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The effects of intermolecular interactions on the overall partition functions of elementary particles

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Abstract

Elementary particles are atomic or sub-atomic particles that make up all kinds of matter. They are classified into two main groups, namely: bosons and fermions. In other words, bosons and fermions are found in all states of matter, viz: solids, liquids and gases. Fermions are constituents of matter while bosons are force carriers. Bosons are particles that transmit interactions or the constituents of radiation. In this work, the canonical ensemble partition functions were determined including the effects on intermolecular interactions. By using hydrogen, helium, bosons and fermions, the partition functions and the thermodynamic properties of internal energy, Helmholtz free energy and entropy were calculated. The partition functions of all systems considered, hydrogen, helium, bosons and fermions were shown to increase in the presence of intermolecular forces, the increase was more pronounced at increased temperatures in some cases. It was also determined that while the internal energies for fermions and bosons decreased, Helmholtz free energies for the particles decreased with temperature. It was found that, at ultra cold condition of below about 200 K, the entropy of bosons is $1.15x10^{-21}$ *J/K* while that of the fermions is $0.435x\ 10^{-21}$ *J/K*. This is understandable since the bosons condense at ultra cold conditions so their Entropy is lower.

Key Words: Intermolecular Interactions, Canonical Ensemble Partition Function, Elementary Particles, bosons, fermions

1. Introduction

In nature real particle gases do not obey the perfect gas equations. Some of these particles/gases are elementary in nature. They are elementary because they are a part of the make- up of every known substance as constituents of matter.They are grouped as Bosons and Fermions .The laws governing these particles are studied under the advanced aspect of Thermodynamics referred to as Statistical Thermodynamics. Statistical Thermodynamics is the study of the techniques used to average the behavior of particles, so that by ignoring details of characteristics of individual particles the gross effects of detail are discovered. Consider a low-density gas phase. A gas filling volume *V* is composed of *N* similar molecules. If the molecules are far enough apart, the forces between molecules are small compared to the forces within a molecule. At first consideration, intermolecular forces are negligible. This does not mean that the forces are completely non-existent; there must be occasional collisions between molecules so that the gas can come to equilibrium. Again, if the collisions are rare enough, the mean potential energy of interaction between molecules may be negligible compared to the mean kinetic energy of molecules (Morse, 1969).

Note here that the energy is conserved and so the total energy remains constant. At ultra cold conditions, the gases are dense and the average distance between molecules will be small. In such situations, the potential energy of interaction cannot be considered negligible.

In either case, the total energy of the system will be the sum of the separate energies ε_i of the individual molecules, each one depending only on its own quantum numbers as discussed in section 2.3. Eq.(2.26) can now be modified to include intermolecular interaction effect as

$$z_{int} = z_r\, z_v\, z_e\, z_n\, z \qquad (1)$$

So that eq.(2.25) becomes

$$z = z_t z_r z_v z_e z_n z_p. \qquad (2)$$

Where $z_p =$ intermolecular (interparticle) partition function.

2. Methodology

The partition functions are formulated both for the case where the intermolecular forces are considered absent and when they are considered present.

2.1 Potential Energy of Interaction

When two particles, say molecules are far apart, they move completely independently. Neither will feel the presence of the other. However, if they come close together, then the intermolecular forces get to work. They will attract one another. The magnitude of the attraction depends on several factors (Matthews, 2004). For example, the forces that hold helium atoms, or covalent substances like iodine together in a liquid or solid are called intermolecular forces. If the forces are between atoms rather than molecules, one can speak about interatomic forces (Smith et al, 2005). Another name given to these forces is van der Waal's forces. For elementary particles such as bosons and fermions, the forces are referred to as interparticle forces. More precisely, they can be referred to as interbosonic and interfermionic forces, as the case may be.

The attraction between the particles tends to bring them together. The outside of a molecule is really a layer of negatively charged electrons called the electron cloud (Biel and Mu-Jeong, 2009). When molecules approach closely, the electron clouds repel each other. It is the great strength of the repulsion that puts a limit on how close the molecules can get. The separation of a positive and a negative charge produces what is called a dipole (Pillai, 2010).

The force of attraction between two temporary dipoles is known as a London Force. Another name for it is dispersion force. London or Dispersion forces are just one type of intermolecular force. Recall that attraction means lowering of energy and repulsion, increase in energy (Callaway, 1996).

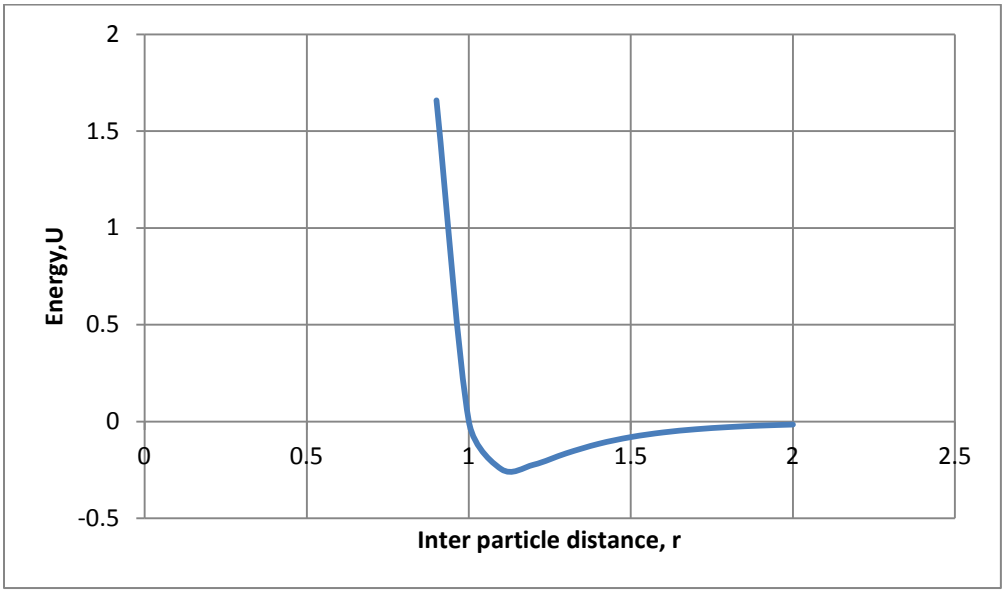


Fig 1 – Potential Energy curve for two particles (atoms or molecules).

In Fig 1, the energy diagram is displayed. Here, there is a minimum in the curve. This is when the attractive and repulsive forces balance each other. The particles are at their equilibrium distance apart. The normal equilibrium distance between molecules is about 200 to 800 pectometers (pm) (Smith, et al, 2005). The shape of the curve gives an idea why it is difficult or sometimes impossible to liquefy gases at high temperatures. This is the reason why bosons and fermions, which are smaller than molecules can be liquefied at very low temperatures, to obtain the ultra cold conditions. The average speed of bosons and fermions at high temperature is usually high (Tukerman, 2003).

If two particles hit each other at a great speed they tend to become squashed together. This is rather like two springs being pushed together. This brings them high up the repulsion part of the curve. Then, they fly apart and go off to make further collisions. At lower temperatures when the speeds are much lower, the force of the collisions can be very much less. The interaction of their electron clouds may take them only part of the way up the repulsion part of the curve. If they do not get too high, they will not spring apart. Rather, they will stick together and oscillate around their equilibrium position.

Considering an ensemble, if there are no forces acting between the molecules of the system, the canonical ensemble partition function, z is given by the expression (Tien and Lienhard, 1971),

$$Z = \frac{z^N}{N!}. \qquad (3)$$

$$\text{where } z = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} V \qquad (4)$$

However, the partition function, *z* pertains to a single molecule (monatomic) moving in a volume *V* which is potential free.

The gas molecules move in a field generated by all molecules and the molecular interactions can be described on pair wise basis as

$U_{(r)} = +\infty$, r $< r_e$

Boltzmann's factor $\exp\left(-\frac{\varphi}{2kT}\right)$, where φ is the potential energy of interaction between any one molecule and all others of the system. The factor $\frac{1}{2}$ is introduced because each pair interaction is to be shared between two molecules in counting the total potential energy. Hence,

$$z = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} V_f \exp\left(-\frac{\varphi}{2kT}\right). \qquad (6)$$

$$Z = \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} V_f^N \exp\left(-\frac{\varphi}{2kT}\right) \qquad (7)$$

Several kinds of force fields are at play between two particles as they undergo an encounter . The potential function for a given type of particle is a combination of the various components.

As in eq. (7), assume a particular molecule of interest wanders through volume *V* and then collides with another molecule thus excluding a volume $\frac{4}{3}\pi r_e^3$ (Fig.1). This volume should be divided by two because the excluded volume arises by the collision of two molecules and only $\frac{1}{2}$ can be assigned to one molecule . Therefore,

$$V_f = V - Nb \quad \text{where } b = \frac{2}{3}\pi r^3 \qquad (8)$$

In the neighbourhood of a particular moving molecule between r = 0 and r = r_e, the density of other moving molecules will be zero. Between r = r_e and r = ∞ it will be constant, N/V. If a random distribution of molecules is

2.2 Lenard-Jones Potential Energy

An ideal gas is characterized by low molecular interactions. Real gases and other fluids are comprised of molecules that have not only the energy of individual molecules, but also energy that is shared among them because of intermolecular forces. This produces intermolecular potential energy, which is associated with collections of molecules, and is the form of energy that reflects the existence of such forces. Two molecules attract each other when they are far apart and repel each other when they are close together. Intermolecular forces represent interactions among the charge distributions of neighbouring molecules.

Fig.1 shows the intermolecular potential energy, U for an isolated pair of spherically symmetric neutral molecules for which U depends on the distance between the molecular centres, i.e. on the molecular separation, *r*. *U* is also a function of the relative orientations of the two molecules.

$$= -V_0\left(\frac{V_e}{r}\right)^6, \quad r \geq r_e \qquad (5)$$

The potential energy minimum occurs at $U = -U_0$ at r = r_e (Fig1). Replacing *V* in eq (3) with V_f, and introducing the assumed throughout the volume, the number of molecules *(dN)* lying near a particular molecule in a spherical shell ranging between r and *r + dr* is

$$dN = 4\pi r^2\, dr\, \left(\frac{N}{V}\right)$$

i.e. volume of the shell × density.

Where r $> r_e$.

The potential energy of interaction between each of these and a central molecule at r = 0 is given by

$$\varphi = -\int_{r_e} U_0\, 4\pi r^2\, dr \left(\frac{r_e}{r}\right)^6 \left(\frac{N}{V}\right) = -\left(\frac{2a_0}{V}\right)N \qquad (9)$$

where $a_0 = \frac{2}{3}\pi U_0 r_e^3$

Applying the above equations into eq (7), gives the complete canonical ensemble partition function:

$$Z = \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} V_f^N \exp\left(\frac{a_0 N^2}{VkT}\right) \qquad (10)$$

Note that eq.(10) is the partition function derived from potential energy of interaction and from it various thermodynamic properties can be evaluated .

Note that while several authors recognize the importance of intermolecular interactions, the partition function for intermolecular interaction was not developed. This work attempted the derivation of intermolecular partition functions from different potential models.

This curve of fig. 1 best fits the Lenard-Jones Potential,

$$U_{(r)} = \frac{A}{r^{12}} - \frac{B}{r^6} \qquad (11)$$

where $U_{(r)}$ is the potential energy at a separation distance. *A* and *B* are constants. The intermolecular force, *F* is proportional to the r-derivative of *U*:

$$F_{(r)} = -\frac{dU_{(r)}}{dr} \qquad (12)$$

A positive *F* represents an intermolecular attraction. Molecules repel each other at small separations and attract each other at modest-to-large separations. The hard-core diameter, *'d'* is a measure of the centre-to-centre distance for which *U* and hence *F* becomes infinite. The collision diameter, σ is the separation for which *U = 0*. The equilibrium separation r_o is the separation for which *U* attains its minimum value of $-\epsilon$. At $r = r_o$, the net intermolecular force is zero. ϵ

is the well depth. Typical ranges of values of σ and ϵ are $\sigma \cong 3$ to 8×10^{-10} m and $\epsilon \cong 0.1 \times 10^{-20}$ J respectively. Commonly, r_o is about 10 to 15% greater than σ. Thus, eq (3.24), the short range Lenard-Jones 12 / 6 pair potential function, is commonly stated as

$$U_{(LJ)} = 4\,\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad (13)$$

Stockmayer improved on the above equation by including the factor μ^2/r^3 which can be shown to be characteristic of a dipole-dipole interaction (Tien and Lienhard, 1971).

$$U_{(LJ)} = 4\,\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - \frac{\mu^2}{r^3} \qquad (14)$$

This provides a semi-qualitative representation of the thermodynamic and transport properties for non-popular substances of relatively simple molecular structure.

Note eq. (7) and recall that $\varphi =$ the potential energy of interaction between any one molecule and all others of the system. Therefore, φ can logically be replaced with $U_{(LJ)}$ of eq.(13) to get

$$Z = \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2} {V_f}^N exp\left\{\frac{-2\epsilon}{kT}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]\right\} \qquad (15)$$

From this partition function, various thermodynamic properties for gases can be derived.

2.3 van der Waals interaction forces

Three distinct types of force contribute to what is now collectively known as van der Waals force (Deeney and O'Leary 2012) between two atoms or molecules; they are dispersion forces, orientation forces and induction forces.

Dispersion forces, also known as London forces, charge fluctuation forces or electrodynamic forces, arise between totally non polar molecules such as helium, methane and carbon dioxide (Jungermann, 2006). These forces are electrostatic in origin which may be understood as follows: For a non polar atom the time average of its dipole moment is zero, yet at instant there exists a finite dipole moment given by the instantaneous positions of electrons about the nuclear protons (Isrealachvili, 1974). This instantaneous dipole moment generates an electric field which polarizes a nearby atom, inducing in it a dipole moment. The resulting interaction between the two dipoles gives rise to an instantaneous attractive force between the two neutral atoms. The dispersion free energy U_{dis} of two atoms of polarizabilities α_1 and α_2 at a distance r apart is given approximately by London equation,

$$U_{dis} = -\frac{3}{2}\frac{h\upsilon_1\upsilon_2}{\upsilon_1+\upsilon_2}\cdot\frac{\alpha_1\alpha_2}{r^6} = -\frac{C_{dis}}{r^6} \qquad (16)$$

Where h is Planck's constant and υ_1 and υ_2 are the characteristic absorption frequencies of the atoms. Orientation forces also known as Keesom forces or dipole-dipole forces arise between molecules which have permanent electric dipoles, and the resulting energy can be represented as

$$U_{ori} = -\frac{C_{ori}}{r^6} \qquad (17)$$

The induction forces also known as Debye forces arise between polar and non polar molecules and the interaction energy can be represented by

$$U_{ind} = -\frac{C_{ind}}{r^6} \qquad (18)$$

The dispersion, orientation and induction energies give the total van der Waals energy between two atoms or molecules, as follows

$$U_{vdw} = U_{dis} + U_{ori} + U_{ind} = -\frac{C_{vdw}}{r^6} \qquad (19)$$

Whereas there may be no orientation and induction forces between two molecules, dispersion forces are always present in which case, eq. (17) can suffice in calculations of van der Waals energy. Thus, the interaction energy equation that should be used is

$$U = -\frac{3}{2}\frac{h\upsilon_1\upsilon_2}{\upsilon_1+\upsilon_2}\cdot\frac{\alpha_1\alpha_2}{r^6} \qquad (20)$$

It is easier to use this expression in this form since gases are involved and the terms of this expression can easily be obtained. Thus, the partition function can be written as in eq. (21) as φ can logically be replaced with U:

$$Z_p = \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2} {V_f}^N exp\left\{\frac{3}{2kT}\frac{h\upsilon_1\upsilon_2}{\upsilon_1+\upsilon_2}\cdot\frac{\alpha_1\alpha_2}{r^6}\right\} \qquad (21)$$

Detailed analysis of eq. (21) especially for liquids and other condensed matter will resort to the theories of Hamaker and the equations of Lifshitz. For interaction in a single gas component, $\alpha_1 = \alpha_2 = \alpha$ and $\upsilon_1 = \upsilon_2 = \upsilon$.

Knowledge of intermolecular interaction energies is essential for the understanding of the properties of gases, the strength and structure of molecular crystals and the magnitude of surface free energies of liquids.

2.4 Interparticle interaction function

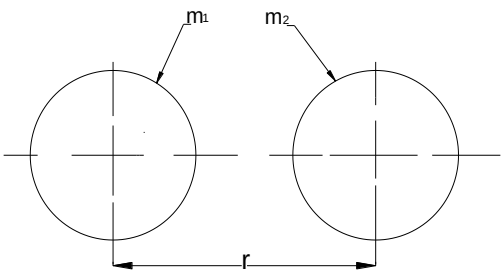


Fig 2 Interparticle interaction force .

Fig 2 is an arrangement of two interacting elementary particles. Their masses are $\mathbf{m_1}$ and $\mathbf{m_2}$ at a distance r apart.

We shall attempt, from quantum mechanics (Massignan, et al., 2005). formulate the interaction between two particles which can be described using a wave equation. Schroedinger had solved this problem, but we shall extend it from the van der Waals interactions. By extending the wave equation for classical fields to photons and generalizing to non-zero rest mass particles, and simplifying using approximations consistent with non-relativistic particles, the time independent Schroedinger equation for two interacting elementary particles has been derived (Tien and Lienhard, 1971, Ward and Volkner, 2008) as

$$\left(-\frac{h^2}{2\mu}\nabla^2 + \frac{R_1}{48r}\right)\psi(r) = \epsilon\psi(r) \qquad (22)$$

Which can be written as (Aruldhas, 2011)

$$\left[\nabla^2 + \frac{2\mu}{h^2}\left(\epsilon + \frac{R_1}{48r}\right)\right]\psi(r) = 0 \qquad (23)$$

Since the potential is spherically symmetric, it is convenient to work in spherical polar co-ordinates

r,θ, and ϕ. ($0 \le r \le \infty,\ 0 \le \theta \le \pi, 0 \le \emptyset \le 2\pi$). Expressing eq(.23) in polar co-ordinates, the following expression is obtained:

$$\left[-\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2\mu}{h^2}\left(\epsilon + \frac{R_1}{48r}\right)\right]R = 0 \qquad (24)$$

where $\nabla^2\psi(r) = \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)$

and $\frac{R_1}{48r}$ was obtained from consideration of van der Waals interactions. Eq. (25) can be expanded and put in the form

$$\left\{\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu}{h^2}\left[\epsilon - \frac{l(l+1)h^2}{2\mu r^2} + \frac{R_1}{48r}\right]\right\}R = 0 \qquad (25)$$

Where $l\,(l+1)/h^2 = L^2$ and L= The orbital angular momentum of a particle and *l* = the quantum number.

Rigorous analysis and solution of resulting equation gives (Bajpai et al, 1982) an asymptotic equation interacting particles of similar and equal, masses, $m_1 = m_2 = m$. The resulting potential is

$$\epsilon = \frac{\pi^2h^2}{4mr^2}$$

$$\therefore \epsilon_i = \frac{\pi^2h^2i}{4mr^2} \qquad (26)$$

The partition function is defined by the expression .

$$:z_i = \sum_{i=0}^{\infty} exp(-\epsilon_i/kT)$$

$$= \sum_{i=0}^{\infty} exp\left[-\left(\frac{\pi^2h^2i}{4mr^2}\right)/kT\right]$$

$$= exp\left[-\left(\frac{\pi^2h^2i(0)}{4mr^2}\right)/kT\right] + exp\left[-\left(\frac{\pi^2h^2i}{4mr^2}\right)/kT\right]$$

$$+ exp\left[-\left(\frac{2\pi^2h^2i}{4mr^2}\right)/kT\right]$$

which is an infinite series with first term, *a=1* and common ratio, $r = exp\left[-\left(\frac{\pi^2h^2}{4mr^2}\right)/kT\right]$ therefore,

$$z_i = \frac{a}{1-r} = \frac{1}{1-exp\left[-\left(\frac{\pi^2h^2}{4mr^2}\right)/kT\right]}$$

$$\therefore z_i = \left\{1 - exp\left[-\left(\frac{\pi^2h^2}{4mr^2}\right)/kT\right]\right\}^{-1} \qquad (27)$$

z_i is the inter-particle partition function of the system of interacting particles and Z is given by eq. (3), and the overall interaction function, Z_{new} is given by the product of equations (10), (15), (21), (27).

2.5 Thermodynamic considerations

It was reported that it is the translational partition function that is most affected by intermolecular interactions. In the absence of intermolecular interactions, the ideal gas condition is obtained. In reality, there is no ideal gas condition; some intermolecular forces do exist, the difference lies in the order of magnitude.

In the absence of intermolecular forces, eq. (4) gives the translational partition function so that the various thermodynamic properties can be determined using the expression for Z_{new}.

From Statistical thermodynamics, various thermodynamic functions can be determined using the above expressions. Hence,

$$\text{Entropy}, S = klnz + kT\left(\frac{\partial lnz}{\partial T}\right)_V, \qquad (28a)$$

$$\text{Internal energy}, U = kT^2\left(\frac{\partial lnz}{\partial T}\right)_V, \qquad (28b)$$

$$\text{Specific heat}, C_v = \frac{\partial}{\partial x}\left(kT^2\frac{\partial lnz}{\partial T}\right)_V \qquad (28c)$$

and Helmholtz Free energy function,

$$F = U - TS \qquad (28d)$$

3. Results and discussion

3.1 Intermolecular Partition Functions

3.1.1 Canonical ensemble

The operational partition function including intermolecular interaction is designated as Z_{new} but when only the translational partition function is considered, the operating equation is designated as Z_{old}.

Making use of data of table 1, figs 3 to 5 were plotted for the partition function, i.e. for eqs. (3) and (4) and the superimposed overall partition function modified for the effect of intermolecular interactions. These plots show the overall

partition function with and without effects of intermolecular interaction forces, being compared with each other. It can be observed that at extremely low temperatures (between 10 K and 300 K) the overall partition function (Z_{old}) for Hydrogen is reduced by intermolecular interactions (Z_{new}) as seen in fig.3 by about 11% at 200 K. This difference increases moderately as temperature increases. As the temperatures go up to about 4,000k (Fig.4) the differences between the partition functions also increase and at about 7000 K, the intermolecular effect becomes more pronounced as shown in Fig.5. This may be explained by the fact that gas, at high temperature, increases in its mean velocity and collisions among the gas molecules and with container walls increase leading to higher pressure.

Table 1. Table of properties (Israelachvili, 1974, Gupta, 1990)

Property	**He**	**Ne**	**H_2**	**C0**	**N_2**
Polarizability, α (10^{-24} cm^3)			0.79	1.95	1.76
Absorption frequency, υ (10^{15} s^{-1})			3.73	3.39	3.77
Dipole moment, m_d ($3.336x10^{-20}$ cm)			0	0112	0
Constants in Lennard-Jones potential: ϵ/k, ^oK $\sigma, \dot{A}$	 10.8 2.57	 35.8 2.75	 36.7 2.96	 100.2 3.76	 95.1 3.70

Boltzmann constant, $k = 1.38x10^{-23}$ J
Planck's constant, $h = 6.626 \times 10^{-34}$ J s
Avogadro's number, $N_o = 6.022 \times 10^{-23}$ mol^{-1}

Element	**Particle mass (kg)**	**wan der Waals radius (m)**
Hydrogen	1.67×10^{-27}	0.37×10^{-10}
Helium	6.65×10^{-27}	0.32×10^{-10}
Argon	6.6×10^{-26}	0.97×10^{-10}
Iodine	4.22×10^{-25}	1.33×10^{-10}
Proton	1.67495×10^{-27}	
Electron	1.67265×10^{-27}	
Neutron	1.66057×10^{-27}	

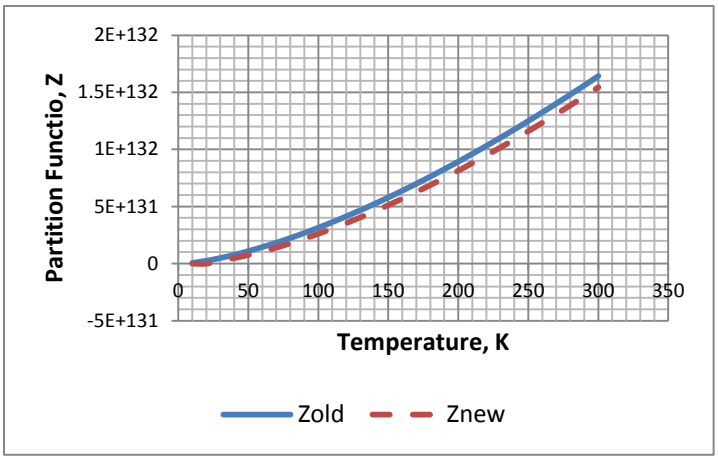


Fig. 3- Partition Function of interacting Hydrogen atoms at low temperatures.

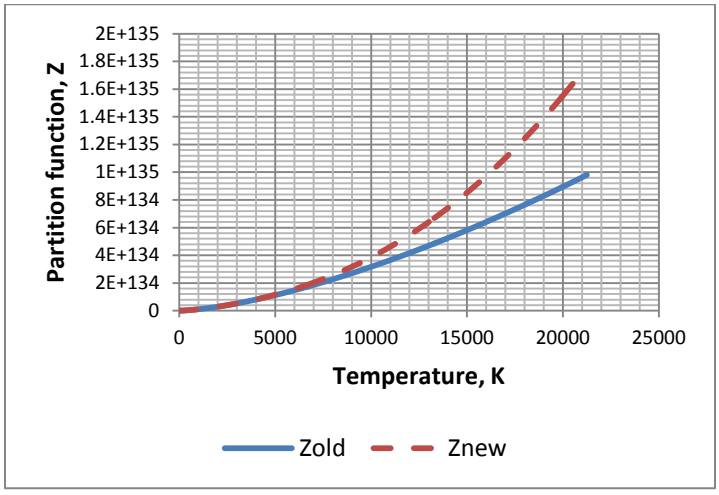


Fig.5 Partition Function of interacting Hydrogen atoms from low temperatures to very high temperatures..

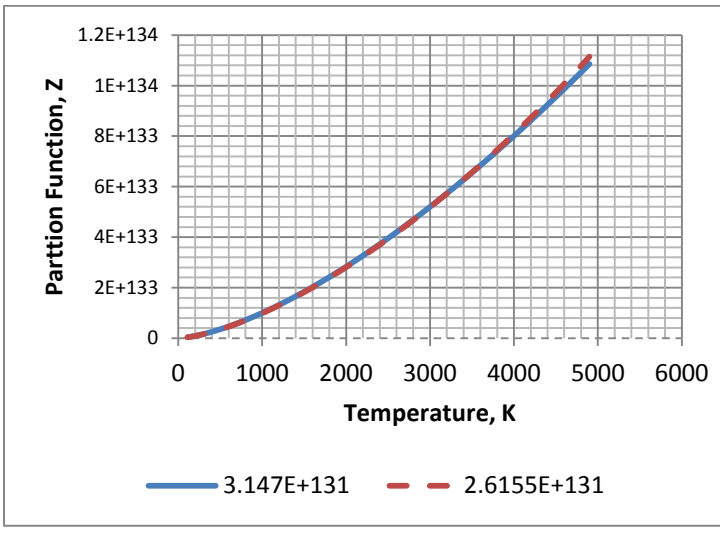


Fig.4 Partition Function of interacting Hydrogen atoms showing that the old and new Partition functions are virtually equal between 100 and 4,000 K.

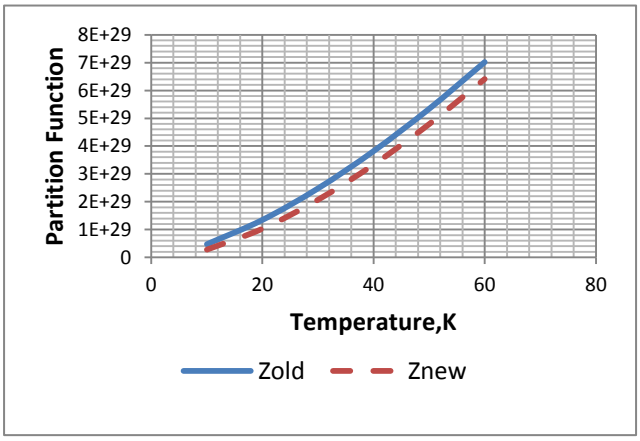


Fig. 6-Partition function of Helium at Ultra-cold conditions, 10-70K.

Just as in the case of Hydrogen, it can be observed that for Helium, the partition function with intermolecular forces (Z_{new}) included is smaller by about 20% at 30 K. The Difference is about 25% at 60 K. At this ultra cold region, Molecular collision activity will be much reduced.

3.1.2 Grand Canonical Ensemble

The consideration of the bosons and fermions is through the number *N* of each elementary particle as it appears in the equations for the partition functions. Appropriate expressions for the bosons and the fermions (Tukerman, 2003) given in eqs. (29) and (30) respectively, were used:

$$n_i = \frac{g_i}{e^{(\epsilon_j-\mu)/kT}-1} \qquad (29)$$

$$n_i = \frac{g_i}{e^{(\epsilon_j-\mu)/kT}+1} \qquad (30)$$

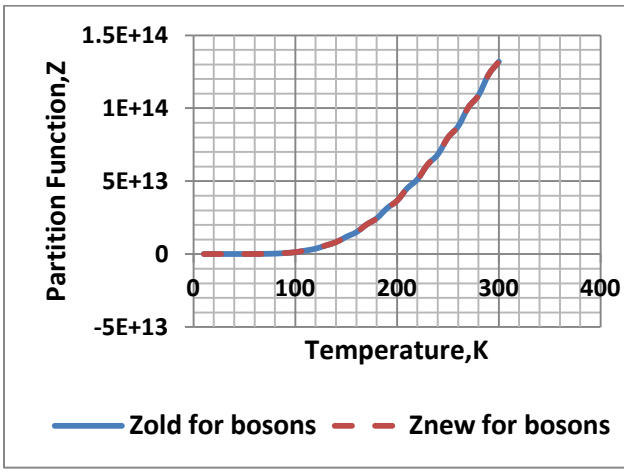
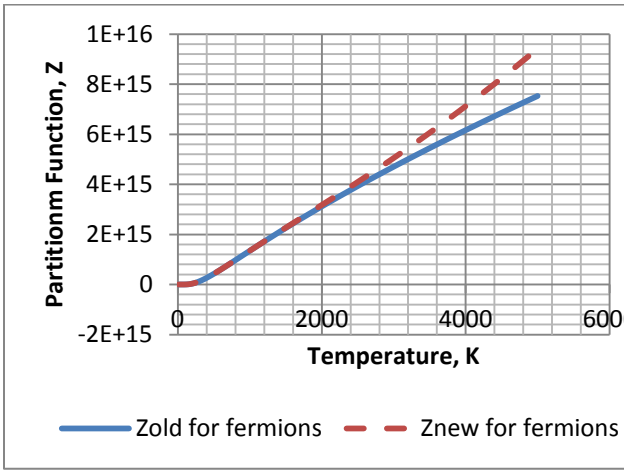


Fig.7 Partition Function of Bosons (Old and New) at temperatures 10-300K



Fig,8-Graphs comparing the two partition functions, old and new(for fermions) with each other at temperatures 10K-5000K.

Fig. 7 and fig. 8 give the partition functions of the bosons and fermions as a function of temperature. At very low temperature (ultracold conditions) the graphs of the partition functions appear to agree but as the temperature increases, differences are observed and as before, with the effect of inter molecular interactions becoming more pronounced. For the fermions (fig. 8), it can be observed that differences begin to occur at about 2500K, where the intermolecular effect is seen to become more pronounced. In fig. 7 for the bosons, the difference is not very pronounced at the temperature limit considered. The effect is expected to become pronounced as the temperature increases further.

3.2 Thermodynamic properties

3.2.1 Canonical Ensemble

The thermodynamic relations will also obviously be affected by the intermolecular interaction forces of the elementary particles. It is bosons that condense at ultra-cold temperature and their thermodynamic relations are highly affected by the intermolecular interaction forces.

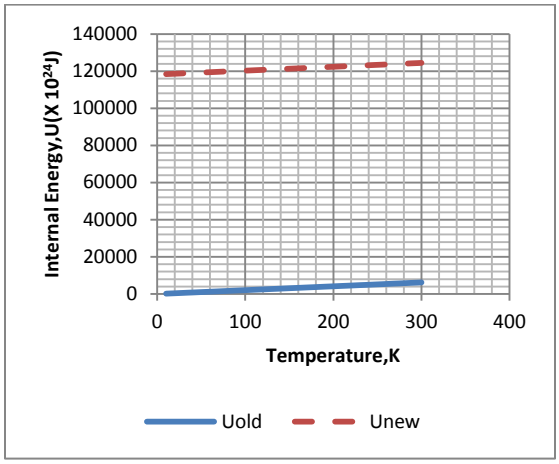


Fig.9- Internal energy of Canonical ensembles using the old and new Z's for hydrogen at temperatures 10-300K.

Since the partition functions were affected by intermolecular forces, it is expected that the thermodynamic relations of elementary particles would also be affected by their intermolecular interaction forces. In fig. 9, the wide difference between the internal energies shows that interparticle interaction affects the internal energies strongly. For Hydrogen, the internal energy with intermolecular effects considered is higher than the internal energy in the absence of intermolecular interactions by up to a factor of 7, with the internal energy variation increasing with increase in temperature. As explained before, higher temperature will witness increased molecular activities.

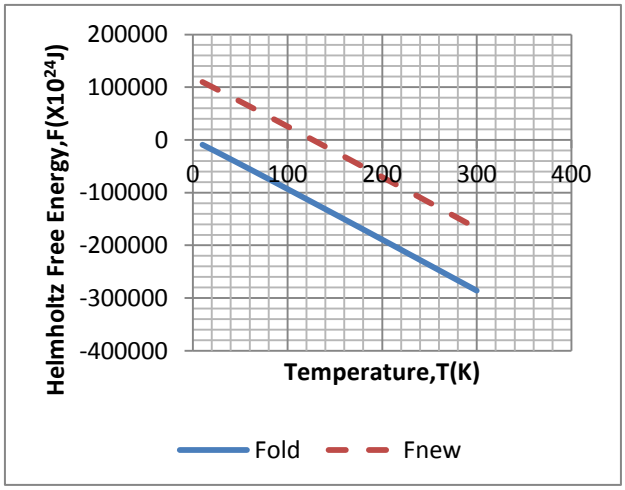


Fig.10 Helmholtz Free Energy of Canonical Ensembles at temperatures 10-350K for Hydrogen atoms.

The Helmholtz free energy *(H)* for hydrogen (fig.10) when intermolecular forces are considered is by a factor of 2.4 higher than in the absence of intermolecular interaction. The striking thing here is that, at ultra-cold conditions, *H* increases with decrease in temperature.

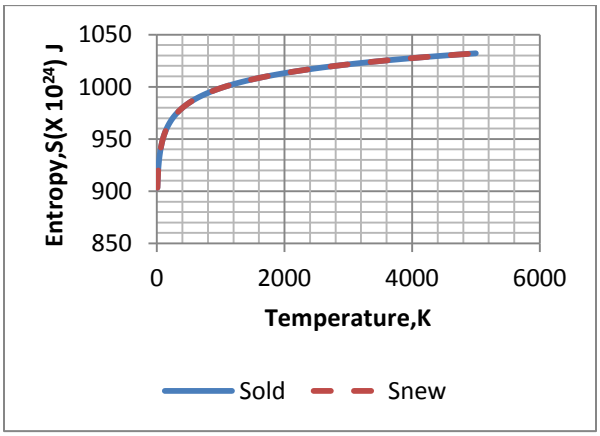


Fig. 11. Entropies of Canonical Ensembles using hydrogen

Both Entropies appear to be equal at all temperatures below 5,000 K for Hydrogen (fig. 11). This means that Intermolecular interaction effect is minimal in temperature range considered. At ultra-cold conditions, entropy increase is dramatic with increase in temperature because of increasing molecular activity with increase in temperature. However, beyond a temperature of about 1000K, there is a gradual reduction in entropy change probably due to attainment of steady state condition in molecular activity at higher temperatures. Note that entropy gives idea of quantity of heat involved (Saha, et. al., 2009).

3.2.2 Grand Canonical Ensemble

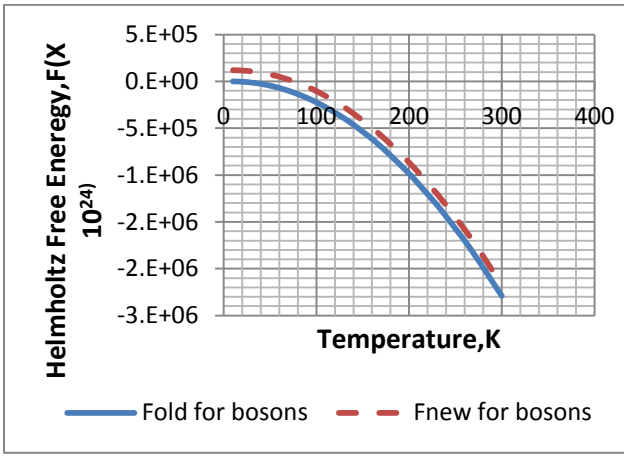


Fig.12. Helmholtz Free Energy of Bosons at temperatures 10-300K

From fig. 12, the free energy extracted from system of particles comprised of bosons when estimated with the intermolecular effects is higher than that obtained without intermolecular interactions. The heat at ultra cold conditions appears to be higher, decreasing with increase in temperature.

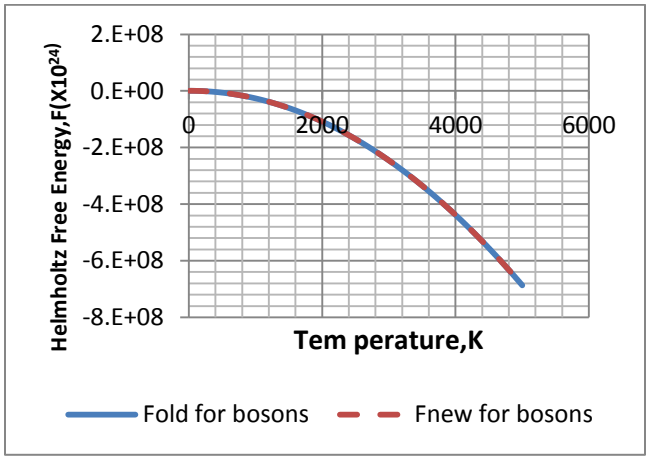


Fig 13. Helmholtz Free Energy of Bosons at 10K-5000K

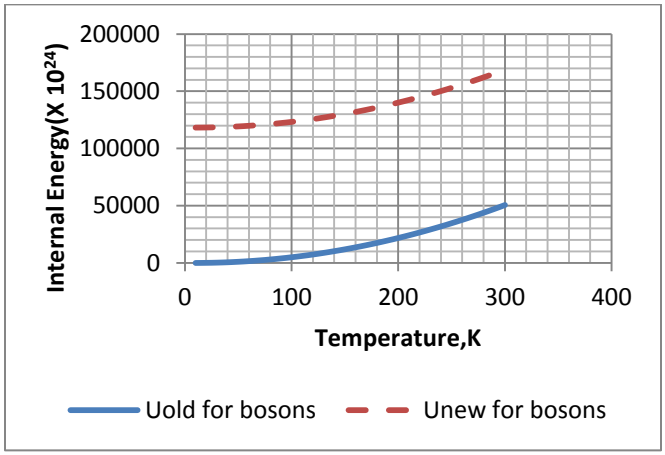


Fig 14. Internal Energy of Bosons at 10-300K.

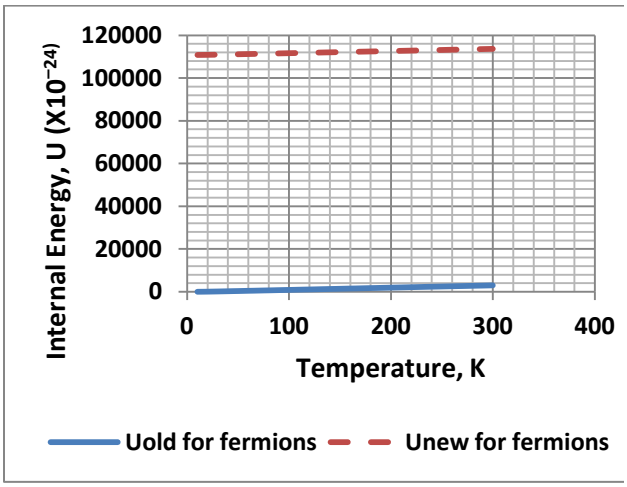


Fig.15 The internal energies of fermions between 10 and 300 K.

The internal energy obtained from the partition function with intermolecular interactions can be seen in broken lines. Large difference is observed in the internal energies, showing profound effects of intermolecular interactions (Christian,. 2004).

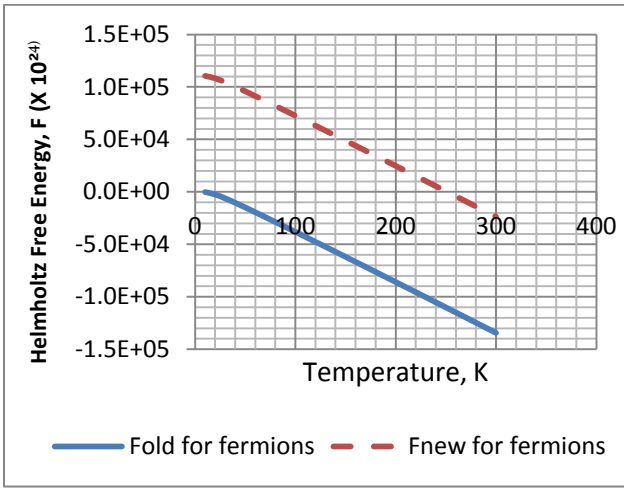


Fig.16 Helmholtz Free Energy, F for fermions

The Helmholtz Free Energy of Fermions calculated (fig. 16) using the partition function with intermolecular forces present can be seen to be higher than the values derived in the absence of intermolecular forces. One also infers that the molecular interaction forces in Fermions increase their Helmholtz Free Energy.

The Internal Energy, U of Fermions calculated (fig. 17) using the partition function with intermolecular interactions included can be seen to be higher than the values derived in the absence of intermolecular interactions. The internal energies, including intermolecular effects are glaringly higher, up to a factor of about 6. The inclusion of intermolecular forces undoubtedly has a profound effect on the internal energy. All the considerations above show that while the internal energy increases with temperature, the Helmholtz free energy decreases for both systems. This is expected from the first law of thermodynamics. From the fact that $F = U - TS$, entropy S was calculated at $T = 200\ K$ to be $0.435x10^{-21}\ J/K$ for the fermions and $1.15x10^{-21}\ J/K$ for bosons.

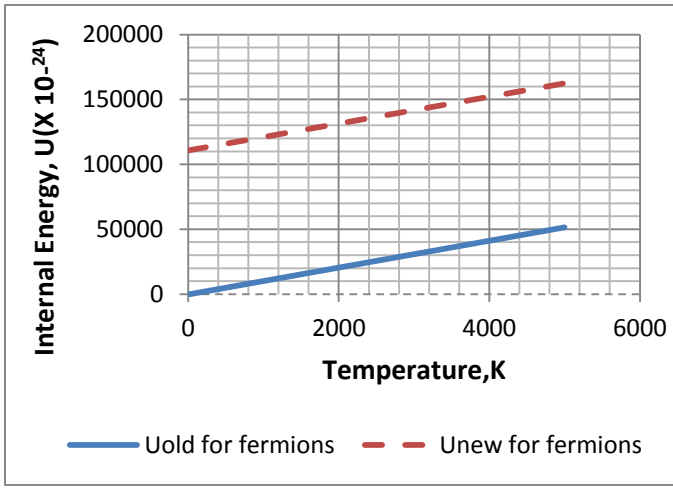


Fig 17 Internal Energies of Fermions at 10-5000K

Conclusion

The partition functions with intermolecular interactions included have been derived. Computations using hydrogen and helium and with bosons and fermions were made. The results show that the partition functions are generally higher when intermolecular interactions are included. These values are not very pronounced at ultra cold conditions (< 50 K). It was observed that from ultracold temperatures to about 1000K, the partition function is generally higher when intermolecular forces are included. The changes in the partition functions increase with increase in temperature. From 1010K to about 4000K the two partition functions are equal. Hence, in computations of partition functions, intermolecular forces should not be neglected.

Bosons condense at ultra cold temperatures and fermions condense at very high temperatures (from about 4000K upwards). The partition functions of bosons and fermions generally increased with increase in temperature. So, generally, intermolecular interactions affect the overall partition function of bosons and fermions.

The thermodynamic functions of enthalpy, internal energy and entropy were also determined for the systems studied. It was found that, while the energies and partition functions of fermions increased with temperature, Helmholtz energies of both bosons and fermions decreased with temperature. It was also seen that the internal energies of both particles increased with temperature. Computations at a temperature of 200 K showed that the entropy of the bosoms was $1.15x10^{-21}$ J/K while that of the fermions was $0.435x10^{-21}$ J/K. This is understandable since the bosons condense at ultra cold conditions. Thus, the thermodynamics of elementary particles is affected both at low and at extreme temperatures by intermolecular interaction forces.

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