DIMENSIONAL TRANSITIONS IN THERMODYNAMIC PROPERTIES

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ABSTRACT

In this work, dimensional transitions in thermodynamic properties of an ideal Maxwell gas confined in a finite domain are studied. When one of the sizes of confinement domain becomes shorter than the thermal de Broglie wavelength of particles, momentum space is subject to a dimensional transition. Dimension of momentum space is defined based on mean probability change per quantum state step. Variation of the dimension with domain sizes is examined. Dependencies of internal energy, specific heat at constant volume and entropy on domain sizes as well as dimension of momentum space are analyzed. Dimensional transitions in momentum space from 3D to 2D and similarly from 2D to 1D and 1D to 0D are considered. It is shown that there is an increment in specific heat at constant volume during the dimensional transitions. Furthermore, all quantities considered here decreases when the confinement increases.

INTRODUCTION

Recent developments in nano science and technology reveal the difference between nano and macro scale material properties. Quantum wells, quantum wires and quantum dots are the remarkable examples for the diversity in transport and optical properties of the same material. Similarly, thermodynamic properties of gases confined in nano domains become size and shape dependent due to wave nature of particles [1-12].

Here, dimensional transitions in thermodynamic properties of an ideal monatomic Maxwell gas confined in a rectangular box are considered. Partition function is used to determine free energy. From expression of free energy; entropy, internal energy and specific heat at constant volume are then derived in exact forms based on expressions of infinite summations. Therefore the expressions are valid even for strongly confined domains although the trivial macroscopic expressions based on integral approximation are valid only for unbounded domains.

To examine the dimensional transitions in thermodynamic properties, dimension of momentum space is defined based on mean probability change per step in quantum state space. Internal energy of excited states is taken into account by eliminating ground state energy from internal energy to consider only thermal contributions instead of size dependent contribution of ground state energy. Similarly instead of considering entropy itself, only the entropy of momentum space is considered by subtracting entropy of the ground state, which is the pure configurational entropy, from the entropy itself. Dimensionless inverse scale factors $\alpha_1, \alpha_2, \alpha_3$ are defined as the ratio of the sizes of rectangular box in each direction (L_1, L_2 and L_3) to L_c. Thermodynamic quantities and their dimensional transitions are examined in terms of these dimensionless scale factors.

THERMODYNAMIC PROPERTIES OF AN IDEAL MAXWELL GAS IN A RECTANGULAR BOX

Free energy expression of an ideal Maxwell gas is given as

$$F = -Nk_b T\left[1+\ln\left(\frac{\zeta}{N}\right)\right] \tag{1}$$

where, N is number of particles, T is temperature, k_b is the Boltzmann's constant and ζ is the partition function. For particles confined in a rectangular box, ζ is defined below [5]

$$\zeta = \zeta\left(\alpha_1,\alpha_2,\alpha_3\right) = \sum_{\{i,j,k\}=1}^{\infty} e^{-(\alpha_1 i)^2-(\alpha_2 j)^2-(\alpha_3 k)^2} \tag{2}$$

Here $\{i,j,k\}$ are the quantum state numbers running from unity to infinity, α_n is the dimensionless inverse scale factor defined as $\alpha_n = L_n/L_c$ where L_n is the size of the box in direction n and $L_c = h/\left(2\sqrt{2mk_bT}\right)$.

Entropy is determined by the derivation of free energy with respect to temperature as follows,

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = Nk_b\left[1+\ln\left(\frac{\zeta}{N}\right)+\frac{\eta}{\zeta}\right] \tag{3}$$

where $\eta = \eta\left(\alpha_1,\alpha_2,\alpha_3\right)$ is given by

$$\eta = \sum_{\{i,j,k\}=1}^{\infty}\left[\left(\alpha_1 i\right)^2+\left(\alpha_2 j\right)^2+\left(\alpha_3 k\right)^2\right]e^{-(\alpha_1 i)^2-(\alpha_2 j)^2-(\alpha_3 k)^2} \tag{4}$$

Free energy and entropy relations are used to obtain internal energy expression as

$$U = F + TS = Nk_b T\left(\frac{\eta}{\zeta}\right) \tag{5}$$

On the other hand, by differentiating the internal energy with respect to temperature, specific heat at constant volume is determined as

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V = Nk_b\left(\frac{\gamma}{\zeta}\right) - Nk_b\left(\frac{\eta}{\zeta}\right)^2 \tag{6}$$

where $\gamma = \gamma(\alpha_1, \alpha_2, \alpha_3)$ is defined as

$$\gamma = \sum_{\{i,j,k\}=1}^{\infty}\left[(\alpha_1 i)^2 + (\alpha_2 j)^2 + (\alpha_3 k)^2\right]^2 e^{-(\alpha_1 i)^2 - (\alpha_2 j)^2 - (\alpha_3 k)^2} \tag{7}$$

To examine the dimensional transition in thermodynamic properties above, dimensionless entropy, internal energy and specific heat at constant volume are introduced as,

$$\tilde{s} = \frac{S}{Nk_b} = 1 + \ln\left(\frac{\zeta}{N}\right) + \frac{\eta}{\zeta} \tag{8}$$

$$\tilde{u} = \frac{U}{Nk_b T} = \frac{\eta}{\zeta} \tag{9}$$

$$\tilde{c}_v = \frac{C_v}{Nk_b} = \frac{\gamma}{\zeta} - \left(\frac{\eta}{\zeta}\right)^2 \tag{10}$$

It should be noted that conditions of $N >> 1$ and $N \ll \zeta$ should be satisfied to use both statistical approach and MB statistics respectively. In case of confinement in two directions (directions 2 and 3), these conditions are expressed as

$$1 \ll N \ll \frac{\sqrt{\pi}}{2\alpha_1} e^{-\left(\alpha_2^2 + \alpha_3^2\right)}. \tag{11}$$

Therefore, MB statistical approach can still be used if the value of α_1 is sufficiently small in spite of large values of α_2 and α_3, $\{\alpha_2, \alpha_3\} > 1$.

DIMENSION DEFINITION AND TRANSITION IN MOMENTUM SPACE

Before examining dimensional transition in thermodynamic properties, dimension in momentum space should be defined with probabilistic approach. Excitation probability of particles in momentum space drastically decreases for the confinement direction and particles lose their excitation chance in that direction. In other words, only the ground state of momentum in confined direction can be occupied by the particles and all the excited states of momentum in that direction become empty. Occupation probability of quantum state *r* is

$$p_r = \frac{e^{-(\alpha_r r)^2}}{\sum_{r=1}^{\infty} e^{-(\alpha_r r)^2}}. \tag{12}$$

Change of probability per change of quantum state number is

$$\Delta p_r = p_r(\alpha_r, r+1) - p_r(\alpha_r, r) \tag{13}$$

The ensemble average of absolute value of Δp_r is

$$\langle|\Delta p_r|\rangle = -\sum_r p_r \Delta p_r \tag{14}$$

When α_r is greater than unity, the probability of ground state goes to unity which means that the whole particles accumulate in ground state. In that case, $\langle|\Delta p_r|\rangle$ also goes to unity since the probabilities of the excited states are zero and probability distribution becomes a single point in probability space. Therefore, this situation corresponds to a zero dimensional probability space. On the contrary, as α_r goes to zero each state becomes equally probable which corresponds one dimensional space. Consequently the dimension of momentum space can be determined by

$$D = 3 - \langle|\Delta p_i|\rangle - \langle|\Delta p_j|\rangle - \langle|\Delta p_k|\rangle \tag{15}$$

Thereby, dimensional transition from 3D to 0D can be examined by Eq.(15) as a function of $\alpha_1, \alpha_2, \alpha_3$. The dimensional transition due to change of domain sizes in directions of 1 and 2 is shown in Fig.1.

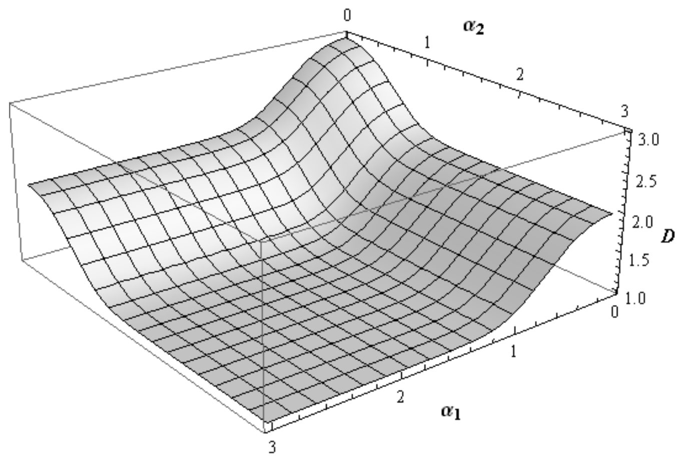

Figure 1: Dimensional transition from 3D to 2D and 1D.

Similarly dimensional transition from 1D to 0D is given in Fig.2.

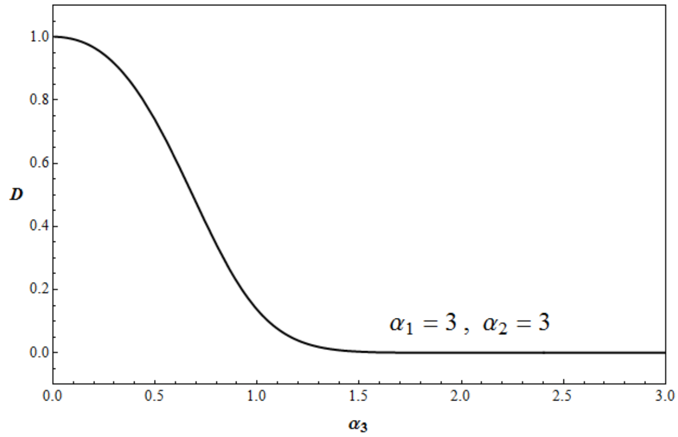

Figure 2: Dimension transition from 1D to 0D.

As seen in Fig.(1) and Fig.(2), even the value of 3 for α_n is enough for a strong confinement and dimensional transition in direction *n*.

DIMENSIONAL TRANSITION IN THERMODYNAMIC PROPERTIES

Internal energy of particles in exited states is calculated as

$$\tilde{u}_{ex} = \tilde{u} - u_o = \frac{\eta}{\zeta} - \alpha_1^2 - \alpha_2^2 - \alpha_3^2 \tag{16}$$

where u_o is the ground state energy. The reason of subtracting u_o is that the ground state energy considerably increases when the domain sizes decreases. Thus thermal energy can stimulates only the particles in excited states instead of particles in ground state. Therefore confinement energy represented by the ground state energy is eliminated if $\tilde{u}_{ex}$ is considered. Similarly dimensionless entropy of particles in excited states is determined by

$$\tilde{s}_{ex} = \tilde{s} - s_o = \ln\zeta + \frac{\eta}{\zeta} \tag{17}$$

By subtracting entropy of the ground state, which is the pure configurational entropy, from the entropy itself, only the entropy of momentum space is considered. In other words, $\tilde{s}_{ex}$ is the measure of disorder in momentum space only. Due to the first term of the right hand side of Eq.(17), however, the value of $\tilde{s}_{ex}$ goes to infinity when α_n goes to zero as expected. Therefore, $\tilde{s}_{ex}$ is normalized by dividing to its value for unconfined domain (3D domain) as follows

$$\hat{s}_{ex} = \frac{\tilde{s} - \tilde{s}_o}{\left(\tilde{s} - \tilde{s}_o\right)_{3D}} \tag{18}$$

Variation of $\tilde{u}_{ex}$, $\tilde{s}_{ex}$ and $\tilde{c}_v$ with domain sizes can be examined by changing α_3 for different set of $\{\alpha_1, \alpha_2\}$ values. Since the variation of dimension with domain sizes is also known, it is possible to examine the variation of thermodynamic quantities also with dimension by matching the values of dimension and thermodynamic properties for the same $(\alpha_1, \alpha_2, \alpha_3)$ values.

RESULTS AND DISCUSSIONS

3D unbounded domain is represented by $\{\alpha_1 = 0,\ \alpha_2 = 0,\ \alpha_3 = 0\}$. Confinement of the domain in one direction needs an increment of α value in that direction from zero to the values higher then unity. By following the same procedures for other directions, it is possible to confine the systems into smaller dimension in momentum space. Therefore the dimension of momentum space can be decreased from 3D to 2D, 1D and 0D.

The change of dimensionless internal energy and specific heat at constant volume of particles in excited states with respect to α_3 are given in Fig.3. and Fig.4 respectively.

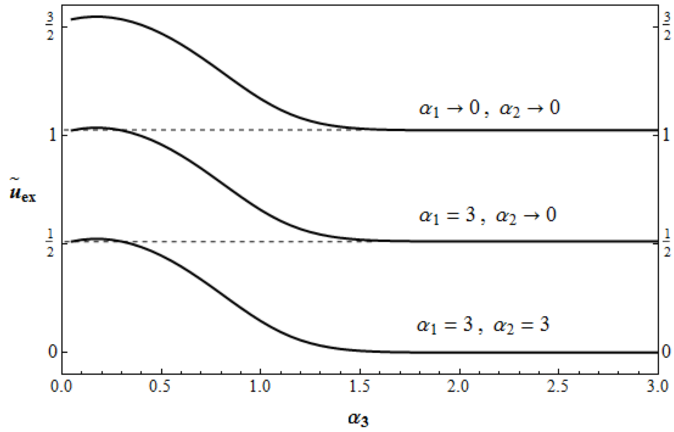

Figure 3: Variation of internal energy of particles in excited states with α_3.

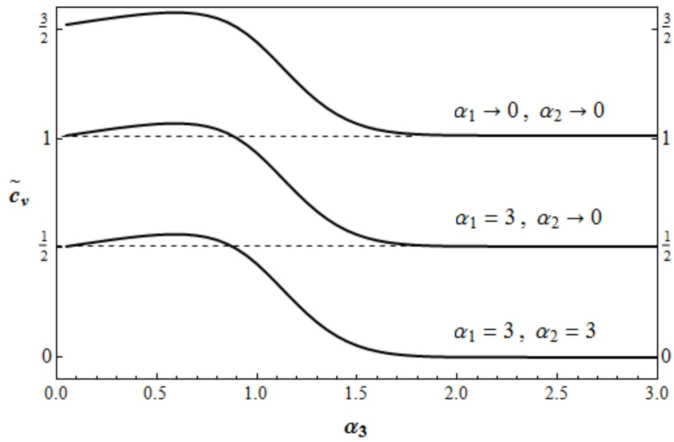

Figure 4: Variation of specific heat at constant volume of particles in excited states with α_3.

In Figure 4., it seems that there is an increment in specific heat at constant volume as an interesting behavior during the dimensional transitions. Functional analysis of Eq.(10) shows that the first term represents the ensemble average of the square of dimensionless energy $\left\langle \left(\varepsilon/k_bT\right)^2 \right\rangle$ while the second one represents the square of ensemble average of dimensionless energy $\left\langle \varepsilon/k_bT \right\rangle^2$. Therefore Eq.(10) can be rewritten as

$$\tilde{c}_v = \left\langle \left(\varepsilon / k_b T \right)^2 \right\rangle - \left\langle \varepsilon / k_b T \right\rangle^2 \tag{19}$$

The first term in Eq.(19) increases faster than the second one up to a critical value of $\alpha = 0.56$ and then the first one approaches to the second one. Therefore the contribution of momentum component to the heat capacity becomes negligible for each direction when the related alpha value gets higher and higher values. In this case, also the dimension of momentum space decreases a unit value. This increment in specific heat is a pure quantum size effect which may be experimentally verified.

In Fig.5, variation of normalized dimensionless entropy of the particles in excited states with α_3 is given for different set of $\{\alpha_1, \alpha_2\}$ values.

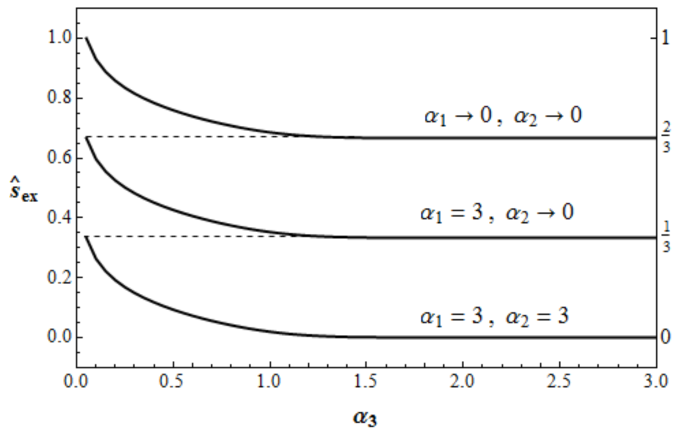

Figure 5: Variation of normalized entropy of gas in excited states with α_3

Normalized entropy of the particles in excited states decreases with increase of α_3. For each confinement process, change in $\tilde{s}_{ex}$ is 1/3. For the case of $\{\alpha_1 = 3,\ \alpha_2 = 3\}$, $\tilde{s}_{ex}$ goes to zero when α_3 goes to higher values then unity. Because all particles occupy ground state which has zero entropy. On the other hand, it should be noted that in case of $\{\alpha_1 = 3,\ \alpha_2 = 3,\ \alpha_3 = 3\}$, Eq.(11) becomes

$$N \ll e^{-\left(\alpha_1^2 + \alpha_2^2 + \alpha_3^2\right)} \ll 1 \tag{20}$$

Therefore, number of particles should be much less then unity to use Maxwell statistics which is physically meaningless. Consequently, although the expressions mathematically give the consistent results for $\{\alpha_1 = 3,\ \alpha_2 = 3,\ \alpha_3 = 3\}$ they represent a physically impossible condition.

As a result of increasing values of α_1, α_2 and α_3, dimensional transitions occur from 3D to 2D, 2D to 1D and 1D to 0D. Dimensionless internal energy and specific heat of particles in excited states versus to dimension is given in Fig. 6 and Fig. 7 respectively. Both $\tilde{u}_{ex}$ and $\tilde{c}_v$ decrease 1/2 for each unit dimensional transition.

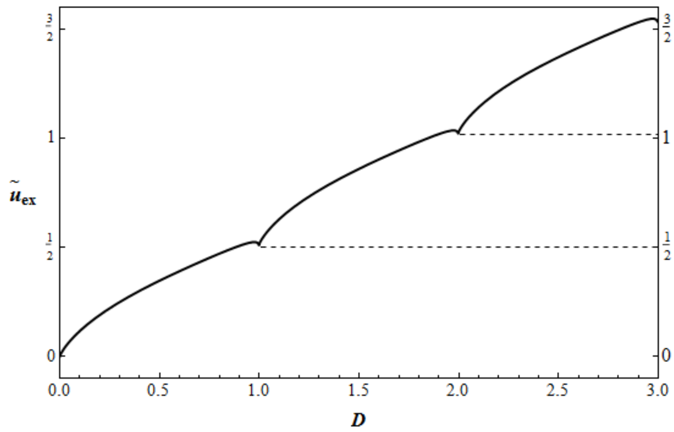

Figure 6: Variation of internal energy of gas in excited states with confined domain dimension

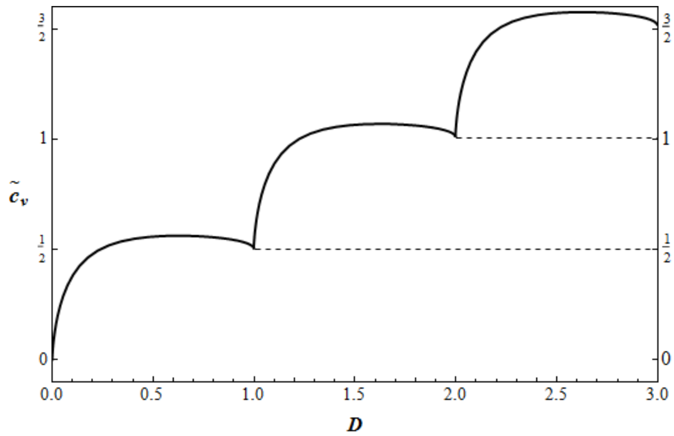

Figure 7: Variation of specific heat at constant volume of gas in excited states with confined domain dimension

In Fig.8 dimensional transition of normalized entropy of particles in excited states is shown. As expected, entropy value decreases with decreasing dimension.

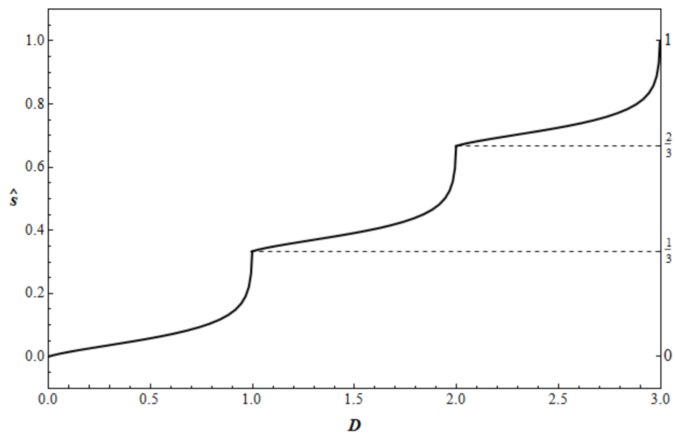

Figure 8: Variation of normalized entropy of gas in excited states with confined domain dimension

NOMENCLATURE

Symbol	Quantity	SI Unit
C_v	Heat capacity at constant volume	$J\,K^{-1}$
$\tilde{c}_v$	Dimensionless Specific heat at constant volume	
F	Free energy	J
h	Planck's constant	J s
k_B	Boltzmann's constant	$J\,K^{-1}$
L	Domain length	m
L_c	Half of the most probable wave length	m
m	Particle mass	kg
S	Entropy	$J\,K^{-1}$
$\tilde{s}$	Dimensionless entropy	
$\tilde{s}_{ex}$	Dimensionless entropy of particles in excited states	
$\tilde{s}_o$	Dimensionless entropy of ground state	
T	Temperature	K
U	Internal energy	J
$\tilde{u}$	Dimensionless internal energy	
$\tilde{u}_{ex}$	Dimensionless internal energy of particles in excited states	
$\tilde{u}_o$	Dimensionless energy of ground state	
α_n	Dimensionless inverse scale factor	
ζ	Partition function	

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