3, surface tension of a gas causes an outward quantum force on the moving wall to minimize the quantum surface energy. Derivative of free energy with respect to $L_z$ gives the quantum force as,

$$\hat{\mathbf{F}} = \left(\frac{\partial F}{\partial L_z}\right)_{N,V,T} \mathbf{e}_z = \hat{p}_z = 2\bar{\delta}L_y \mathbf{e}_z = \sigma 2L_y \mathbf{e}_z$$ \hspace{1cm} (23)

The effective thickness of the wall is $2\bar{\delta}$ because of the QBL around infinitesimally thin moving wall. Thus, quantum force $\hat{\mathbf{F}}$ acting on the wall in outward direction can easily be expressed by means of the normal component of stress tensor (pressure) or surface tension as in equation (23). In other words, quantum force can be explained by a normal force due to gas pressure acting on the effective area of the movable wall ($2\bar{\delta}L_y$). If quantum forces of gases are experimentally verified, this can be one of the macroscopic manifestations of quantum boundary layer and quantum surface energy.

**Discrete nature of thermodynamic quantities:** If the confinement is strong enough, then alpha values are greater than unity. In that case, the discrete nature of momentum states becomes very dominant and makes the thermodynamic quantities of an ideal Fermi gas discrete. In figure 4, the relation between number of particles and dimensionless chemical potential is shown just to give an idea. It is clearly seen that only some certain values of chemical potential are available since the number of particles has an integer value. The similar behavior can be observed in internal energy. The most interesting results is obtained for the specific heat at constant volume. There are lots of peaks in the relation between specific heat and number of particles, see Figure 5.

![Figure 4: Number of Fermi particles strongly confined in an anisometric rectangular domain versus dimensionless chemical potential, $\Lambda = \mu/k_B T$.](image)

All the results summarized above show that thermodynamics in nano scale is completely different than that in macro scale. QSE on thermodynamics cause entirely new behaviors and effects that can be experimentally verified for the exploration of nano world as well as used to design some new nano devices.

**REFERENCES**


