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The application of closed Bragg-Williams equation to elementary particles.

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Abstract

The Bragg-Williams equation is actually a form of van der Waal's equation of gases presented in the form of an infinite Maclaurin's series. The problem with such expressions is that discrepancies tend to arise during computations of an infinite series. To make computation easier and in addition obtain more accurate results, a closed form of Bragg-Williams equation was obtained using geometric progressions. The comparison of the closed and open Bragg-Williams equations shows that the point at which the two equations agree increases with increase in the power of θ in the open expression. The increase in the dimensionless quantity, *Pb/kT,* with increase in powers of θ suggests that the pressure of the gas is increased since *kT* is constant at a given temperature. Increase in pressure means that the interaction energy of the gas represented by *Pb* is increased. By relating the number of particles to bosons and fermions, it is seen that this energy is less for bosons and more for fermions. Thus, interaction energy between the fermions particles will be expected to be more than for the bosons in a given matter. Increase in pressure can guarantee increase in other thermodynamic quantities. .

Key words: Bragg-Williams, bosons, fermions, virial coefficient, van der Waals equation.

1. Introduction.

Elementary particles are atomic or sub-atomic particles that make up all kinds of matter (Goshal 2009). 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.(Gupta 1990) Fermions are constituents of matter while bosons are force carriers. Bosons are particles that transmit interactions or the constituents of radiation.(Leggett 2001, Dalfovo et al 1999) It can therefore be deduced that bosons are actually what is seen when light is emitted or when energy is exchanged. This means that there are actually particles in light and other forms of energy, for example, heat. Therefore, matter is really transferred in the course of every energy transmission (Lewenstein et al 2007). Bosons can also be said to be quanta of energy and fermions quanta of mass.

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. 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. 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. 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.

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.

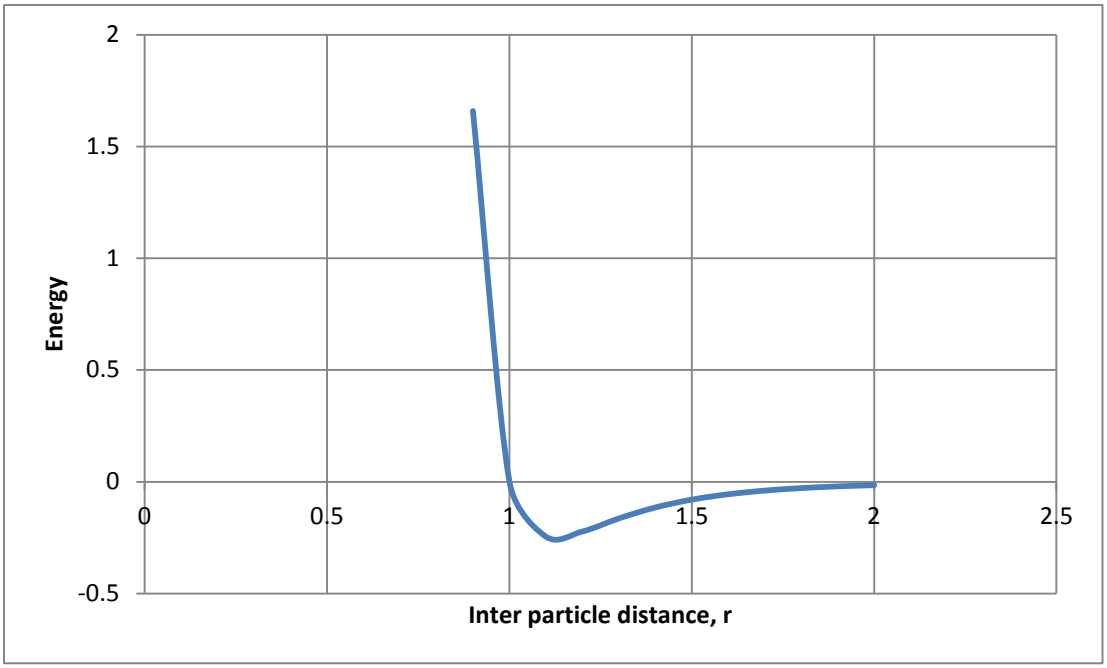


Fig 1 – Potential Energy curve for two particles (atoms or molecules).

In Fig 3.1, 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).The shape of the curve gives an idea why it is difficult or sometimes impossible to liquefy gases at high temperatures.(Smith et al 2005). 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. 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 (Matthews 2004). 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 (Pillai, 2010).

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.

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.

Assume a particular molecule of interest wanders through volume V and then collides with another molecule thus excluding a volume $\frac{4}{3}\pi r_e^3$ .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,

$V_f = V - Nb$ where $b = \frac{2}{3}\pi r^3$ (1)

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 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 $\times$ density.

Where r$>$ r_e .

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

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

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

2. van der Waals interaction

The potential energy of interaction was obtained as in eq. (2) and from the application of thermodynamic principles, the pressure and hence van der Waals equation can be obtained in a series form. By application of simple strategy, the Helmholtz function, F can be determined using the relation (Tien and Lennard 1971)

$F = -kT\,lnZ$, as

$$F = -kT\left[-N\ln\mathrm{N} + \mathrm{N} + \frac{3}{2}\mathrm{Nln}\left(\frac{2\pi\mathrm{mkT}}{\mathrm{h}^2}\right) + \mathrm{Nln}(\mathrm{V} - \mathrm{Nb}) + \frac{\mathrm{N}^2\mathrm{a}_0}{\mathrm{VkT}}\right] \qquad (3)$$

But, from Thermodynamics, the pressure is related to Helmholtz energy F, as

$$\mathrm{P} = -\left(\frac{\partial F}{\partial V}\right)_T \qquad (4)$$

Differentiating eq(31) with respect to V at constant T, then

$$\mathrm{P} = -\left(\frac{\partial F}{\partial V}\right)_T = kT\left(\frac{N}{V-Nb} - \frac{N^2 a_0 kT}{V^2(kT)^2}\right), \text{ i.e.,}$$

$$P = kT\left(\frac{N}{V-Nb} - \frac{N^2 a_0}{V^2 kT}\right). \qquad (5)$$

If $\frac{N}{V} = \varrho = Particle\ density$

Then Eq (5) becomes

$$\frac{P}{kT} = \frac{\varrho}{1-\varrho b} - \frac{N^2 a_0}{V^2 kT} \qquad (6)$$

Recast $\frac{\varrho}{1-\varrho b}$ into Maclaurin's series:

Let $f(\varrho) = \frac{\varrho}{1-\varrho b} = (1-\varrho b)^{-1}$.

$$\therefore f(\varrho = f(0) + \acute{f}(0)\varrho + \frac{f''(0)}{2!}\varrho + \frac{f'''(0)}{3!!}\varrho^3 + \frac{f^{iv}(0)}{4!!}\varrho^4 + \frac{f^{v}(0)}{5!!}\varrho^5 + \ldots\ldots\ldots\ldots\ldots\ldots..$$

$f(0) = 1$, $\acute{f}(0) = b$, $f''(0) = 2b^2$, $f'''(0) = 3!b^3$, $f^{iv}(0) = 4!b^4$,

$f^{v}(0) = 5!b^5$.

$$\therefore f(\varrho) = 1 + b\varrho + b^2\varrho^2 + b^3\varrho^3 + b^4\varrho^4 + b^5\varrho^5 + \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$\frac{\varrho}{1-\varrho b} = \varrho + b\varrho^2 + b^2\varrho^3 + b^2\varrho^3 + b^3\varrho^4 + b^4\varrho^5 + b^5\varrho^6 + \ldots\ldots\ldots\ldots\ldots\ldots\ldots..$$

$$\frac{P}{kT} = \frac{\varrho}{1-\varrho b} - \frac{N^2 a_0}{V^2 kT}$$

$$= \varrho + b\varrho^2 + b^2\varrho^3 + b^2\varrho^3 + b^3\varrho^4 + b^4\varrho^5 + b^5\varrho^6 + \ldots - \frac{N^2 a_0}{V^2 kT}$$

$$= \varrho + b\varrho^2 + b^2\varrho^3 + b^2\varrho^3 + b^3\varrho^4 + b^4\varrho^5 + b^5\varrho^6 + \ldots. - \frac{\varrho^2 a_0}{kT}$$

$$= \varrho + \left(b - \frac{a_0}{kT}\right)\varrho^2 + b^2\varrho^3 + b^2\varrho^3 + b^3\varrho^4 + b^4\varrho^5 + b^5\varrho^6 + \ldots\ldots \qquad (7)$$

Since $N = \frac{g_i}{e^{\alpha+\beta\epsilon i}-1}$ for bosons Eq (6) becomes

$$\frac{P}{kT} = \frac{\varrho}{1-\varrho b} - \frac{a_0}{kT}\left(\frac{g_i}{V(e^{\alpha+\beta\epsilon i}-1)}\right)^2 \qquad (8)$$

For fermions, it becomes

$$\frac{P}{kT} = \frac{\varrho}{1-\varrho b} - \frac{a_0}{kT}\left(\frac{g_i}{V(e^{\alpha+\beta\epsilon i}+1)}\right)^2 \qquad (9)$$

$\left(b - \frac{a_0}{kT}\right)$ in eq. (7) is the second virial coefficient. Thus, multiplying eq.(8) by b and putting $\theta = \varrho b$, the equation becomes

$$\frac{Pb}{kT} = \theta + \left(1 - \frac{U_0}{kT}\right)\theta^2 + \theta^3 + \cdots\ldots\ldots\ldots\ldots.. \qquad (10)$$

Equation (10) is known as the Bragg-Williams equation for gas model. In computations, one does not know how far to go in the series. This work therefore sought to obtain the Bragg-Williams equation in a closed form to facilitate computation.

It is noted that at high temperatures, the approximation regarding the random distribution of molecules is quite good. Hence, the value of the second virial coefficient calculated from eq.(10) agrees quite well with the value for imperfect gases. In eq.(10), the terms after the second term can be represented as

$$S_n = \theta^3 + \theta^4 + \theta^5 + \cdots\ldots + \theta^n + \cdots \ldots\ldots \qquad (11)$$

Where S_n is the sum of the geometrical progression θ^3 , θ^4. θ^5,…… θ^n.

Here, the first term of the geometric progression is θ^3 and the common ratio is θ (Kreyzig 1990; Stroud 1996), thus

$$S_n = \frac{\theta^3(1-\theta^n)}{1-\theta} \qquad (12)$$

For such elementary particles as bosons and fermions, b is very small. Therefore, the term θ^n is considered negligible, and recall that $\varrho b = \theta$, , then eq.(10) becomes

$$\frac{Pb}{kT} = \theta + \left(1 - \frac{U_0}{kT}\right)\theta^2 + \frac{\theta^3}{1-\theta} \quad (13)$$

However, if θ^n is not negligible. eq, (10), becomes

$$\frac{Pb}{kT} = \theta + \left(1 - \frac{U_0}{kT}\right)\theta^2 + \frac{\theta^3(1-\theta^n)}{1-\theta} \quad (14)$$

This is the closed form of van der Waals equation obtained through modification of Bragg-Williams equation.

3. Prediction of pressure of gas

The Bragg-Williams equation for a gas as given in eq. (10) gives the van der Waals equation in a dimensionless form; the equation can be used to predict the pressure in a gas. This equation is not in a closed form and in computations one has to apply different powers of θ until the equation converges.

Bragg-Williams equation was however brought to a closed form as given in eq.(13). The highest power of θ in this equation is 3. With powers of θ denoted by $n = \alpha$ in eq.(10), equations (10) and (14) were plotted as shown in fig.1 as a function of θ for various values of α. The term $\frac{U_0}{kT}$ in the equations mentioned above was calculated by assuming critical values (Omenyi 2011) for volume, V and temperature, T. For b = $\frac{V_c}{3N}$ and $and\ a_0 = \frac{9}{8}\left(\frac{kT_cV_c}{N}\right)$

where V_c = Critical volume and T_c = Critical temperature, the critical constants in terms of U_0 and r_e are: $V_c = 3b$; $T_c = \frac{8a}{27bk}$; $P_c = \frac{a_0}{27b^2} and$

$\frac{V_c}{r_e^3} = 2\pi = 6.28$; $\frac{kT_C}{u_0} = \frac{8}{27}$. . Thus, in eqs. (10) and (14), $\frac{U_0}{kT}$ can be taken as $\frac{27}{8}$.

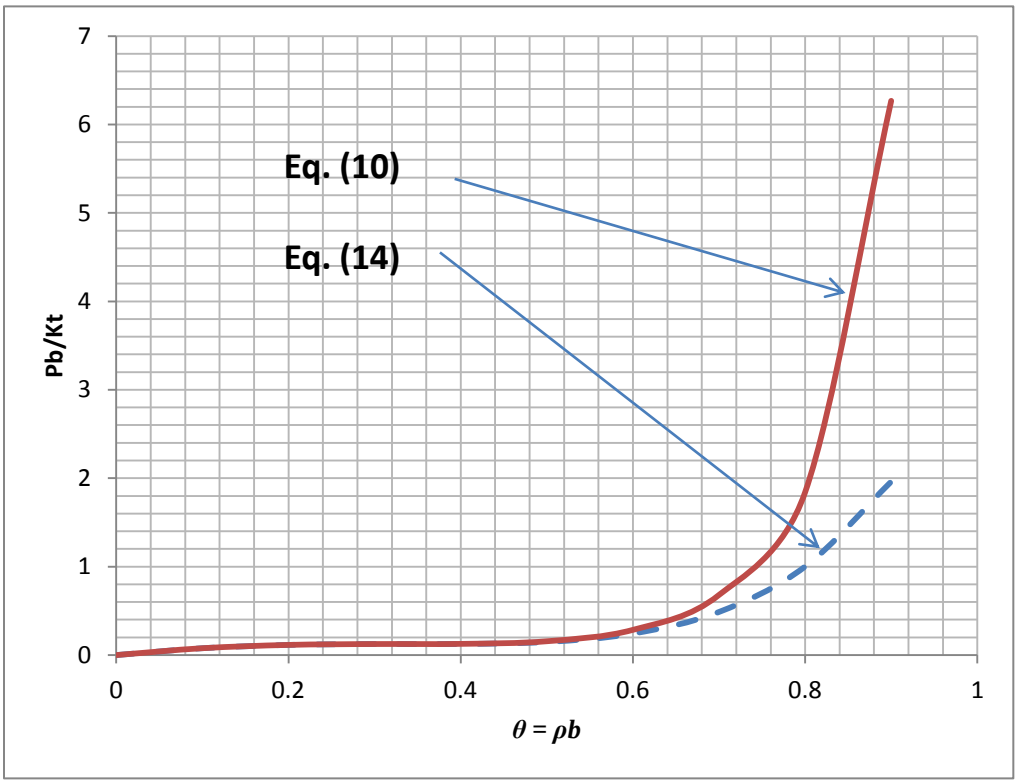


Fig. 2a A plot of equations (10) and (14) for $\alpha = 7$.

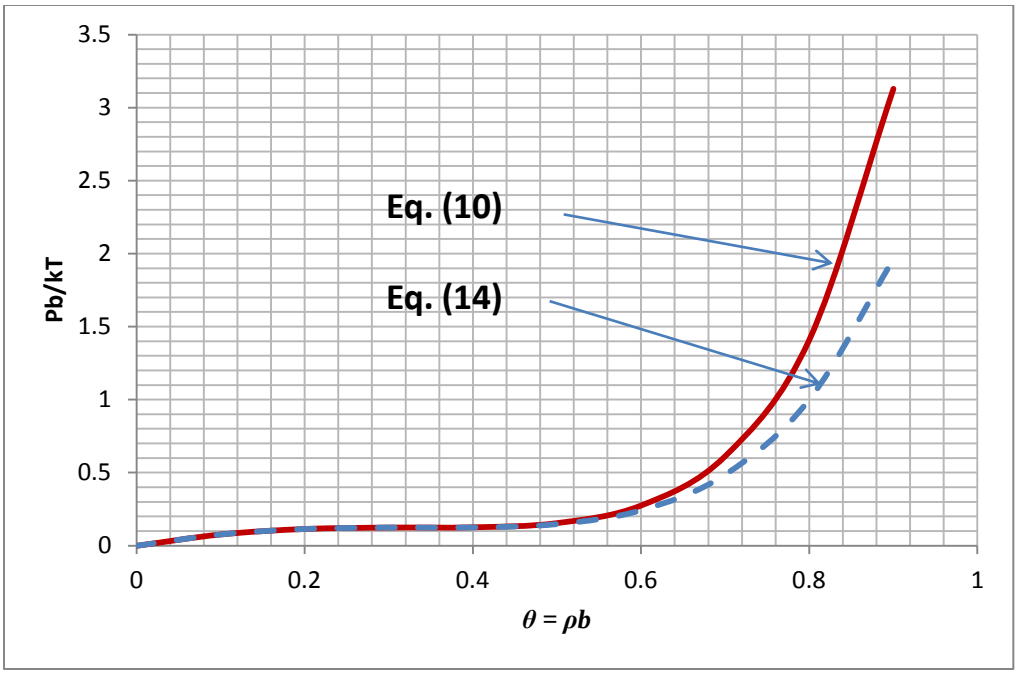


Fig.2b A plot of equations (10) and (14) for $\alpha = 10$

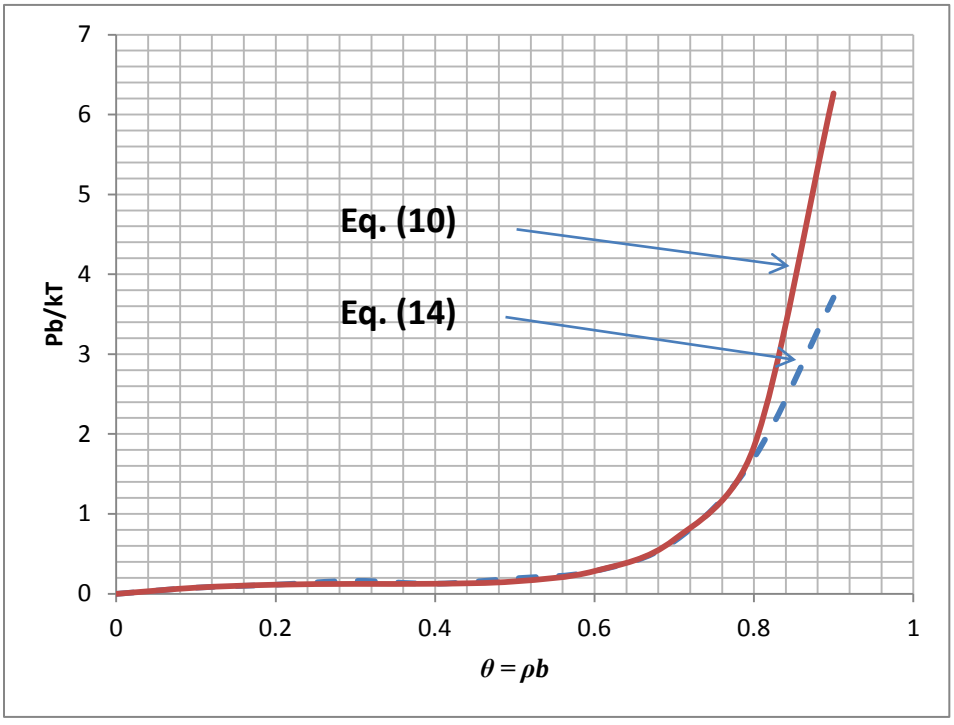


Fig.2c A plot of equations (10) and (14) $\alpha = 15$

A look at the graphs of fig. 2, show that the curves for the two equations are coincident up to a certain value of θ. The values of θ at which the two graphs begin to diverge and the corresponding values of *Pb/kT* were determined for various values of α and plotted in fig.3.

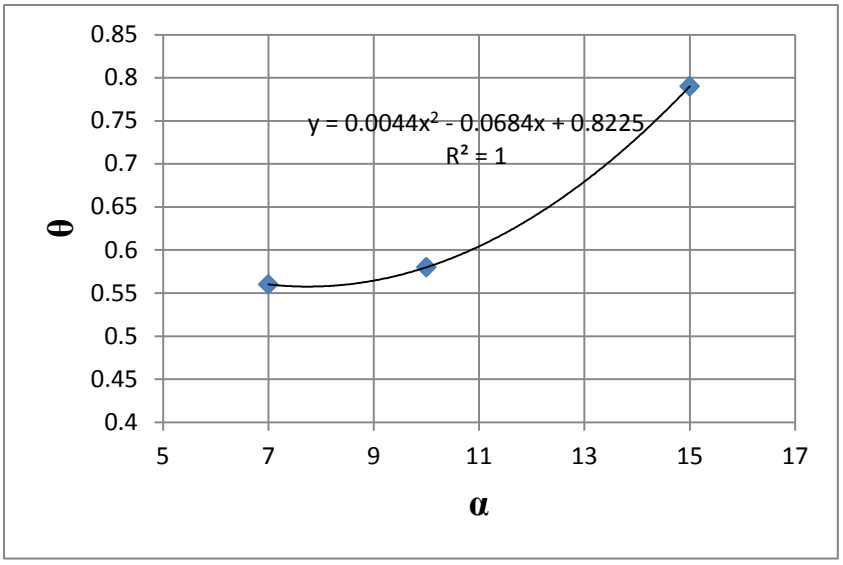


Fig.3a. Variation of θ with α

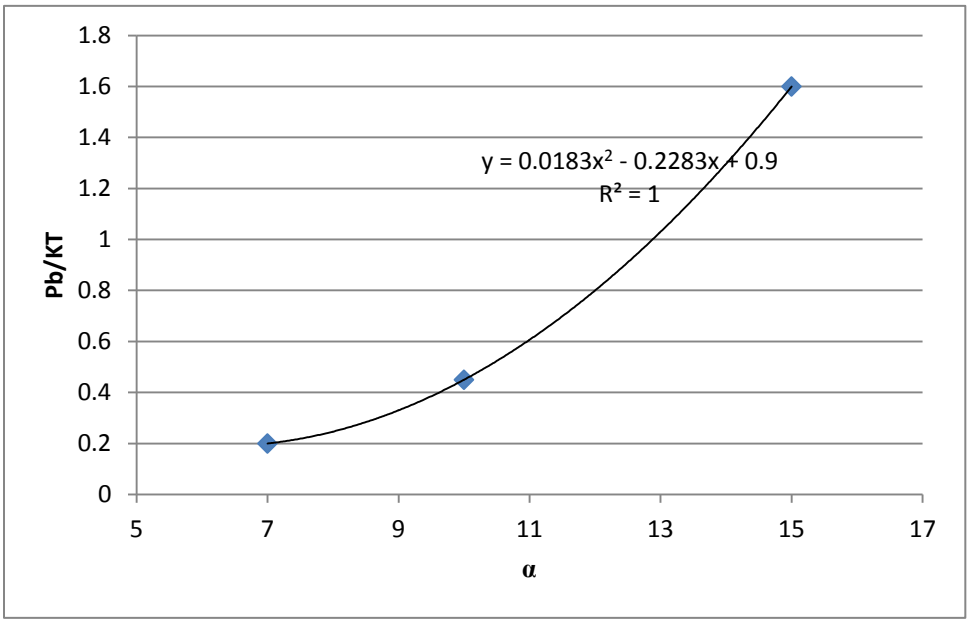


Fig.3b. Variation of *Pb/kT* with α

Figs.3a & b show that each of *Pb/kT* and θ is a monotonically increasing function of α. Increase in α leads to an increase in the values of θ and also of *Pb/kT* at which the two curves are coincident.

Note that $\theta = \varrho b$, $\frac{N}{V} = \varrho$ = particle density, b = $\frac{2}{3}\pi r^3$ so that $\theta = \frac{2}{3}\pi r^3 \frac{N}{V}$. The values of N can be determined from N = $\frac{g_i}{V(e^{\alpha+\beta\epsilon i}-1)}$ for bosons and N = $\frac{g_i}{V(e^{\alpha+\beta\epsilon i}+1)}$ for fermions (Steuerman, 2011). For the same volume V, then N for bosons is larger than N for fermions and hence θ at which the two curves diverge will be larger for bosons than for fermions. It is then obvious from eqs. (10) and (14) that the pressure will be higher for fermions than for bosons for a given container volume.

It is clear that increase in θ is due to increase in number of gas molecules N since volume of container V is constant. With $V_f = V - Nb$ one sees that V_f is decreased as α and hence θ are increased.

The increase in the dimensionless quantity, *Pb/kT*, with increase in α suggests, as expected in view of eqs.(10) and (14), that the pressure of the gas is increased since *kT* is constant at a given temperature. Increase in pressure means that the interaction energy of the gas represented by *Pb* is increased. This energy is less for bosons and more for fermions. Thus, interaction energy between the fermions particles will be expected to be more than for the bosons in a given matter. Increase in pressure can guarantee increase in other thermodynamic quantities and these, in view of the discussion above, will be more in fermions than in bosons.

4. Conclusion

The Bragg-Williams equation is actually a form of van der Waal's equation of gases presented in the form of an infinite Maclaurin's series. The problem with such expressions is that discrepancies tend to arise during computations of an infinite series. To make computation easier and in addition obtain more accurate results, a closed form of Bragg-Williams equation was obtained using geometric progressions.

This paper tried to point out the fact that working with a power series solution could be somewhat cumbersome, especially, when there is an alternative closed expression that could serve the same purpose and still give a good result. When the graphs were juxtaposed with each other, the two expressions agreed depending on the highest power in the series.

In practice, certain of the constants in the expressions are not calculated from some assumed pair potential, but are used as adjustable parameters chosen to give best fit to the experimental data over some range of temperature and density. The results were applied to the analysis of elementary particles, bosons and fermions.

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