



## QUANTUM MECHANICAL SECOND VIRIAL CO-EFFICIENT FOR HARD CONVEX BODY

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**Abstract-** We have expressed the quantum-mechanical second virial co-efficient for hard convex bodies (HCB) in terms of the surface-to-surface co-ordinate than more customary centre-to-centre co-ordinate representation and separated into two terms. The first,  $B_{direct}$  represents Virial for a Boltzmann gas, and the second  $B_{exch}$ , embodies the departure from Boltzmann statistics. Numerical computation of second virial co-efficient of  $He^3$  and  $He^4$  has been done by using the potential defined in terms of support function at low temperature. This result has been compared with the result of hard sphere (HS) model for L.J. potential.

**Keywords-** Hard convex fluid, support function  $h(x)$ , Virial co-efficient

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### Introduction

In this paper we have deduced the expression for second

Virial co-efficient for HCB model an expressed the same in terms of phase shifts which is found to be more convenient for the purpose of our numerical calculation. We have separated the second virial co-efficient expression in two terms. The first expression is the contribution of a Boltzmann gas and the second is an exchange term embodying the effects of Quantum statistics. These expressions have been used for the theoretical calculation of second virial co-efficient for  $He^4$  and  $He^3$  at low temperature employing the intermolecular potential expressed in term of  $h(x)$  [1]. The phase shifts need for our calculations that have been already calculated for this HCB co-ordinate system employing this potential [2].

These theoretical results have been compared with the Lennard-Zones potential for hard sphere model. The mathematical simplicity of our model makes it especially amenable to highly accurate numerical calculation.

### Analysis of Second Virial Co-efficient for hard convex body

The effects of quantum mechanics on the second virial co-efficient can be formally separated into direction effects which obtain for a Boltzmann gas and exchange contributions associated with the Bose-Einstein and Fermi-Dirac character of gas [3]. This separation arises very naturally in the formalism developed by Lee and Yang [4] and allows us to consider the sum of a direct term

$$B_{direct} = \pm \left(\frac{N}{2}\right) \int dr \left[ 2^{\frac{3}{2}} \left(\lambda_T^3\right) \left\langle \left| e^{-\beta H_{rel}} \right|_{-r} \right\rangle - 1 \right] \quad (1)$$

Which in the limit  $\hbar \rightarrow 0$  gives us the classical answer, of an exchange term

$$B_{exch} = \pm \left(\frac{N}{2}\right) \left[ \frac{1}{(2S+1)} \right] \int dr \cdot 2^{\frac{3}{2}} \left(\lambda_T^3\right) \left\langle \left| e^{-\beta H_{rel}} \right|_{-r} \right\rangle \quad (2)$$

$H_{rel}$  is the relative Hamiltonian,  $\beta^{-1}$  is Boltzmann's constant times the temperature,  $\lambda_T$  is the thermal wave length defined as  $h / (2\pi m k T)^{1/2}$ ,  $N$  is Avogadro's constant,  $S$  is the spin of the individual component, and the sign is negative for Bose-Einstein statistics and positive for Fermi-Dirac cases.

For getting hard convex body Models expression in terms of surface-to-surface co-ordinate representation along the unit vector  $\hat{e}$  and the relative position of the atom is specified by the shortest surface-to-surface distance  $K$  measured along the common surface normal  $\hat{K}$  [Fig-1]. The two vectors, in the system are  $\hat{K}$  the apse vector, and  $\hat{e}$  is the director axis. In this case the scalar is

$$x = \hat{K} \cdot \hat{e} = \cos \theta \quad (3)$$

When  $x$  is defines the orientation of HCB'S.

The full Jacobian for the transfer from centre-to-centre to surface-to-surface co-ordinate system is given [5]

$$dr^3 = \left| \frac{\partial r}{\partial \theta} \cdot x \frac{\partial r}{\partial \phi} \cdot K \right| d\theta d\phi dk = S(x, K) d\theta d\phi dk \quad (4)$$

Where  $\theta$ ,  $\Phi$ , are the polar and azimuthally angles respectively. The weight function  $S(x, K)$  for each value of the surface-to-surface distance  $K$  is Jacobian determinant. The resulting expression for the

[Eq-4] has been expressed in terms of a support function  $h(x)$  which is defined as the projection

$$h(x) = h(\hat{K} \cdot \hat{e}) = \hat{K} \cdot \vec{\rho} = b\sqrt{1 + \varepsilon x^2} \quad (5)$$

here  $x$  has been defined as [Eq-3] and

$$\varepsilon = \left(\frac{a}{b}\right)^2 - 1 \quad (6)$$

Where  $a$  is the major axis and,  $b$  is the minor axis.

The properties of hard convex bodies (HCB's) necessary for our analysis are summarized by Kihara and others [7]. The mathematical properties of HCB's are easily demonstrated by means of a support function  $h(x)$  where  $\rho$  is the vector extending from the centre of the body to the point on the surface.

$$\rho = \hat{K} h(x) + (1 + \hat{K} \hat{K}) \cdot \hat{e} h^1(x) \quad (7)$$

Where  $h^1(x) = \frac{dh(x)}{dx}$

The support function for convex surface comprised of two convex separated by surface-to-surface separation distance  $\bar{K}$  is  $\bar{K} \cdot \vec{r}(K)$  Where

$$\vec{r}(K) = \vec{\rho}_1(\hat{K}) - \vec{\rho}_2(-\hat{K}) \quad (8)$$

To avoid the overlapping situation [8], the [Eq-8] has been transferred to

$$r(\hat{K}) = \hat{K} [K + h(x)] \quad (9)$$

With  $h(x) = h(x_1) + h(x_2)$

The resulting expression for  $B_{dir}$  and  $B_{exh}$  will be found to be more convenient for the numerical calculation in term of derivatives of Phase shifts.

Introducing the wave number  $g$  related to the relative kinetic energy of a system of reduced mass  $\mu$ ,

$$E = \frac{P^2}{2\mu} = \frac{\hbar k^2}{2\mu}$$

the difference in the densities of states of the interacting and non-interacting system is also known as the phase shifts and hence it may be expressed as the integration over  $g$  such as [2] which are determined from the solution of the radial wave equation for positive energies.

$$\int \left[ \frac{e^{-\hbar^2 g^2}}{8\pi^2 \mu \hbar k T} \right] \left[ \left( \frac{d}{dg} \eta \right)^1 - \left( \frac{d}{dg} \eta \right)^0 \right] \int \left[ \frac{1}{\pi} \frac{e^{-\hbar^2 g^2}}{8\pi^2 \mu \hbar k T} \right] \left( \frac{d}{dg} \eta \right) dg \quad (10)$$

By means of partial integration we may express terms of the phase shifts themselves instead of their derivatives. The final expression for the second virial co-efficient has been expressed in terms of the Phase shift.

The expression may be refined by taking the influence of the symmetry requirements to account. i.e. for the quantum statistical ideal gas. The second virial co-efficient becomes

$$B = B_{direct} + B_{exch} + B_{ideal}$$

Where  $B_{ideal}$  [8] is the quantum virial co-efficient for ideal gas and is expressed in the term of surface-to-surface ( $K, \theta, \Phi$ ) co-ordinate for ideal gas.

$$B_{ideal} = \pm \frac{c\Delta^*}{16\sqrt{T^*} \sqrt{\pi}} \left\{ \frac{\Delta^{*2}}{4\pi^2 T^*} \frac{L_1}{2} + \frac{\Delta^*}{\pi^2 T^{*2}} \frac{1}{2} \right\} [2L_1 + \varepsilon (L_2 - M_2)] + 2 \left[ \frac{L_3}{2} - \varepsilon \left( \frac{L_5 - M_5}{2} \right) + \frac{\varepsilon^2}{8} \left( \frac{L_7 - 2M_7 + N_7}{2} \right) \right] \quad (11)$$

In which the positive sign holds for system with symmetric eigen function (Bose-Einstein Statistics) and the negative sign for system with anti-symmetric eigen function (Fermi-Dirac Statistics)

$$\Delta^* = \frac{\hbar}{b\sqrt{mE}}$$

is the maximum mechanical parameter,  $m$  is the mass of helium,  $\hbar$  is the planks constant and  $T^* = \frac{kT}{E}$ . The final expression for the second virial co-efficient for  $B_{dir}$  is

$$B_{direct} = \left[ - \left( \frac{1}{2} N 2^{\frac{3}{2}} \right) \cdot (\lambda_r)^5 \cdot \left( \frac{2l+1}{4} \right) \right] [(-1)^l] \left[ \int_0^x \left( \frac{1}{\pi} \eta(g) \cdot 2g \right) \left[ e^{-\frac{(\lambda_r)^2 g^2}{2\pi}} dg + \left( \sum e^{-\varepsilon \eta_l} - 1 \right) \right] \right] \times \int_0^1 b \left[ \left( L_0 \right) + 2b \left( L_{\frac{1}{2}} \right) + \frac{2}{b} + 8b \right] dx \times \left( 2b^2 \varepsilon L_{\frac{3}{2}} \right) \left[ 2 \left( 1 + x^2 \right) + \left( \frac{1}{\varepsilon} + L_{\frac{3}{2}} - M_{\frac{3}{2}} \right) + \left( \frac{\varepsilon L_{\frac{5}{2}}}{4} \right) \left( \frac{1}{2} - x^2 + \frac{x^4}{2} \right) \right] + \left[ \frac{6}{\beta} b L_1 \left[ 2 + \varepsilon L_{\frac{3}{2}} + \varepsilon M_{\frac{3}{2}} \right] - \beta \left[ 1 + \left( 2b^3 L_{\frac{3}{2}} - \varepsilon M_{\frac{3}{2}} \right) \frac{\varepsilon^2 L_{\frac{5}{2}}}{8} - \frac{\varepsilon^2 L_{\frac{5}{2}}}{4} + \frac{\varepsilon^2 N_{\frac{3}{2}}}{4} \right] \right] + [2b^3 L_0 + (b^3 \varepsilon L_1 + b^3 \varepsilon M_1)] \pm B_{ideal} \quad (12)$$

Where  $Nb^3 = C$

$$\int_0^1 (1 + \varepsilon x^2)^{\frac{1}{2} - P} dx = L_P \quad (13)$$

$$\int_0^1 (x^2) (1 + \varepsilon x^2)^{\frac{1}{2} - Q} dx = M_Q \quad (14)$$

$$\int_0^1 (x^4) (1 + \varepsilon x^2)^{\frac{1}{2} - R} dx = N_R \quad (15)$$

The above results are valid if the nuclear spin of the atom is zero. We will have the similar expression for the  $B_{exch}$ , since the nuclear spin is not zero in this case, the nuclear spin weights must be taken into account. However, we will do not then mention it here.

### Result and Discussion

The quantum mechanical study of the Virial co-efficient of the HCB fluid will be done next. The phase shift needed for the calculation of these properties of HCB fluid is the resolution of the radial wave equation described by the HCB co-ordinate system. This has already been done [2]. The potential [1] for HCB in terms of support function  $h(x)$

$$\phi(k) = 4E \left[ \frac{h(x)}{K^{12}} - \frac{h(x)}{K^6} \right] \quad (16)$$

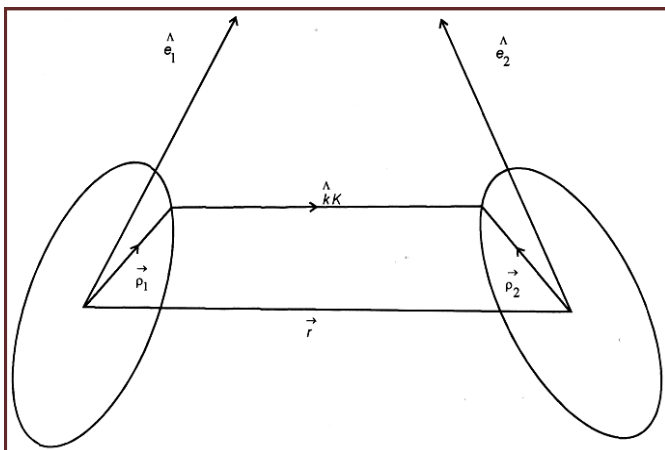
has been used. For the calculation of the second virial co-efficient, we have taken the phase shift at  $l = 0$ . It is of some interest to note

that since LJ3 (very nearly the equivalent of MR5 exp-sin potential [9] in terms of the (very low-temperature second Virial co-efficient) definitely has a low-lying discrete level, the question of whether He<sup>4</sup> really has a discrete level is still open. It is immediately apparent from the behavior of low energy potentials for this potential has a low-lying negative discrete level. The exact position of this level and proceeding to a general investigation of such levels for the Lennard-Jones 12-6 potential was done. We have taken this result [9] for our calculation because our potential corresponds to the Lennard-Jones for hard sphere. We have taken the value of the location of the discrete level for E/k=-0.036850 for calculation of B<sub>dir</sub> and B<sub>exh</sub>. The final expression for the calculation of second virial co-efficient for B<sub>dir</sub> and B<sub>exh</sub>, (12) have been used [Table-1], [Table-2] model and plotted against temperature in [Fig-2] and [Fig-3]. The constant parameters a, b, E and Δ used for calculation have been already done [1].

**Constant Parameters of Ratio a/b**

Y	Major axis (a) in cm.	Major axis (b) in cm.	Δ	E (in erg)
2.201	2.744 x 10 <sup>-8</sup>	1.372 x 10 <sup>-8</sup>	2.5044	1.411 x 10 <sup>-15</sup>

This results have been compared with the results for low temperature of HS model [Table-3] and [Table-4] of second virial co-efficient calculated for Lennard-Jones potential [10] [Fig-2] and [Fig-3]. The Figure with circle symbol is for Lennard-Jones [1,2-7] potential and with square symbol is for HCB model potential.



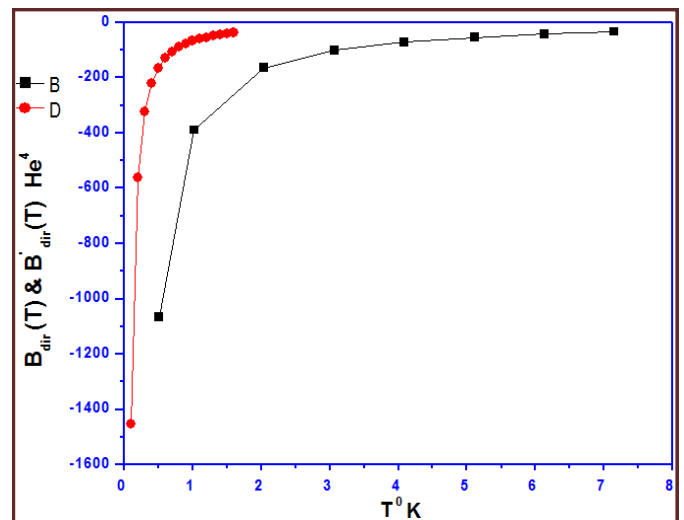
**Fig. 1-** The apse - vector based co-ordinate system for two ellipsoids. The orientations  $\hat{e}$  and  $\hat{e}$  are measured with respect to the minimum surface-to-surface  $\hat{k}$ .

**Table 1-** Calculated values of B<sup>direct</sup> for HCB model Potential

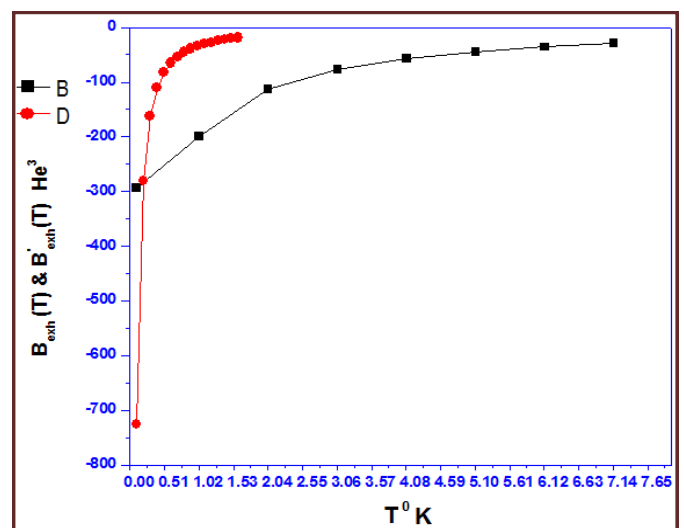
T (Kelvin)	B <sub>dir</sub> (T)
0.1	-1451
0.2	-560.061
0.3	-324.56
0.4	-221.596
0.5	-165.362
0.6	-130.472
0.7	-106.951
0.8	-90.138
0.9	-77.586
1	-67.898
1.1	-60.216
1.2	-53.99
1.3	-48.854
1.4	-44.551
1.5	-40.899
1.6	-37.765

**Table 2-** Calculated values of B<sub>exh</sub> for HCB model Potential

T (Kelvin)	B <sub>exh</sub> (T)
0.1	-725.339
0.2	-280.031
0.3	-162.28
0.4	-110.798
0.5	-82.681
0.6	-65.236
0.7	-53.475
0.8	-45.069
0.9	-38.794
1	-33.949
1.1	-30.103
1.2	-26.995
1.3	-24.427
1.4	-22.276
1.5	-20.45
1.6	-18.882



**Fig. 2-** Graph of Calculated Second Virial Coefficients for the Isotopes of He<sup>4</sup> at very low temperature with circle symbol for HCB Potential [Table-1] and with square symbol for Lennard-Jones (6-12) Potential [Table-3].



**Fig. 3-** Comparative Graph of Calculated Second Virial Coefficients for the Isotopes of He<sup>3</sup> at very low temperature with circle symbol for HCB Potential [Table-2] and with square symbol for Lennard-Jones (6-12) Potential [Table-4].

Table 3- Calculated values of  $B_{direct}$  for HS model for LJ Potential

T(Kelvin)	$B_{dir}$ (T)
0.51	-1066
1.02	-389
2.04	-164
3.07	-101
4.09	-71.6
5.11	-54.1
6.13	-42.4
7.15	-34.2

Table 4- Calculated values of  $B_{exh}$  for HS model for LJ Potential

T(Kelvin)	$B_{exh}$ (T)
0.51	-293
1.02	-199.3
2.04	-113.5
3.07	-76.52
4.09	-56.7
5.11	-44.24
6.13	-35.67
7.15	-29.35

### Conclusion

The value of quantum second Virial co-efficient computed for HCB fitted well with the experimental result. So we may safely conclude that the calculation of all other parameters may be done very safely for HCB model.

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### References

- [1] Giri V.S. and Akhouri B.P. (2003) *Indian J. Phys.*, 77B, 233.
- [2] Giri V.S. and Sinha N.K. (2005) *Indian J. Phys.*, 79, 195.
- [3] Joseph O., Charles H., Curstissand F. and Bird Byron R. (1966) *Molecular Theory of Gases and Liquids*, John Wiley & Sons INC, New York Chapman & Hall Limited, London.
- [4] Lee T.D. and Yang C.N. (1959) *Phys. Rev.*, 113, 1165.
- [5] Kumar B., James C. and Evans G.T. (1988) *J. Chem. Phys.*, 8 11.
- [6] She R.S.C. and Evans G.T. (1986) *J. Chem. Phys.*, 85, 1513.
- [7] Kihara T. *Adv. (1963) Chem. Phys.*, 5, 147.
- [8] Talbot J. and Kirelson D., Allen M.P., Evans G.T. and Frenkel (1990) *J. Chem. Phys.*, 92, 20.
- [9] Kilpatrick J.E., Keller W.E. and Hammel E.F. (1955) *Phy. Rev.*, 97, 1.
- [10] de Boer J. (1940) *Contribution to the Theory of Compressed Gases*, Doctoral Dissertation, University of Amsterdam.