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Department of Physics, Suraj Singh Memorial College, Ranchi,
Jharkhand, India

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Preface

Hard Convex Body models have been proven useful in several areas in chemical physics. The geometric properties of convex bodies made it possible for one to perform analytical calculation of reaction rates, transport coefficients and contact radial distribution function. We are performing the calculations of transport coefficient (viscosity).

Isotropic symmetric and orientational correlations for hard-convex bodies exhibit simpler behaviour in the surface to surface than in the more customary centre to centre coordinate representation. For the hard convex bodies, the isotropic symmetric part behaves much like that of a hard sphere fluid. It is the support function h(x) which defines the analytical properties of hard-convex bodies. The intermolecular potential field has been pro- posed in terms of support function. The constant parameters, phase, and cross-section for ratio of major and minor axis of HCB model for helium molecules have been calculated in terms of this potential. These results have been used for knowing the co-effcient of viscosity of helium.

The theoretical results for viscosity of helium have been compared with the available experimental results. The theoretical results for ratio $\frac{a}{b} = 2$ agrees well with the experimental results.

This work has three important publications. The titles of the paper and the name of the journals are:

1. Constant Parameter of Hard Convex Fluid: Indian Journal of Physics (International journal, Springer) 77 B (2): 233-236, Year 2003

2. Cross Sections for Helium Molecules: RUJOST Vol. III No.3, May 2021

3. Viscosity of Isotopes of Helium with HCB model: Asian J. Research in Chemistry....9(912): 974-4150, Year 2017

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Contents

Introduction

The purpose of this book is to give an idea of evaluation of transport coefficient (viscosity) for the fluid of hard convex bodies. The properties of hard convex bodies necessary for our analysis are due to Kihara and others. In quantum mechanical calculation of the transport phenomenon, the major problem is the evaluation of phase shifts (Allen et al. 1996; Allen et al. 1993; Chapman and Cowling 1970). The cross sections, the viscosity and thermal conductivity are determined from the calculated values of phase shifts. These cross sections are required while calculating the integral associated with the interaction between molecules.

The set of coordinates specifying separation and orientation of pair of HCB'S involve the minimum surface to surface separation K, measured along the common surface normal $K\hat{}$ and angles measured relative to the surface normal. The necessary properties of HCB'S are easily demonstrated by means of support function h(x). In order to make calculation of phase shifts it is necessary to specify the intermolecular potential function in the radial wave equation. The intermolecular potential field has been proposed in terms of the support function. This has been generalised on the supposition that it is a function of the shortest distance between the surface to surface of the molecules retaining the Lennard-Jones potential characteristics.

The theoretical expression for the classical and quantum mechanical second virial coefficients for HCB'S has been derived in terms of the proposed intermolecular potential. In order to make use of these theoretical expressions, it is necessary to know the constant parameters of the intermolecular potential. The constant parameters of the potential function have been determined empirically by fitting the theoretical virial coefficients with the quantum correction to experimental virial coefficient data.

The classical and quantum mechanical theoretical second virial coefficient have been calculated with these known parameters. The agreement between the theory and experiment is as good as can be expected.

The radial wave equation for a pair of interacting bodies have been written in reduced form by using the parameters in the proposed potential as a basis for determination of phase shifts. The values of the quantum mechanical parameters, which we need for the computation of the phase shifts from the radial wave equation, have also been calculated. The phase shifts have been computed from the solution of this radial wave function.

After the phase shift computation from this radial wave equation, the cross section Q for viscosity calculations have been computed by the formulae given by Kramers.The result of these calculations has been applied in case of He^3 and He^4. If He^3 had no molecular spin, Fermi Dirac statistics should have been applied. As He^3 has a spin of $\frac{1}{2}\hbar$ one has to take a 3:1 mixture of cross sections according to Fermi-Dirac statistics respectively. The values of the viscosity have been calculated from this cross section. The viscosity have been calculated by using the values of the cross sections. The viscosity of He^3 is considerably greater than that of He^4.

The subject of this research work has been divided into five chapters.

In chapter I, a brief discussions on the intermolecular forces, the inter molecular potential, the collision integrals, the diffraction effects, the phase shifts and finally the viscosity are given.

In Chapter II, the intermolecular potential has been proposed in terms of the support function. The definitions of the support function and the coordinate systems to be considered in the rest of the thesis have been reviewed.

In chapter III, the general expression for the classical, and quantum statistical second virial coefficient for HCB’S have been derived.

In chapter IV, the constant parameters have been calculated by successive approximation method.

In chapter V, the radial wave expression for the proposed intermolecular potential have been derived and reviewed its solution for phase shifts. From these calculated values of phase shifts, the cross section for helium has been calculated.

In chapter VI, the quantum mechanical transport coefficient (viscosity) for hard convex fluid has been calculated and results have been compared.

Chapter I

1 Intermolecular forces

When molecules are near enough to influence one another, we need to concern ourselves with the balance between the forces of attraction and repulsion (Evans 1991; Gluckman et al. 1972; Majda and Osher 1979). We know that such forces exist, for otherwise there would be nothing to bring molecules together into the solid and liquid states, and all matter would be gaseous. A study of the forces between atomic or molecular species constitutes the subject of intermolecular forces.

People have speculated about the nature of intermolecular forces ever since the ideas of atoms and molecules first existed. Our present ideas, that molecules attract at long range but repel strongly at short range, began to emerge in the nineteenth century due to the experimental work of Rudolf J. E. Clausius and Thomas Andrews.

The force of interaction F between two spherical non-polar molecules is a function of the intermolecular separation r. It is more convenient to use the potential energy of interaction $\phi(r)$ rather than the force of interaction $F(r)$. These two functions are simply related as:

$$F(r) = -\frac{d\phi}{dr} \tag{1}$$

$$\emptyset(r) = \int_r^{\infty} F(r)dr \tag{2}$$

1.1 Classification of intermolecular interactions

We can identify a number of physical phenomena that are responsible for attraction and repulsion between molecules (Mott and Massey 1933); Watson 1922; Chapman and Cowling 1970). They can be separated into two main types: long-range, where the energy of interaction behaves as some inverse power of r, and short-range, where the energy decreases in magnitude exponentially with distance.

The long-range effects are of three kinds: electrostatic, induction and dispersion.

The electrostatic effects: The electrostatic effects are the simplest to understand in general terms: they arise from the straightforward classical interaction between the static charge distributions of the two molecules. They are strictly pairwise additive and may be either attractive or repulsive.

Induction effects: The induction effects arise from the distortion of a particular molecule in the electric field of all its neighbours, and are always attractive. Because the fields of several neighbouring molecules may reinforce each other or cancel out, induction is strongly non-additive.

Dispersion effect: Dispersion is an effect that cannot easily be understood in classical terms, but it arises because the charge distributions of the molecules are constantly fluctuating as the electrons move. The motions of the electrons in the two molecules become correlated, in such a way that lower energy configurations are favoured and higher-energy ones disfavoured. The average effect is a lowering of the energy, and since the correlation effect becomes stronger as the molecules approach each other, the result is an attraction. Further contributions to the energy arise at short range that is, at distances where the molecular wave functions overlap significantly and electron exchange between the molecules becomes possible. The most important is described as exchange-repulsion or just exchange. It can be thought of as comprising two effects: an attractive part, arising because the electrons become free to move over both molecules rather than just one, increasing the uncertainty in their positions and so allowing the momentum and energy to decrease; and a repulsive part, arising because the wave function has to adapt to maintain the Pauli antisymmetry requirement that electrons of the same spin may not be in the same place, and this costs energy. The latter dominates, leading to a repulsive effect overall.

1.2 The Pair Potential

Consider the two atomic or molecular species, A and B. The two species A and B concerned are ions. We simply calculate their mutual Coulomb potential energy. We will consider the very simple case of a pair of like atoms such as argon atoms.

$$\emptyset_{AB} = \frac{1}{4\Omega \in_0} \frac{Q_A Q_B}{r_{AB}} \tag{3}$$

We know from experiment that the general form of their mutual potential energy must be that shown in Figure 1.

The pair potential is written as $\phi(r)$, where r is the separation between the two atoms. That is, it must have an attractive region at long range, where the force $-\frac{\partial \emptyset(r)}{\partial r}$ is negative, and a steeply repulsive region at close range to account for the low compressibility of condensed materials.

There is a separation r_m where the energy is a minimum, and a closer distance σ where the energy of interaction goes through zero before climbing steeply. These are conventional notations, as is the symbol ε for the depth of the attractive well. The precise form of the function $\phi(r)$will depend on the particular molecules concerned, but these general features will be almost universal. For some pairs of molecules, in some relative orientations, the interaction energy may be repulsive at all distances, but unless the molecules are both ions with the same sign of charge, there will always be orientations where the long-distance interaction is attractive.

1.3 Empirical intermolecular potential functions

The choice of considering the intermolecular potential depends on two factors

1. The degree of realism desired and
2. The numerical difficulties in calculating the potential function. The different potential functions are given in Figure 1.

Different potentials, angle independent and angle dependent are summarised here.

Angle Independent Potentials

a. Rigid spheres

$$\phi(r) = \begin{cases} \infty & \sigma < r \\ 0 & \sigma > r. \end{cases} \tag{4}$$

The simplest approximation is to treat atoms as impenetrable hard spheres, i.e., where σ is the hard-sphere diameter. This potential gives a representation of the short and long range forces. The potential remains of considerable utility as a reference for the development of hard-sphere equations of state. From this equation the virial coefficients and transport coefficients have been calculated classically as well quantum mechanically.

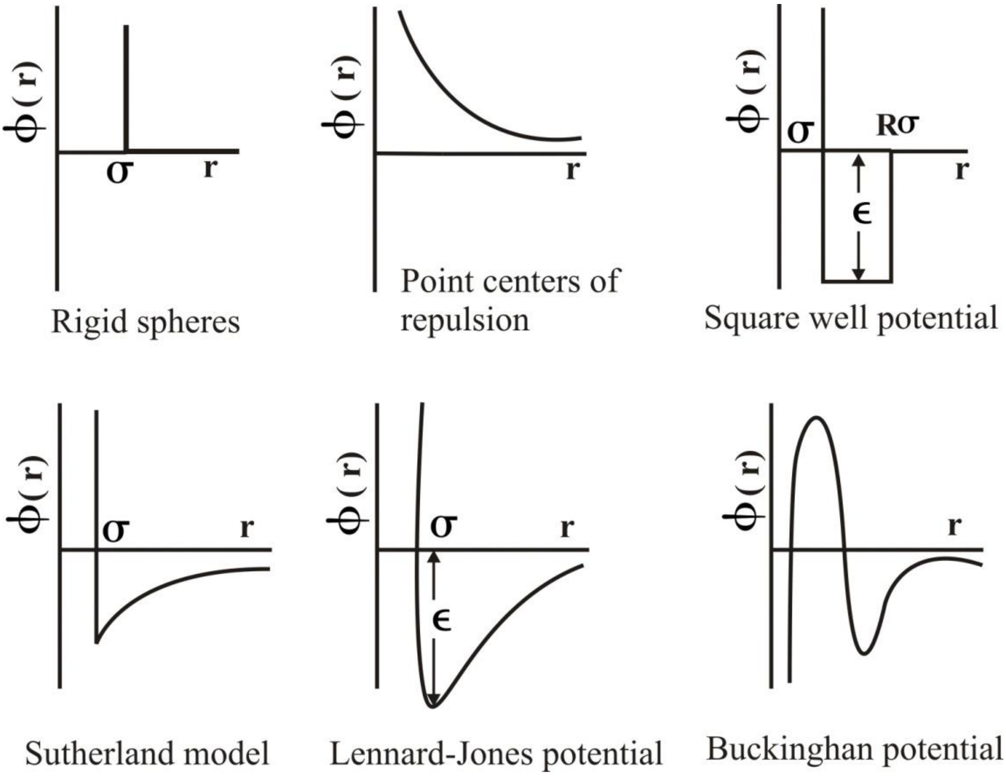


Figure 1

b. The square well potential

$$\phi(r) = \begin{cases} \infty & \sigma < r, \\ -\varepsilon & \sigma < r < R\sigma, \\ 0 & r > R\sigma. \end{cases} \tag{5}$$

This model represents rigid spheres of diameter σ surrounded by an attractive core of strength ε which extends to separations $R\sigma$. Thus, the ideas of attractive and repulsive forces are taken into account. The square-well potential represents a mathematically idealised model of molecular interactions. The properties of the square-well fluid have been investigated widely and it remains a useful starting point for the development of fluid state theory. The virial coefficients and transport coefficients have been calculated using this potential.

c. Sutherland potential

$$\phi(r) = \begin{cases} \infty r < \sigma \\ -cr^{-\gamma} r \geq \sigma. \end{cases} \tag{6}$$

This potential has also a form similar to rigid spheres of diameter σ which follow the inverse square law of attraction. The second virial coefficient and transport properties have also been calculated for this potential.

d. Buckingham potential

$$\phi(r) = be^{-ar} - cr^{-6} - cr^{-8} \tag{7}$$

This is more realistic but complicated to handle it numerically. This equation has been used for equation of state calculations but not for transport coefficients.

e. Yukawa potential

$$\phi(r) = \begin{cases} \infty & r \leq \sigma \\ -\frac{\in\sigma}{r}\left[-z\left(\frac{r}{\sigma} - 1\right)\right] & r > \sigma. \end{cases} \tag{8}$$

where is an attractive term, σ is the hard-sphere diameter and z is an adjustable parameter. The inverse power of this potential indicates that it can be applied to ionic systems.

f. Leenard -Jones potential

$$\phi(r) = \epsilon\left[\left(\frac{m}{n-m}y^{-n} - \frac{n}{n-m}y^{-m}\right)\right] \tag{9}$$

where n and m are constants, $y = r/\sigma$, and σ is the separation corresponding to minimum energy. Here, indicates the energy at the bottom of the potential well that accounts for molecular attraction , while σ establishes the particle diameter that provides a barrier for molecular repulsion. The most common form of the Lennard-Jones potential is obtained when n = 12 and m = 6.

$$\phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right) - \left(\frac{\sigma}{r}\right)^6\right]^{12} \tag{10}$$

Equation (10) is referred as the Lennard -Jones potential (6-12) potential σ is the value of r for which $\emptyset(r) = 0$. ϵ is the maximum energy of attraction which occurs at $r = 2^{\frac{1}{6}}\sigma$ .This potentil is good enough for nonpolar molecules. The second and third virial coefficients have been calculated with this potenial efficiently. The transport coefficients have also been used employing this potential both classically and quantum mechanically.

f. Truncated Lennard-Jones Potential

The advantage of this potential is that it provides a more realistic representation of repulsive interaction than assuming an infinitely steep potential.

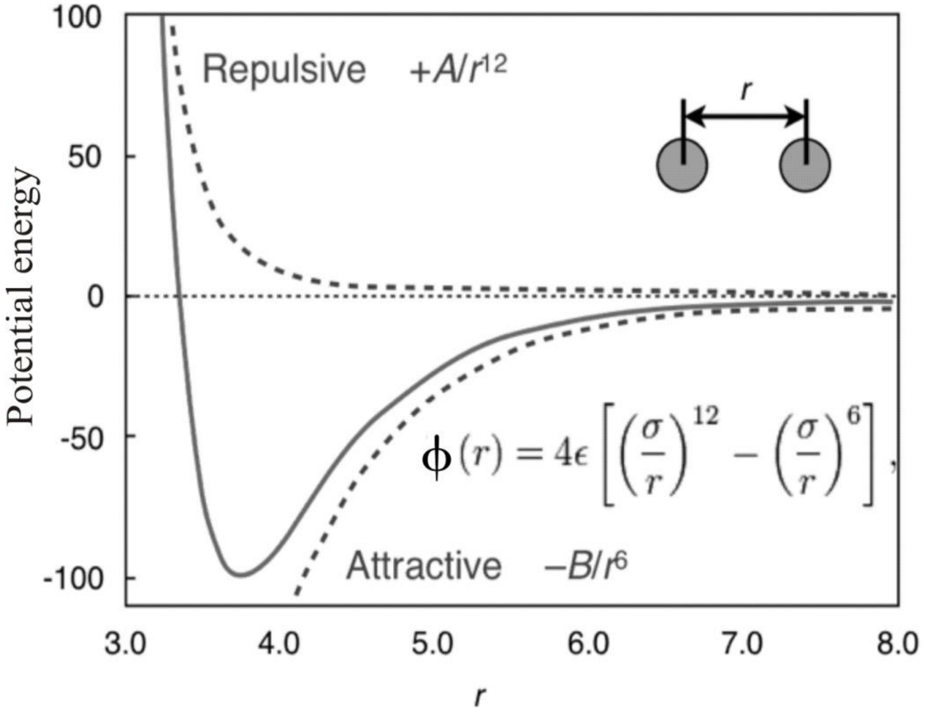


Figure 2

$$\phi(r) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} + \varepsilon\right] & r \leq 2^{\frac{1}{6}}\sigma \\ 0 & r \geq 2^{\frac{1}{6}}\sigma. \end{cases} \tag{11}$$

Angle dependent Potentials

a. Rigid Ellipsoidal of Revolution

The Kihara potential is a slightly more complicated alternative to the Lennard-Jones potential. This is used for studying the effect of non-spherical potential fields on physical properties. Oblate ellipsoids represent flat molecules and the prolate ellipsoids represent elongated molecules. The second virial coefficients and transport coefficients have been calculated for these type of molecules.

b. Kihara potential

The Kihara spherical core potential is a slightly morecomplicated alternative to the Lennard-Jones potential.

$$\phi(r) = \begin{cases} \infty & r \leq \sigma \\ \left[\left(\frac{a-b}{r-d}\right)^{12} - \left(\frac{a-d}{r-d}\right)^{6} + \epsilon\right] & r > d. \end{cases} \tag{12}$$

where d is the diameter of an impenetrable hard core at which u(r) = . The Kihara potential can be also applied to non-spherical molecules by using a convex core of any shape. The Kihara potential has been studied extensively and it has been used to calculate the second virial coefficient more accurately than the Lennard-Jones potential.

c. Stockmayer potential

$$\phi\left(r, \theta_a, \phi_b - \phi_a\right) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - \frac{\mu_a\mu_b}{r^3}\, g\left(\theta_{a,}\theta_{b,}\phi_b - \phi_a\right) \tag{13}$$

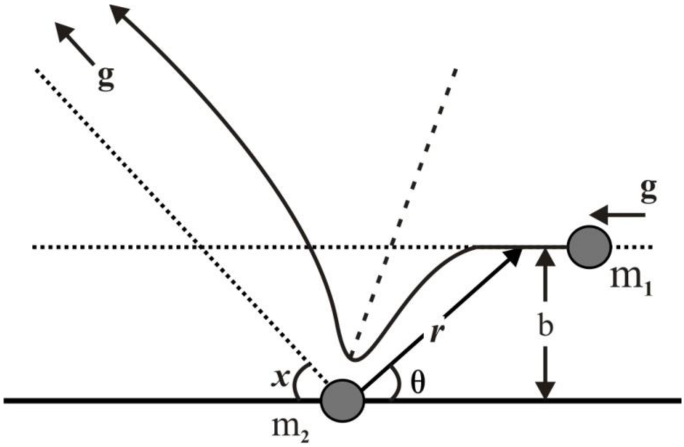
This potential is the sum of Leenard -Jones potential (6-12) and interaction of two point dipoles. Second and third virial coefficients have been calculated with this but no transport coefficients.

2. Collision Integrals

The intermolecular potentials used should incorporate both attractive forces between molecules at long ranges and repulsive forces between these same molecules at short range. Taking attractive and repulsive forces together gives an opportunity for improved predictions of transport properties. This consideration is also useful in the study of non ideal gas.

It is well known that, an intermolecular potential describing the interaction between two particles depends not only on their separation distance but also on their relative orientation. The case of relative orientations become significant for those molecules which have permanent dipole moments. But for convenience we must take an intermolecular potential, $\phi\ (r)$, that depends only on the distance r , separating the two particles. The trajectory of these two particles are described completely by the use of a coordinate system. The resulting trajectory is shown in Figure 3.

We know from the conservation of momentum that the relative speed V_R must be the same sufficiently before and after impact for this two-body



Particle trajectory in impact region for inter molecular potential $\phi(r)$

Figure 3

problem. Using spherical polar coordinates, we can define the impact parameter b as the distance of closest approach (this is the case when the intermolecular potential ϕ (r) = 0). Also we can define the angle of deflection χ which is caused by interaction between the particles. From the Figure it is observed that the distance, r and the angle, θ, has been expressed as function of time. This is achieved by considering the conservation laws. The conservation of energy is described by

$$\frac{1}{2}\mu g^2 = \frac{1}{2}\mu\left(\dot{r}^2 + r^2\dot{\theta}\right) + \phi(r) \tag{14}$$

and the conservation of angular momentum

$$\mu b g = \mu r^2 \dot{\theta} \tag{15}$$

where μ is the reduced mass. For rigid sphere model and far from the impact region the intermolecular potential, $\varphi(r) = 0$. Combining (14) and (15), we obtain

$$\dot{r}^2 + g^2\left(\frac{b}{r}\right)^2 + \frac{2\phi(r)}{\mu} = g^2 \tag{16}$$

Equations (15) and (16) can be sequentially solved at a given temperature to determine r and θ as function of time For this we have to considered the input parameter as g , $\phi(r)$, μ , and b . From this solution, we may determine the angle of deflection, χ, at a given temperature, which must be expressed in the form, $\chi(\gamma,\ \phi,\ b)$, where

$$\gamma = \left(\frac{\mu}{2kT}\right)^{\frac{1}{2}} g \tag{17}$$

The appropriate collision integral in the notation of Chapman-Enskog has the form as

$$\Omega^{l,s} = \left(\frac{\mu}{2kT}\right)^{\frac{1}{2}} \int_0^\infty e^{-\gamma^2}\gamma^{2s+3}\, Q^{(l)}(g)d\gamma \tag{18}$$

where the cross section is

$$Q^{l}(g) = 2\pi \int_0^\infty 1 - \ cos^{l}\, X)\, bdb \tag{19}$$

and the parameter

$$X(g,b) = \ \pi - 2b \int_{r_m}^\infty \frac{\frac{dr}{r^2}}{\sqrt{1-\frac{b^2}{r^2}-\frac{\emptyset r}{\frac{1}{2}\mu g^2}}} \tag{20}$$

2.1 Diffraction effects

The diffraction effect may be taken into account by replacing bdb in the equation (19) by $(g,\chi)sin\chi d\chi$. The classical expression of cross section i.e., equation (19) can be written in quantum mechanics,

$$Q^{(l)}(g) = \frac{2\pi}{g}\int_0^\pi (1\ -\ cos^{n}\chi)\alpha(g,\chi)\sin\chi d\chi \tag{21}$$

The quantity α $(g,\ \chi)$ gives the probability of an angle of deflection χ. When the expression for Boltzmann statistics is substituted into equation (21), we obtain after algebraically the following expressions for the quantum mechanical cross-sections:

$$Q^{(1)} = 2\left(\frac{2\pi}{k^2}\right)\sum_{l=0,1,2\ldots}^{\infty} (l+1)sin^2(\eta_{l+1} - \eta_l) \tag{22}$$

$$Q^{(1)} = 2\left(\frac{2\pi}{k^2}\right)\sum_{l=0,1,2\ldots}^{\infty}\frac{(l+1)(l+2)}{\left(l+\frac{3}{2}\right)}sin^2(\eta_{l+2}-\eta_l) \tag{23}$$

The quantity l and k are quantum numbers characteristic of the angular momentum and the relative kinetic energy of a two molecule collision, and the $\eta_l\,(k)$ are the phase shifts in the radial wave function for a binary collision.

3 The phase shifts: two particle molecular collision in Quantum Mechanics

Quantum mechanical calculation of transport coefficients requires knowledge of quantum theory of equation of state. Here we will consider the collision of particles for which the potential is angle independent. It is shown classically in Figure (1) that a quantity- the angle of deflection (χ) - characterizes a given collision. However, quantum mechanics theory i.e., on the atomic- molecular scale, is more accurate. We know from the uncertainty principle of Heisenberg that the simultaneous determination of the position and momentum of a particle cannot be made. Thus, it is not possible to determine exactly the angle of deflection in a collision. In the following development it is found that the phase shift of the radial wave function characterizes a binary quantum mechanical collision. This quantity, then which is analogous to the classical angle of deflection, determines the final quantum mechanical expression describing the physical properties of real gases at low temperature.

The Schrodinger equation for $\phi\,(r)$, may be written as

$$\frac{d^2\psi(\mathrm{r})}{dr^2}+\left[-\frac{l(l+1)}{r^2}+\frac{2\mu}{\hbar}\left(E-\ \emptyset(r)\right)\right]\psi(\mathrm{r}) \tag{24}$$

In the case of ideal gas, $\phi\,(r) = 0$ and equation (24) becomes

$$\frac{d^2\psi^0(r)}{dr^2}+\left[-\frac{l(l+1)}{r^2}+\frac{\mu^2g^2}{\hbar^2}\right]\psi^0(\mathrm{r}) = 0 \tag{25}$$

Where the total energy E has been equated to $\frac{1}{2}\mu g^2$. Equation (25) can be compared to the Bessel equation

$$\frac{d^2\psi^0(r)}{dr^2} + \left(\alpha^2 - \frac{4p^2-1}{4r^2}\right)\psi^0(\mathrm{r}) = 0 \tag{26}$$

with the identifications

$$\alpha^2 = \frac{\mu^2 g^2}{h^2} \quad and \quad p = \left(l + \frac{1}{2}\right) \tag{27}$$

where α is the wave number of the deBroglie wave and $\alpha\hbar$ is the relative momentum in quantum mechanics consideration whereas μg is the relativemomentum in classical mechanics.

The general solution to Bessel's equation is of the form

Finally for large r, we have asymptotically,

$$r\psi_{\alpha l} = \left[A_l^2(\alpha) + B_l^2(\alpha)\right]^{\frac{1}{2}} sin\left[\alpha r - \frac{1}{2} l\pi + \eta_l(\alpha)\right] \tag{28}$$

where the argument of the sin in equation (28) now contains the phase shift.

$$\eta_l = \tan^{-1}(-1)^l[B_l(\alpha)/A_l(\alpha)] \tag{29}$$

Which represents the net result of encounter. This quantity is analogous to the angle of deflection in the classical one.

4 Phase shifts for simple potentials

a. Rigid sphere: The phase shift is :

$$\eta_l(\alpha) = \tan^{-1}\left[(-1)^{l+1}\frac{J_{l+\frac{1}{2}}(\alpha\sigma)}{J_{-l-\frac{1}{2}}(\alpha\sigma)}\right] \tag{30}$$

which for $l = 0$ reduces to $\eta_0(\alpha) = -\alpha\sigma$.

b. square well potential: The phase shift is

$$\eta_0(\alpha) = \tan^{-1}\left[\frac{\alpha}{\alpha'} tan\frac{\alpha'\sigma}{2}\right] - \frac{3}{2}\alpha\sigma \tag{31}$$

Where

$$h^2\alpha^2 = 2 \qquad and \qquad ħ^2\alpha'^2 = 2\mu(E + \varepsilon) \tag{32}$$

c. Lennard -Jone potential: The expression of phase shift is given in chapter V.

5 Molecular Transport: The viscosity

We can express the formulae of dynamic viscosity as:

$$\eta = \frac{1}{3}nml\bar{V} \tag{33}$$

After having adequate knowledge of collision theory, the physical quantity required for this are:

1. The mean free path: It describes the mean distance travelled by any given particle between collisions. The expression is

$$l = \frac{kT}{\sqrt{2}\pi\sigma^2 P} \tag{34}$$

2.The mean relative speed: In case of center of mass, the motion of any particle pair is equivalent to that for a single particle of reduced mass, μ, moving at relative speed,

$$\bar{V_r} = \left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}} \tag{35}$$

3. The gravimetric density: It is expressed as

$$\rho = \frac{mP}{kT} \tag{36}$$

Thus analogously we can write,

$$\eta = \frac{2\sqrt{mkT}}{3\pi^{\frac{3}{2}}\sigma^2} \tag{37}$$

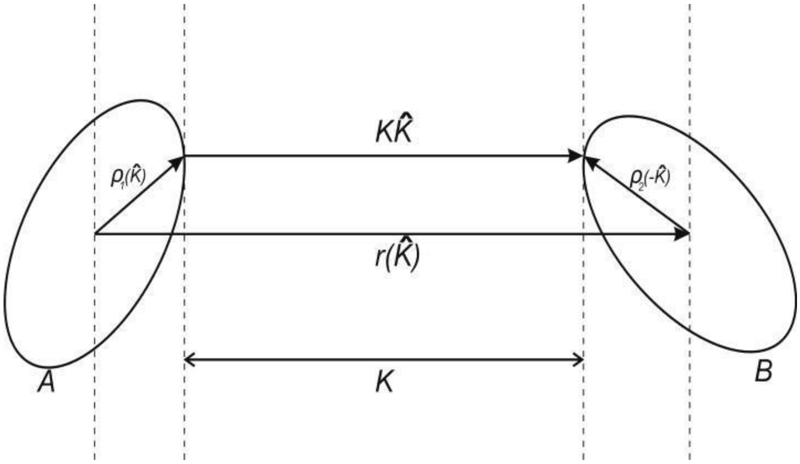
Here the factor for rigid sphere model $\frac{2}{3\pi}$ is required to be changed in rigorous rigid sphere model by $\frac{5}{16}$ and rigorous intermolecular potential model by $\frac{5}{16\Omega^{(2,2)}}$ Where, $\mathbf{\Omega}^{(2,2)}$ is given by expression (18).

Chapter II

1 Support function

Just as the simplest model for a spherical molecule is a rigid impenetrable sphere, so also for a non-spherical molecules, hard convex molecules can be regarded as a rigid impenetrable objects. A body is called convex if any line segment whose end points are inside lies entirely in that body. The necessary properties of HCB are summarized by Kihara and others.

Convex body is that each point on its surface has a unique surface normal,K. Figure 1 shows our co-ordinates system for a pair of convex bodiesˆ separated by a surface to surface separation K measured along K. Ideallyˆ one would like to have a support function that could represent convex shapes ranging from ellipsoids to spherocylinders.The analytic properties of HCB are easily demonstrated by means of a support function h(x) which is defined as the projection,



$$h(x) = h\left(\hat{K}.\hat{E}\right) = \hat{K}.\vec{\rho} = b(1+\varepsilon x^2) \tag{1}$$

where

$$\hat{K}.\hat{e} = cos\theta \tag{2}$$

and $\hat{e}$ is the director axis. The quantity

$$\varepsilon = \left(\frac{a}{b}\right)^2 - 1 \tag{3}$$

Here, ’a’is the major axis and ‘b’ is the minor axis. The vector $\vec{\rho}$ is extending from the centre of the body to the point on the surface and is

$$\vec{\rho} = \widehat{K}\mathrm{h(x)} + \left(1 - \widehat{K}\widehat{K}\right).\hat{e}h'(x) \tag{4}$$

$$h'(x) = \frac{dh(x)}{dx} = \frac{b^2\varepsilon x}{h(x)} \tag{5}$$

The support function for convex surface comprised of two convex bodies separated by surface to surface separation distance K is $\widehat{K}$. We consider aˆ system consisting of N HCBs in a box of volume V and at a temperature T. The i^{th} particle of the system has mass *m* and a centre of mass position vector is the i^{th} particle of the system has mass *m* and a centre of mass position vector is $\vec{r}_{i.}$ If $\vec{r}_{ij}$ denotes the vector emanating from the centre of particle i and extending to the centre of particle j.

$$r_{ij} = \vec{r_j} - \vec{r_i} \tag{6}$$

$$\overrightarrow{r_{12}}\left(K,\widehat{K}\right) = \widehat{K}\,K + \vec{\rho}_1\left(\widehat{K}\right) + \vec{\rho}_2\left(-\widehat{K}\right) \tag{7}$$

where $\vec{\rho}_1\left(\widehat{K}\right)$ $and\, \vec{\rho}_2\left(-\widehat{K}\right)$ emanates from the mass centre of particle1 and 2, respectively.

2 Intermolecular potential

The intermolecular potential has been generalized on the supposition that it is a function of the shortest distance between the surface to surface of the molecules retaining the Lennard -Jones potential characteristics. The expression for intermolecular pair potential for HCB model as:

$$\phi(K) = 4E\left[\left(\frac{h(x)}{K}\right)^{12} - \left(\frac{h(x)}{K}\right)^{6}\right] \tag{8}$$

The pair potential has been expressed in terms of minimum surface to surface separation K, the support function h(x) and E (the minimum energy). So, the potential is now characterized by three constant parameters a, b, and E. The potential well minimum occurs at $K = 2^{\frac{1}{6}}h(x)$and

$$\phi(K) = \begin{cases} 0 \ \ if\ h(x) = K, \\ \infty \qquad if\ K = 0 \end{cases}$$

The support function *h*(*x*) for $\frac{a}{b} = 1$ reduces to a or b, and the intermolecular potential for HCB reduces to HS intermolecular potential which has exactly the same surface to surface distribution as the HCB.

3 The coordinate system

The dynamic properties of hard convex body fluid can be described more conveniently by a convex coordinate (*K, θ,* φ) in place of conventional coordinate (*r, θ,* φ).The two vectors in system are the apse vector $\widehat{K}$ and the director axis $\hat{e}$. The director axis of the convex body points along the unit vector *ê* and the relative position of the atom is specified by the shortest surface to surface distance K measured along the common surface normal *K*,. *θ and* φ are the polar and azimuthal angles of the apse vector $\widehat{K}$ with respect to some space fixed coordinate frame. At arbitrary intermolecular separation, the full Jacobian of the transformation from center to center to surface to surface is

$$\overrightarrow{dr}_{12} = \left|\frac{\partial\vec{r}}{\partial\theta} \times \frac{\partial\vec{r}}{\partial\emptyset}.\widehat{K}\right| d\theta d\phi dK \tag{9}$$

$$= S^{12}(x, K)d\widehat{K}dK \tag{10}$$

where $d\widehat{K} = Sin\theta d\theta d\phi$=dxdϕ

$$\overrightarrow{dr}_{12} = S^{12}(x, K)dxd\phi dK \tag{11}$$

After some algebra, one can show the Jacobian as

$$S^{12}(x,K) = j(j + f_1 + f_2) + f_1 f_2 Sin^2\alpha \tag{12}$$

where, $\alpha = \phi_2 - \phi_2$,

$$j = K + h(x_1) - x_1 h'(x_1) + h(x_2) - x_2 h''(x_1)$$

and $f_i = h''(x_i)\left(1 - x_i^2\right)$.

$$\mathrm{d}\vec{r}_{12} = dKdxd\alpha[j^2 + j(h''(x_1)(1 - x_1^2) + h''(x_2)(1 - x_2^2) + sin^2\alpha h''(x_1)h''(x_2)(1 - x_1^2)(1 - x_2^2)] \tag{13}$$

The function x may be defined as: $x_n = \widehat{K}.\hat{e}_n$and so $x_1 = \widehat{K}.\hat{e}_1$and $x_2 = \widehat{K}.\hat{e}_2$. But for isotropic -symmetric situation x_2 will become $\widehat{K}.\hat{e}_2$for a pair of molecules and $\hat{e}_2$may be replaced by $\hat{e}_1$. So, $x_2 = x_1$ and $h(x_2) = -h(x_1)$. Therefore, j will tend to zero for the overlapping situation and so to avoid this situation $h(x_1) + h(x_2)$ may be replaced by $h(x)$ and $f_1 + f_2$ by f . Thus j becomes

$$j = K + h(x) - xh'(x) \tag{14}$$

and

$$f = h''(x)(1 - x^2) \tag{15}$$

where

$$h''(x) = \frac{d^2h(x)}{dx^2} = \frac{b^4\in}{h^3(x)} \tag{16}$$

This will make the integral rapidly convergent. The expression for separation distance is given by

$$\overrightarrow{dr_{12}} = dKdxd\alpha\left[j^2 + jf + \frac{1}{4}f^2 sin^2\alpha\right] \tag{17}$$

Using equations (14)-(17) and (5), $\overrightarrow{dr_{12}}$may be written as

$$\overrightarrow{\mathrm{dr}}_{12} = \left[K^2 + \frac{2kb^2}{h(x)} + \frac{b^4}{h^2(x)} + \frac{b^4 \in K}{h^3(x)} - \frac{b^4 \in K}{h^3(x)} + \frac{b^6 \in}{h^4(x)} - \frac{b^6 x^2 \in}{h^4(x)} + \frac{b^8 + \in^2 \sin^2\alpha}{4h^6(x)} - \frac{b^8 + \in^2 x^2 \sin^2\alpha}{2h^6(x)} + \frac{b^8 + \in^2 x^4 \sin^2\alpha}{4h^6(x)}\right] dK dx d\alpha \tag{18}$$

This expression will be utilised while calculating the second virial coefficients in forthcoming chapter.

Chapter III

1 The virial coefficient

The observed deviations from the ideal gas law were interpreted qualitatively by van der Waals by assuming that the molecules are attracted to one another at large distances and repelled at very small distances. At very high density the gas particle interact more vigorously. Accordingly, the gas becomes less ideal and more real. This deviation from ideal behavior gives a more complicated equation of state for real gases, which is the virial equation of state written generally in the form

$$\frac{PV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \cdots \qquad (1)$$

Where $\frac{PV}{RT}$ is the compressibility factor, $V^{\,2}$ denotes the molar specific volume. The coefficients $B(T)$,$C(T)$, $D(T)$...are called the second, third and fourth virial coefficients. By means of statistical mechanics these virial coefficient may be expressed in terms of the intermolecular potential function. Therefore, it is possible to obtain a quantitative interpretation of the deviations from the ideal gas law in terms of the forces between molecules. The second virial coefficient $B(T)$ in equation (1) accounts for deviations from ideal gas behavior up to about 20 bar near room temperature. Similarly, C(T) must be included to deal with pressure up to about 100 bar. Also, D(T) has the order of 1000 bar. Higher virial coefficients must, of course, be considered to account for even greater pressures. It is well known that the compressibility factor is almost invoked to model real gas behavior. Equation (1) represents a dimensionless correlation, therefore, it can define the principle of corresponding states both classically and statistically.

Two forms of the equation of state are used to study the fluids properties. One is developed from virial theorem and the other is developed from the statistical mechanics relation of pressure and partition function. We will develop the equation of state of real gases by the statistical mechanical approach of virial expansion with the use of grand canonical ensemble.

2 Equation of state for real gases

The fundamental relation for the grand canonical ensemble is

$$PV = kTln\Xi \qquad (2)$$

Where

$$ln\Xi = \lambda\left(\frac{\partial ln\Xi}{\partial\lambda}\right)_{T.V} = N \tag{3}$$

and

$$\Xi = \sum_N \lambda^N Q(T, V, N) \tag{4}$$

which is a general relation between the grand canonical ensemble and canonical ensemble. We have $Q = Z^N$ for distinguishable particles and appropriate for the crystalline solid. This is inappropriate for an ideal gas composed of N indistinguishable particles. Therefore for the indistinguishable particles we have

$$Q = \frac{Z^N}{N!} \tag{5}$$

Using (4), equation (3) is written as

$$\Xi = \sum_N \frac{(\lambda \mathrm{Z})^N}{N!} \tag{6}$$

Substituting (2) in (3) we get

$$PV = kTln[\sum_{N=0}^{\infty} \lambda^N Q(T, V, N)] \tag{7}$$

For $N = 0$, the value of Q (T, V, N) from equation (4) is one. Hence equation (7) is written as:

$$PV = kTln[1 + \sum_{N=1}^{\infty} \lambda^N Q(T, V, N)] \tag{8}$$

2.1 Canonical partition function of real gases

The canonical partition function is given by

$$Q = \sum_i \exp\,(-E_i/kT) \tag{9}$$

The system consisting of non-polar or moderately polar molecules, the energy associated with the ith system quantum state is written as

$$E_i(T, V, N) = E_i^* + \emptyset(r_1, r_2 \ldots\ldots r_N). \tag{10}$$

where, E_i^* is the energy of the assembly of particles and $\emptyset(r_1, r_2 \ldots \ldots r_N)$ is the configuration energy. Substituting (9) in (8), we get for canonical partition function as

$$Q(T,V,N) = \sum_i \exp\left(-\frac{E_i}{kT}\right) \cdot \frac{1}{V^N} \cdot \iint \ldots \int e^{-\emptyset/kT}\, dr_1 dr_2 \ldots . dr_N . \tag{11}$$

The summation part of equation (10) is nothing but the canonical partition function of independent particle which is equivalent to the equation (4). Accordingly, we have

$$Q(T,V,N) = \frac{Z^N}{N!}\left(\frac{Q_N}{V^N}\right) \tag{12}$$

Where is the configurational integral written as:

$$Q_N = \iint \ldots \int e^{\phi/kT} dr_1 dr_1 \ldots \ldots \ldots dr_N \tag{13}$$

2.2 **The virial equation of state**

$$PV = kTin\left[1 + \sum_{N=1}^{\infty}\left(\frac{Q_N}{N!}\right)\mathrm{z}^N\right] \tag{14}$$

where

$$\mathrm{z} = \frac{\lambda \mathrm{Z}}{V} \tag{15}$$

with Z as molecular partition function of the assembly of hypothetical gas. From equation (3) and (15), we have the relation where

$$\mathrm{z} = \frac{\mathrm{N}}{V} \tag{16}$$

where the parameter *z* is the particle density. Expanding equation (14) in terms of the particle number density for ideal and real gases by using the logarithmic seriesln$(1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3}$ this equation becomes

$$\frac{PV}{kT} = Q_1 z + \frac{1}{2!}(Q2 - Q_1^2)z^2 + \frac{1}{3!}(Q_3 - 3Q_1Q_2 + 2Q_1^3)z^3 + \cdots \tag{17}$$

Let us write,

$$\frac{P}{kT} = \sum_{l=1}^{\infty} b_l z^l \tag{18}$$

Comparing equations (17) and (18) gives

$$b_1 = \frac{Q_1}{V} = 1 \tag{19}$$

$$b_2 = \frac{Q_2 - Q_1^2}{2!\,V} \tag{20}$$

$$b_3 = \frac{Q_3 - 3Q_1Q_2 + 2Q_1^3}{3!\,V} \tag{21}$$

Here, coefficients b_l are known as cluster integrals. The determination of b_2 requires the evaluation of configuration integrals for only two particles and dermination of cluster integral b_3 requires only three particles. From equation (3) the actual number density is

$$n = \frac{N}{V} = \frac{\lambda}{N}\left(\frac{\partial \ln \Xi}{\partial \lambda}\right)_{T,V} \tag{22}$$

Equation (22) with elimination of λ can be written as

$$n = \frac{z}{V}\left(\frac{\partial \ln \Xi}{\partial \lambda}\right)_{T,V} \tag{23}$$

Substituting for ln Ξ from equation (2), we have

$$n = \frac{z}{kT}\left(\frac{\partial \mathrm{P}}{\partial \lambda}\right)_{T,V} \tag{24}$$

Substituting for P from equation (18) into equation (24), we have

$$z = \sum_{l=1}^{\infty} l b_1 z^l, \tag{25}$$

Equation (25) has a series for the number density of a real gas in terms of that corresponding to the ideal gas. We know require to write by inverting equation (25) as

$$z = \sum_{l=1}^{\infty} a_l \, n^l \tag{26}$$

Substituting (26) into equation (25), we have

$$b_1 a_1 = 1 \ \rightarrow a_1 = \frac{1}{b_1} = 1$$

$$b_1 a_2 = -2 b_2 a_1^2 \rightarrow a_2 = -2 b_2, b_2 = -\frac{-a_2}{2}$$

$$b_1 a_3 = -4 b_2 a_1 a_2 - 3 b_3 a_1^3 \rightarrow a_3 = 8 b_2^2 - 3 b_3, b_3 = -\frac{1}{3}(2 a_2^2 - a_3)$$

Thus using equation (26) the total density expansion for z is:

$$z = n - 2 b_2 n^2 + (8 b_2^2 - 3 b_3) n^3 + \cdots \tag{27}$$

Inserting equation (27) into equation (18)

$$\frac{P}{kT} = b_1 z + b_2 z^2 + b_3 z^3 + \cdots = z - \frac{1}{2} a_2 z^2 + \frac{1}{3}(2 a_2^2 - a_3) z^3 + \cdots \tag{28}$$

$$= (a_1 n + a_2 n^2 + a_3 n^3 + \cdots) - \tfrac{a_2}{2}(a_1 n + a_2 n^2 + a_3 n^3 + \cdots)^2 + \tfrac{1}{3}(2 a_2^2 - a_3)(a_1 n + a_2 n^2 + a_3 n^3 + \cdots)^3$$

$$= (a_1 n + n^2 \left(a_2 - \tfrac{a_1 a_2}{2}\right) + n^3 \left(a_3 - a_1 a_2^2 + \tfrac{1}{3}(2 a_2^2 - a_3) a_1^3\right) + \cdots$$

$$= n + n^2(-b_2) + n^3 \left(\tfrac{2\left(8 b_2^2 - 3 b_{3)} - 4 b_2^3\right)}{3}\right) + \cdots$$

$$= n + n^2(-b_2) + n^3(4b_2^3 - 2b_3) +$$

Thus we have

$$\frac{P}{kT} = n + n^2(-b_2) + n^3(4b_2^3 - 2b_3) + \qquad (28)$$

We have the relation between the specific volume v and the number density *n* as

$$n = \frac{N_A}{\vartheta} \qquad (29)$$

Inserting equation (29) into equation (28) we have

$$\frac{P}{kT} = 1 - b_2\left(\frac{N_A}{\vartheta}\right)(4b_2^2 - 2b_3)\left(\frac{N_A}{\vartheta}\right)^2 + \cdots \qquad (30)$$

Comparing equation (30) with equation (1) we have relations for second virial coefficient and third virial coefficient as:

$$B(T) = -b_2 N_A \qquad (31)$$

and

$$C(T) = (4b_2^2 - 2b_3)N_A^2 \qquad (32)$$

It is clear that the second virial coefficient requires only two configuration integral and the collisions is binary and for the third virial coefficient requires only three configuration integral and the collisions is both binary and tertiary.

2.3 The second virial coefficient

The expression for first configurational integral is

$$Q_1 = \int_V dr_1 = V \qquad (33)$$

$$Q_1 = \iint exp\left[-\frac{\emptyset(r_{12})}{kT}\right] dr_1 dr_2 \qquad (34)$$

Inserting equation (33) and (34) in (20) we have

$$b_2 = \frac{1}{2V} \iint_v \left[e^{-\emptyset(r_{12})/kT} - 1 \right] dr_1\, dr_2 \tag{35}$$

The Mayer cluster function is

$$f_{ij} = e^{-\phi(r_{ij})/kT} - 1 \tag{36}$$

Equation (35) is written as

$$b_2 = \frac{1}{2V} \iint_V f_{12}\, dr_1 dr_2 \tag{37}$$

Equation(37) can be written as

$$b_2 = \frac{1}{2V} \int_V dr_c \int_V f_{12} dr_{12}, \tag{38}$$

where the first integration is for center of mass and the second is for relative distance between any two particles. When substituting equation (33) for the integral occurring with center of mass, the second cluster integral becomes

$$b_2 = \frac{1}{2} \int_V f_{12} dr_{12} \tag{39}$$

Using equation (31), we have the expression for second virial coefficient as

$$B(T) = -\frac{N_A}{A} \int_V f_{12} dr_{12} \tag{40}$$

Substituting for f_{12}, we have

$$B(T) = \frac{N_A}{2}\int_V \left[1 - e^{-\emptyset\frac{(r_{12})}{kT}} dr_{12}\right] \tag{41}$$

It is given that $dr_{12} = 4\pi r^2 dr$, the second virial coefficient may be written as:

$$B(T) = 2\pi N_A \int_V \left[1 - e^{-\emptyset\frac{(r_{12})}{kT}} r_{12}^2 dr_{12}\right] \tag{42}$$

Thus, information on the intermolecular potential or in turn the second virial coefficient can be gathered by knowing alternatively the other. Now here we summarizing the second virial coefficients for some important potentials viz hard sphere, square well, Leenard Jones potential and Sutherland potential model for angle independent potential and the second virial coefficient for spherical molecules.

a. The second virial coefficient for rigid sphere (see Chapter I for the expression (4) for potential) is:

$$B(T) = 2\pi N_A \int_0^{\sigma} r^2 dr = \frac{2\pi}{3} N_A \sigma^3 \tag{43}$$

which is designated as

$$b_0 = \frac{2\pi}{3} N_A \sigma^3 \tag{44}$$

The virial coefficient is a function of temperature, as is obvious because of $B(T)$. The rigid sphere model is generally used at very high temperatures.

b. The second virial coefficient for square well potential (see Chapter I for the expression(5) for potential) is:

$$\mathrm{B(T)} = 2\pi \mathrm{N_A}\left[\int_0^{\sigma} \mathrm{r^2 dr} + \int_0^{\lambda\sigma}\left(1 - \frac{\mathrm{e}^{\epsilon}}{\mathrm{kT}}\right)\mathrm{r^2 dr}\right] \tag{45}$$

$$B(T) = b_0 \left[1 - (\lambda^3 - 1)\left(e^{\frac{\varepsilon}{kT}} - 1\right)\right] \tag{46}$$

This temperature dependence reflects the combined attractive and repulsive components of the square well potential.

c. The second virial coefficient for Leenard Jones potential (see Chapter I for the expression(10) for potential) is:

$$B(T) = 2\pi N_A \int_0^{\infty} \left[1 - exp\left[-\left(\frac{\epsilon}{kT}\right) . f\left(\frac{r}{\sigma}\right)\right]\right] \tag{47}$$

Here, in equation (47), we have used alternatively the generic form of equation (10) of Chapter I, which has the form $\emptyset(r) = \epsilon f\left(\frac{r}{\sigma}\right)$

d. The second virial coefficient for the Sutherland potential (see Chapter I for the expression (10) for potential) is:

$$B(T) = \frac{2\pi N_A \sigma^3}{3} - 2\pi NA \int_0^{\infty} \left[exp\left(\frac{-cr^{-\gamma}}{kT}\right) - 1\right] r^2 dr \tag{48}$$

The Sutherland model is a special case of the Leenard -Jones potential with infinitely steep repulsion. At low temperatures this model gives a negative virial coefficient.

Similar to spherical molecules the non-spherical molecules can also be taken as a rigid impenetrable objects but of various shapes. Kihara followed the work of Isihara and explained the calculations of any rigid convex molecule such as elongated and flat molecules interacting by means of Leenard -Jones potential. This potential was considered when the distance of molecules are least separated.

a. Isihara rigid convex molecule.

The second virial coefficient of rigid convex molecules may be written as

$$B = 4N_A v_m f \tag{49}$$

Where v_m is the volume of a single molecule. According to Isihara the expression for f is

$$f = 1 + \left[\frac{\bar{R}}{4v_m} - \frac{3}{4}\right] \tag{50}$$

Where

$$\bar{R} = \frac{1}{4\pi}\int \frac{1}{2}(R_1 + R_2)d\omega \tag{51}$$

Here, R_1 and R_2 are the principle radii of curvature, and *dw* is the surface element on a unit sphere. The value of *f* for various non spherical models are: *f* = 1 (Sphere),

$f = \frac{11}{8}$ (Cube), *f* = 1.926 (Regular Tetrahedron) , *f* = 1.330 (Regular Octehedron) and$f = \frac{\pi u^2+(\pi+3)al+l^2}{8al}$ (Cylinder).

b. Kiharas model

1. For the generalized spherocylider molecules the second virial coefficient is given by

$$B(T) = \int_{\rho=0}^{\rho=\infty} \left[1 - e^{-\emptyset(\rho)/kT}\right] db_l(\rho) + b_l(0) \tag{52}$$

This expression has a term of second virial coefficient as $b_l(\rho)$ for rigid spherocylinder. Where *l* is the core length and *ρ* is the minor axis of rigid spherocylinder. The expression is:

$$b_l = 4N_A v_m(l,\rho) f(l,\rho) \tag{53}$$

$$f = 1 + \left[\frac{8}{3}\xi^2 + 4\xi\right] - 1(prolate) \tag{53}$$

and

$$f = 1 + \frac{\left(\frac{\pi^2}{4} - 2\right)\xi + \frac{\pi}{4}}{\frac{8}{3}\xi^3 + 4\xi + 2\pi\xi^2}(oblate) \tag{54}$$

Prolate spherocylinders are generated when the cylinder is rotated about one axis (length -wise) and oblate spherocylinders are generated when the cylinder is rotated about the other axis (diameter-wise). Here, in equations (54) and (55), the value of $= \frac{\rho m}{l}$. Actually these equations were used by Kihara to obtain the expressions for second virial coefficient of angle dependent Leenard -Jones intermolecular potential. According to him, the inter- molecular potential is characterized by three quantities: the length l and the parameters σ and of the Leenard -Jones (6-12) potential. He actually chosen the parameter $\rho_{m=}2^{\frac{1}{6}}\sigma$, in place of the collision diameter σ. The distance ρ_m is the shorter (minor-axis) dimension of the spherocylider. When l = 0 the intermolecular potential reduces to the ordinary spherically symmetric Leenard -Jones (6-12) potential.

Respective insertion of $b_l(\rho)$ in equation (52) and then integrating, we obtain the following relations for both Prolate and Oblate spherocylinders,

$$B(T) = \frac{2\pi N_A \rho_m^3}{3} F_3\left(\frac{\epsilon}{kT}\right) + \pi^2 N_A \rho_m^2 l F_2\left(\frac{\epsilon}{kT}\right) + \frac{\pi N_{A\rho_m}}{4} F_1\left(\frac{\epsilon}{kT}\right) \tag{56}$$

and

$$\mathrm{B(T)} = \frac{2\pi \mathrm{N_A} \rho_\mathrm{m}^3}{3} \mathrm{F}_3\left(\frac{\epsilon}{\mathrm{kT}}\right) + \frac{\pi^2 \mathrm{N_A} \rho_\mathrm{m}^2}{2} \mathrm{lF}_2\left(\frac{\epsilon}{\mathrm{kT}}\right) + \frac{\pi \mathrm{N_A}}{2}\left(1 + \frac{\pi^2}{8}\right) \mathrm{p_m} l^2 \mathrm{F1}\left(\frac{\epsilon}{\mathrm{kT}}\right) + \frac{\pi^2 \mathrm{N_A} \mathrm{L}^3}{16} \tag{57}$$

in which

$$F_k = -\frac{k}{12}\sum_{0}^{\infty} \frac{2^j}{j!}\left(\frac{\varepsilon}{kT}\right)^{\left(\frac{l}{2}+\frac{k}{12}\right)} \Gamma\left(\frac{6j-k}{12}\right) \tag{58}$$

2.Kihara's ellipsoidal molecules This model may be generalised to include the repulsive and attractive intermolecular forces as that of spherocylinder molecules. The second virial coefficient is

$$B(T) = \frac{2}{3} N_A \rho_m^3 \left[K_0\left(\frac{\varepsilon_0}{kT}\right) + \varepsilon_0^2 K_1\left(\frac{\varepsilon_0}{kT}\right) + \varepsilon_0^4 K_2\left(\frac{\varepsilon_0}{kT}\right) + \cdots\right] \tag{59}$$

In equation (59), the coefficients of k_i are given by $K_0 = F_3 K_1 = k_1 F_1 K_2 = k_1 F_1 + k_2 F - 1$

The k_i for the prolate ellipsoid are

$$k_1 = \frac{1}{2}, \quad k_2 = \frac{-7}{120}, \quad k_3 = \frac{7}{240}, \quad k_4 = \frac{-1201}{67200}, \quad k_5 = \frac{1643}{134400}$$

and

for the oblate ellipsoid are

$$k_1 = 1, \qquad k_2 = \frac{-1}{15}, k_3 = 0, \; k_4 = \frac{-2}{525}, \quad k_5 = \frac{2}{525}$$

The eccentricity is

$$\varepsilon_0 = \frac{l}{\sqrt{l^2 + \rho_m^2}}$$

3 The second virial coefficient for angle dependent potential

The second virial coefficient in classical mechanics in terms of the distance r between the centre of the two molecules and the three angles needed to specify the mutual orientation of the two molecules (i.e. in the conventional spherical polar co-ordinate $(r, \; \theta, \phi)$) may be written as

$$B(T) = -\frac{N}{4}\int_0^\infty \int_0^{2\pi} \int_0^\pi \left[e^{-\emptyset\frac{r}{kT}} - 1\right] sin\theta_1 \, d\theta_1 \sin\theta_2 d\theta_2 d\alpha \, r_{12}^2 dr_{12} \qquad (60)$$

where $\alpha = \phi_2 - \phi_1$.It is known that this formula is also true in the quantum mechanical theory of the equation of state when the factor $\left[e^{-\phi(r)/kT} - 1\right]$ is replaced by its quantum mechanical analog $[S(r) - 1]$. Where $S(r)$ is the slater sum. Thus the quantum analogue of Eq.(60) is

$$B(T) = -\frac{N}{4}\int_0^\infty \int_0^{2\pi} \int_0^\pi \left[e^{-\emptyset\frac{r}{kT}} - 1\right] sin\theta_1 \, d\theta_1 \sin\theta_2 d\theta_2 d\alpha \, r_{12}^2 dr_{12} \qquad (61)$$

The Slater sum *S*(*r*) is defined by

$$S(r) = N! \, \lambda^{3N} \textstyle\sum_\rho \, \phi_\rho^*(r^N) e^{-\frac{\phi(r)}{kT}} \phi_\rho(r^N) \qquad (62)$$

where $\lambda = \frac{h}{\sqrt{2\pi mKT}}$is the de-Broglie wavelength of average thermal energy and the function $\Phi(r^N)$ are a complete orthonormal set of eigen functions and H is the quantum mechanical Hamiltonian operator. It's classical counterpart and is commonly referred to as the

Boltzmann factor which is the limiting case of the more rigorous quantum statistics as $\lambda \rightarrow 0$.

$$\lim_{\lambda\to 0} S(r) = e^{-\emptyset(r)/KT} \tag{63}$$

For isotropic-symmetric system, equation (60) and (61) reduces to

$$B_{CL}(T) = -\frac{N}{4}\int_0^{\infty}\int_0^{2\pi}\int_0^{\pi}\left[e^{-\emptyset\frac{r}{kT}} - 1\right] r^2 sin\theta d\theta d\alpha dr \tag{64}$$

$$B(T) = -\frac{N}{4}\int_0^{\infty}\int_0^{2\pi}\int_0^{\pi}\left[exp\big(S(r)\big) - 1\right] r^2 sin\theta d\theta d\alpha dr \tag{65}$$

A series expansion of $S(r)$ is

$$\begin{aligned}\mathrm{S(r)} = \mathrm{e}^{-\phi(r)/kT}\Bigg[1 + \frac{h^2(kT)^{-2}}{48\pi^2 m}\left(-\Delta\phi + \frac{(kT)^{-1}}{2}(\Delta\phi)^2\right) - \frac{h^4(kT)^3}{3840\pi^4\mu^2}\Big[-\Delta\Delta\phi + \\ \frac{(kT)^{-1}}{6}\left(2\Delta(\nabla\phi)^2 + 4(\nabla\phi.\nabla\Delta\phi) + 5(\Delta\phi)^2\right) \\ -\frac{(kT)^{-2}}{6}\left(5(\Delta\phi)(\nabla\phi)^2 + 3(\nabla\phi\cdot\nabla(\nabla\phi))^2\right) + \\ \frac{5}{24}(kT)^{-3}(\nabla\phi)^4\Big]\Bigg] + \cdots +\end{aligned} \tag{66}$$

Where Δ is the infinitesimal interval and ∇ is the del operator and $\Phi(r)$ is the intermolecular potential. The quantum mechanical second virial coefficient may be written as the classical mechanical second virial coefficient plus correction terms. The quantum statistical correction can be represented with sufficient accuracy by the two following terms of the expansion down to moderately low temperatures. Since the terms involving higher order permutations would have to be considered in the third and higher virial coefficient but do not affect the second virial coefficient. If we next write the second virial coefficient in the form

$$B(T) = B_{CL}(T) + B_1(T) + B_2(T) + \cdots \tag{67}$$

Then, after introduction of polar coordinates and integration by parts, it follows from equation (66) and equation (67) that $B_{CL}(T)$ is just the classical expression (64) and

$$B_1(T) = -\frac{N}{4}\frac{h^2}{48\pi^2 m(kT)^3}\int_0^\infty \int_0^{2\pi} \int_0^\pi \left(\frac{d\phi}{dr}\right)^2 \left[e^{-\frac{\phi(r)}{kT}}\right] \sin\theta d\theta d\alpha r_{12}^2 dr_{12} \tag{68}$$

$$\mathrm{B}_2(T) = -\frac{N}{4}\frac{h^2}{1920\,\pi^4 m^2(kT)^4}\int_0^\infty \int_0^{2\pi} \int_0^\pi \left[\left(\frac{d^2\phi}{dr^2}\right)^2 + \frac{2}{r^2}\left(\frac{d\phi}{dr}\right)^2 + \frac{10}{9rkT}\left(\frac{d\phi}{dr}\right)^3 - \frac{5}{36(kT)^2}\left(\frac{d\phi}{dr}\right)^4\right]\left[e^{-\frac{\phi(r)}{kT}}\right] \sin\,\theta d\theta d\alpha r_{12}^2 dr_{12} \tag{69}$$

The expression (68) may be refined somewhat by taking the influence of the symmetry into account i.e., for a quantum statistical ideal gas $\phi(r) = 0$. The expression (67) may also be written as

$$B(T) = B_{CL}(T) + B_1(T) + B_2(T) + B_{id}(T) + \cdots) \tag{70}$$

where B_{id} is the second virial coefficient of the ideal gas. The symmetry character of the eigen function which results from the statistics of the particles are of importance when the DE Broglie wavelength of the molecules is of the order of magnitude of the average distance between the molecules.

4 The second virial coefficient of HCB fluid

The transformation from (r, θ, ϕ) to (K, θ, ϕ) coordinates in equation (12). The Jacobian $S^{12}(x, K)$ for this transformation from centre to centre coordinates to the surface to surface coordinates is a function of K and the new angles. Therefore, in this new language the equation (64) and (65) may be expressed as

$$B_{CL}(T) = -\frac{N}{4}\int_0^\infty \int_0^{2\pi} \int_0^1 \left[\exp\left(\frac{-\phi(K)}{kT}\right) - 1\right]\left[j^2 + jf + \frac{1}{4}f^2\sin^2\,\alpha\right] dx d\alpha dK \tag{71}$$

$$B(T) = -\frac{N}{4}\int_0^\infty \int_0^{2\pi} \int_0^1 \left[\left(S(K)\right) - 1\right]\left[j^2 + jf + \frac{1}{4}f^2\sin^2\alpha\right] dx d\alpha dK \tag{72}$$

It follows from equations (66) and (72) that $(T) = B_{CL} + B_1 + B_2$, where B_{CL} is the expression (71)

$$B_1(T) = -\frac{N}{4}\frac{h^2}{48\pi^2 m(kT)^3}\int_0^\infty \int_0^{2\pi} \int_0^\pi \left(\frac{d\phi}{dK}\right)^2 \left[e^{-\frac{\phi(K)}{kT}}\right]\left[j^2 + jf + \frac{1}{4}f^2 \sin^2\alpha\right] dx d\alpha dK \tag{73}$$

$$\mathrm{B}_2(T) = -\frac{N}{4}\frac{h^2}{1920\,\pi^4 m^2 (kT)^4}\int_0^\infty \int_0^{2\pi} \int_0^\pi \left[\begin{array}{c} \left(\frac{d^2\phi}{dr^2}\right)^2 + \frac{2}{r^2}\left(\frac{d\phi}{dK}\right)^2 + \frac{10}{9rkT}\left(\frac{d\phi}{dr}\right)^3 \\ -\frac{5}{36(kT)^2}\left(\frac{d\phi}{dr}\right)^4 \end{array}\right] \left[e^{-\frac{\phi(K)}{kT}}\right]\left[j^2 + jf + \frac{1}{4}f^2 \sin^2\alpha\right] dx d\alpha dK \tag{74}$$

The expression for $B_{CL}(T), B_1(T), B_2(T)$ and $B_{id}$for the potential

$$\Phi(K) = 4E\left[\left(\frac{h(x)}{K}\right)^{12} - \left(\frac{h(x)}{K}\right)^{6}\right] \tag{75}$$

may be expanded in a rapidly converging infinite series of gamma functions. The computation of the second virial coefficient for this potential may be carried out with the aid of this series expansion.

4.1 The expression for $\boldsymbol{B_{CL}(T)}$

Using equation (19) of chapter II, the expression for B_{CL}may be written as

$$\mathrm{B_{CL}} = \frac{N}{4}\int_0^{\infty}\int_0^{2\pi}\int_0^{1}\left[1 - e^{-\phi(K)/kT}\right]\left[K^2 + \frac{2Kb^2}{h(x)} + \frac{b^4}{h^2(x)} + \frac{\epsilon b^4 K}{h^3(x)} - \frac{Kb^4x^2\epsilon}{h^3(x)} + \frac{b^6\epsilon}{h^4(x)} - \frac{b^6x^2\epsilon}{h^4(x)} + \frac{\epsilon^2 b^8}{4h^6(x)}\sin^2\alpha - \frac{\epsilon^2 b^8 x^2}{2h^6(x)}\sin^2\alpha + \frac{\epsilon^2 b^8 x^2}{4h^6(x)}\sin^2\alpha\right] dK dx d\alpha \tag{76}$$

The first term of integral (76) is

$$\frac{N}{4}\int_0^{\infty}\int_0^{2\pi}\int_0^{1}\left[1 - e^{\frac{-\phi(K)}{kT}}\right] K^2 dK dx d\alpha \tag{77}$$

Since

$$\int_0^{\infty}\left[1 - e^{\frac{-\phi(K)}{kT}}\right] K^P dK = \frac{1}{(p+1)kT}\int_0^{\infty} K^{P+1}\frac{d\phi}{dK} e^{\frac{-\phi(K)}{kT}} dK \tag{78}$$

$$= -\frac{1}{2}\sum_0^{\infty}\frac{1}{S!}\left(\frac{4E}{kT}\right)^{\frac{S}{2}+\frac{R}{12}} h^R(x)\Gamma\left(\frac{S}{2} - \frac{R}{12}\right) \tag{79}$$

where $R = P + 1$ So integral (77) may be expressed in a series of gamma functions by the relation

$$-\frac{N}{48}\pi b^3 K_3\int_0^1 (1 + \epsilon x^2)^{\frac{3}{2}} dx \tag{80}$$

where

$$K_3 = \sum_0^{\infty}\frac{1}{S!}\left(\frac{4E}{kT}\right)^{\frac{S}{2}+\frac{3}{12}} h^R(x)\Gamma\left(\frac{S}{2} - \frac{3}{12}\right) \tag{81}$$

Here, the integral $\int_o^1 h^R(x)dx$ has been divided by 2 to avoid the contribution in the integral due to overlapping situation. Similarly, all the term of expression (76) may be expressed in a series of gamma functions. These relations are:

$$-\frac{N}{24}\pi b^3 K_2 \int_0^1 (1+\epsilon\cdot x^2)^{\frac{1}{2}}dx \tag{82}$$

where

$$K_2 = \sum_0^\infty \frac{1}{S!}\left(\frac{4E}{kT}\right)^{\frac{S}{2}+\frac{2}{12}} h^R(x)\Gamma\left(\frac{S}{2}-\frac{2}{12}\right) \tag{83}$$

$$-\frac{N}{48}\pi b^3 K_2 \int_0^1 (1+\epsilon\cdot x^2)^{-\frac{1}{2}}dx \tag{84}$$

Where

$$K_1 = \sum_0^\infty \frac{1}{S!}\left(\frac{4E}{kT}\right)^{\frac{S}{2}+\frac{1}{12}} h^R(x)\Gamma\left(\frac{S}{2}-\frac{1}{12}\right) \tag{85}$$

The other terms are

$$-\frac{N}{48}\pi b^3 \epsilon K_2 \int_0^1 (1+\epsilon\cdot x^2)^{-\frac{1}{2}}\,dx \tag{86}$$

$$-\frac{N}{48}\pi b^3 \epsilon K_2 \int_0^1 x^2(1+\epsilon\cdot x^2)^{-\frac{1}{2}}\,dx \tag{87}$$

$$-\frac{N}{48}\pi b^3 \epsilon K_1 \int_0^1 (1+\epsilon\cdot x^2)^{-\frac{3}{2}}\,dx \tag{88}$$

$$-\frac{N}{48}\pi b^3 \epsilon K_1 \int_0^1 x^2(1+\epsilon \cdot x^2)^{-\frac{3}{2}}\, dx \tag{89}$$

$$-\frac{N}{382}\pi b^3 \epsilon^2 K_1 \int_0^1 (1+\epsilon \cdot x^2)^{-\frac{5}{2}}\, dx \tag{90}$$

$$-\frac{N}{192}\pi b^3 \epsilon^2 K_1 \int_0^1 x^2(1+\epsilon \cdot x^2)^{-\frac{5}{2}}\, dx \tag{91}$$

$$-\frac{N}{384}\pi b^3 \epsilon^2 K_1 \int_0^1 x^4(1+\epsilon \cdot x^2)^{-\frac{5}{2}}\, dx \tag{92}$$

Finally, the expression for B_{CL} using (81-85) can be written as

$$\mathrm{B}_{\mathrm{CL}}(T) = -\frac{C}{48}L_{-1}K_3 - \frac{C\epsilon}{48}\left[\frac{2}{\epsilon}L_0 + (L_1 - M_1)\right]K_2 - \frac{C\epsilon^2}{48}\left[\frac{1}{\epsilon^2}L_1 + \frac{1}{\epsilon}(L_2 - M_2)\right.$$
$$\left. + \frac{1}{4}\left(\frac{L_3}{2} - M_3 + \frac{N_3}{2}\right)\right]K_1 \tag{93}$$

where

$$\mathrm{C} = \mathrm{N}\pi b^3, L_P = \int_0^1 (1+\epsilon x^2)^{\frac{1}{2}-P} dx,\ \ M_P = \int_0^1 x^2(1+\epsilon x^2)^{\frac{1}{2}-Q} dx,$$
$$N_P = \int_0^1 x(1+\epsilon x^2)^{\frac{1}{2}-R} dx \tag{94}$$

4.2 Expressions for quantum correction $B_1(T)$ and $\mathbf{B}_2(T)$

$$\mathrm{B}_1(T)=\frac{N}{4}\frac{h^2}{48\pi^2 m(kT)^3}\int_0^{\infty}\int_0^{2\pi}\int_0^{1}\left(\frac{d\phi}{dK}\right)^2 e^{\frac{-\phi(K)}{kT}}\left[K^2+\frac{2Kb^2}{h(x)}+\frac{b^4}{h^2(x)}+\frac{\epsilon b^4K}{h^3(x)}-\frac{Kb^4x^2\epsilon}{h^3(x)}\right.$$

$$\left.+\frac{b^6\epsilon}{h^4(x)}-\frac{b^6x^2\epsilon}{h^4(x)}+\frac{\epsilon^2b^8}{4h^6(x)}\sin^2\,\alpha-\frac{\epsilon^2b^8x^2}{2h^6(x)}\sin^2\alpha+\frac{\epsilon^2b^8x^2}{4h^6(x)}\sin^2\alpha\right]dKdxd\alpha$$

(95)

Consider the first integral of expression (96)

$$\frac{N}{4}\frac{h^2}{48\pi^2 m(kT)^3}\int_0^{\infty}\left(\frac{d\phi}{dK}\right)^2 e^{\frac{-\phi(K)}{kT}}K^2dK \qquad (96)$$

which may be written as

$$-\frac{h^2}{48\pi^2 m(kT)^2}\int_0^{\infty}\frac{d}{dK}\left[e^{-\frac{\phi(K)}{kT}}\right]\frac{d\phi(K)}{dK}K^2dK \qquad (97)$$

$$=-\frac{h^2(6-1)}{48\pi^2 m(kT)^2}\int_0^{\infty}K\left[\frac{12\lambda}{K^{13}}-\frac{6\mu}{K^7}\right]\left[e^{-\frac{\phi(K)}{kT}}\right]dK \qquad (98)$$

$$-\frac{6h^2}{48\pi^2 m(kT)^2}\int_0^{\infty}K\frac{12\lambda}{K^{13}}\left[e^{-\frac{\phi(K)}{kT}}\right]dK \qquad (99)$$

$$=\ I_1\ +\ I_2$$

Where, $\lambda\ =\ 4Eh^1(x)\ and\ \mu\ =\ 4Eh^6(x)$. This expression may be expressed in a series of gamma function. The resulting expressions have the form:

$$I_1=-\frac{(6-1)h^2}{576\pi^2(kT)m}\sum_{S=0}^{\infty}\frac{1}{S!}\left(\frac{4E}{kT}\right)^{\frac{S}{2}+\frac{1}{12}}h(x)\Gamma\left(\frac{S}{2}-\frac{1}{12}\right) \qquad (100)$$

$$\mathrm{I}_2 = +\frac{36h^2}{1152\pi^2 mE}\frac{S}{2}\sum_{S=0}^{\infty} \frac{1}{S!}!^{S+\frac{1}{6}+2} h(x)\Gamma\left(\frac{S}{2}-\frac{1}{12}\right)T^{*-\left(\frac{6\,S+13}{12}\right)}$$

$$-\frac{6h^2}{2304\pi^2 mE}\sum_{S=0}^{\infty} \frac{1}{S!}2^{S+\frac{1}{6}+2}h(x)\Gamma\left(\frac{S}{2}-\frac{1}{12}\right)T^{*-\left(\frac{6S+13}{12}\right)} \qquad (101)$$

where $T^* = \frac{kT}{E}$ and $R = P + 1$

Finally, we have

$$I_1 + I_2 = -\frac{h^2}{mE}\sum_{S=0}^{\infty}\frac{1}{S!}\left(\frac{11-36S}{2304\pi^2}\right)2^{S+\frac{1}{6}+2}h(x)\Gamma\left(\frac{S}{2}-\frac{1}{12}\right)T^{*-\left(\frac{6\,S+13}{12}\right)} \qquad (102)$$

Similarly, all the terms of the expansion (95) can be expressed in a series of gamma functions. These terms are

$$-\frac{N\pi b^3}{4}\Delta^{*2}K_1\int_0^1 (1+\epsilon\cdot x^2)^{\frac{1}{2}}\,dx \qquad (103)$$

$$-\frac{N\pi b^3}{2}\Delta^{*2}K_0\int_0^1 (1+\epsilon\cdot x^2)^{\frac{1}{2}}\,dx \qquad (104)$$

$$-\frac{N\pi b^3}{2}\Delta^{*2}K_1\int_0^1 (1+\epsilon\cdot x^2)^{\frac{-3}{2}}\,dx \qquad (105)$$

$$-\frac{N\pi b^3}{4}\epsilon\Delta^{*2}K_0\int_0^1 (1+\epsilon\cdot x^2)^{\frac{-3}{2}}dx \qquad (106)$$

$$-\frac{N\pi b^3}{4}\epsilon\Delta^{*2}K_0\int_0^1 x^2(1+\epsilon\cdot x^2)^{\frac{-3}{2}}dx \tag{107}$$

$$-\frac{N\pi b^3}{4}\epsilon\Delta^{*2}K_{-1}\int_0^1 (1+\epsilon\cdot x^2)^{\frac{-5}{2}}dx \tag{108}$$

$$-\frac{N\pi b^3}{4}\epsilon\Delta^{*2}K_{-1}\int_0^1 x^2(1+\epsilon\cdot x^2)^{\frac{-5}{2}}dx \tag{109}$$

$$-\frac{N\pi b^3}{32}\epsilon^2\Delta^{*2}K_{-1}\int_0^1 (1+\epsilon\cdot x^2)^{\frac{-5}{2}}dx \tag{110}$$

$$-\frac{N\pi b^3}{16}\epsilon^2\Delta^{*2}K_{-1}\int_0^1 x^2(1+\epsilon\cdot x^2)^{\frac{-7}{2}}dx \tag{111}$$

$$-\frac{N\pi b^3}{8}\epsilon^2\Delta^{*2}K_{-1}\int_0^1 x^4(1+\epsilon\cdot x^2)^{\frac{-7}{2}}dx \tag{112}$$

where, $\Delta^*= \frac{h}{b\sqrt{mE}}$ is the quantum mechanical parameter.

$$K_1 = -\sum_{S=0}^{\infty}\frac{1}{S!}\left(\frac{11\times 1-36S}{2304\pi^2}\right)2^{S+\frac{13}{6}}\Gamma\left(\frac{6S-1}{12}\right)\left(\frac{E}{kT}\right)^{\left(\frac{S}{2}+\frac{13}{12}\right)} \tag{113}$$

$$K_0 = -\sum_{S=0}^{\infty}\frac{1}{S!}\left(\frac{11\times(0)-36S}{2304\pi^2}\right)2^{S+2}\Gamma\left(\frac{6S}{12}\right) \tag{114}$$

$$= -\sum_{S=0}^{\infty} \frac{1}{S!}\left(\frac{11\times(-1)-36S}{2304\pi^2}\right) 2^{S+\frac{13}{12}}\Gamma\left(\frac{6S+1}{12}\right)\left(\frac{E}{kT}\right)^{\left(\frac{S}{2}+\frac{13}{12}\right)} \qquad (115)$$

The general form can be written as

$$K_{n'} = -\sum_{S=0}^{\infty} \frac{1}{S!}\left(\frac{11n'-36S}{2304\pi^2}\right) 2^{S+\frac{13}{6}}\Gamma\left(\frac{6S-n'}{12}\right)\left(\frac{E}{kT}\right)^{\left(\frac{S}{2}+\frac{13}{12}\right)} \qquad (116)$$

where $n' = -1,0,1$.

$$\begin{aligned} \mathrm{B}_1(T) = &-\frac{C}{48}\Delta^{*2}L_0K_1 - \frac{C\epsilon}{48}\Delta^{*2}\left[\frac{2}{\epsilon}L_1 + (L_2 - M_2)\right]K_0 - \frac{C\epsilon^2}{48}\Delta^{*2}\left[\frac{1}{\epsilon^2}L_2\right. \\ &\left. + \frac{1}{\epsilon}(L_3 - M_3) + \frac{1}{4}\left(\frac{L_4}{2} - M_4 + \frac{N_4}{2}\right)\right]K_{-1} \qquad (117) \end{aligned}$$

Simplifying in a very similar way as above, the expression for second quantum correction term equation (74) can be written in terms of series gamma function as

$$\begin{aligned} \mathrm{B}_2(T) = &-\frac{C}{48}\Delta^{*4}L_1K_{-1} - \frac{\mathrm{C}\,\varepsilon}{4}\Delta^{*4}\left[\frac{2}{\epsilon}L_2 + (L_3 - M_3)\right]K_{-2} - \frac{\mathrm{C}\,\varepsilon}{4}\Delta^{*4}\left[\frac{1}{\epsilon^2}L_3\right. \\ &\left. + \frac{1}{\epsilon}(L_4 - M_4) + \frac{1}{4}\left(\frac{L_5}{2} - M_5 + \frac{N_5}{2}\right)\right]K_{-3} \qquad (118) \end{aligned}$$

$$\begin{aligned} \mathrm{K}_{-1} = &-\sum_{S=0}^{\infty} \frac{1}{S!}\left(\frac{767\times(-1) + 4728\times S + 3024\times S^2}{3\times 491520\pi^4}\right) 2^{S+\frac{-1}{6}+4}\Gamma\left(\frac{S}{2} - \frac{-1}{12}\right) \\ &\times\left(\frac{E}{kT}\right)^{\left(\frac{S}{2}+\frac{-1}{12}+2\right)} \end{aligned}$$

(119)

$$\mathrm{K}_{-2} = -\sum_{S=0}^{\infty} \frac{1}{S!}\left(\frac{767 \times (-2) + 4728 \times S + 3024 \times S^2}{3 \times 491520\pi^4}\right) 2^{S+\frac{-2}{6}+4}\Gamma\left(\frac{S}{2} - \frac{-2}{12}\right) \times \left(\frac{E}{kT}\right)^{\left(\frac{S}{2}+\frac{-2}{12}+2\right)}$$

(120)

$$\mathrm{K}_{-3} = -\sum_{S=0}^{\infty} \frac{1}{S!}\left(\frac{767 \times (-3) + 4728 \times S + 3024 \times S^2}{3 \times 491520\pi^4}\right) 2^{S+\frac{-3}{6}+4}\Gamma\left(\frac{S}{2} - \frac{-3}{12}\right) \times \left(\frac{E}{kT}\right)^{\left(\frac{S}{2}+\frac{-3}{12}+2\right)} \tag{121}$$

In general form

$$\mathrm{K}_{-n} = -\sum_{S=0}^{\infty} \frac{1}{S!}\left(\frac{767 \times (-n) + 4728 \times S + 3024 \times S^2}{3 \times 491520\pi^4}\right) 2^{S+\frac{-n}{6}+4}\Gamma\left(\frac{S}{2} - \frac{-n}{12}\right) \times \left(\frac{E}{kT}\right)^{\left(\frac{S}{2}+\frac{-n}{12}+2\right)} \tag{122}$$

Here n= -1,-2,-3.

4.3 The expression for B_{id}

B_{id} is the second virial coefficient of the ideal gas. The influence of the symmetry requirements into account to the first approximation for quantum statistical ideal gas with $\Phi(K) = 0$ reduces the Slater sum as

$$S(r)_{id} = 1 \pm \frac{e^{-2\pi r^2}}{\lambda^2} \tag{123}$$

In which the positive sign holds for system with symmetric eigen functions (Bose-Einstein statistics), the negative sign for system with anti-symmetric eigen function (Fermi-Dirac statistics). By substituting (123) in equation (65) and using equation (19) the expression for B_{id} becomes

$$\mathrm{B}_{id} = \mp \int_0^\infty \int_0^{2\pi} \int_0^1 e^{-k_0^2K^2} \left[K^2 + \frac{2Kb^2}{h(x)} + \frac{b^4}{h^2(x)} + \frac{\epsilon b^4 K}{h^3(x)} - \frac{Kb^4x^2\epsilon}{h^3(x)} \right.$$

$$+ \frac{b^6\epsilon}{h^4(x)} - \frac{b^6x^2\epsilon}{h^4(x)} + \frac{\epsilon^2 b^8}{4h^6(x)}\sin^2\alpha - \frac{\epsilon^2 b^8x^2}{2h^6(x)}\sin^2\alpha$$

$$\left. + \frac{\epsilon^2 b^8 x^2}{4h^6(x)}\sin^2\alpha \right] dKdxd\alpha \qquad (124)$$

where

$$k_0 = \frac{\sqrt{2}\pi}{\lambda}, T^* = \frac{kT}{E}$$

and

$$\lambda = \frac{h}{\sqrt{2}\pi mkT}$$

Simplifying as above, the equation (65) may be written as

$$\mathrm{B}_{id} = \mp \frac{C\Delta^*}{16T^{*\frac{1}{2}}\pi^{\frac{1}{2}}} \left[\frac{\Delta^{*2}}{4\pi^2T^*}L_{\frac{1}{2}} + \frac{\Delta^*}{\pi^{\frac{3}{2}}T^{-\frac{1}{2}}}[2L_1 + +\epsilon(L_2 - M_2)] \right.$$

$$\left. +2\left[L_{\frac{3}{2}} - \epsilon\left(L_{\frac{5}{2}} - M_{\frac{5}{2}}\right) + \frac{\epsilon^2}{8}\left(L_{\frac{7}{2}} - 2M_{\frac{7}{2}} + N_{\frac{7}{2}}\right)\right]\right] \qquad (125)$$

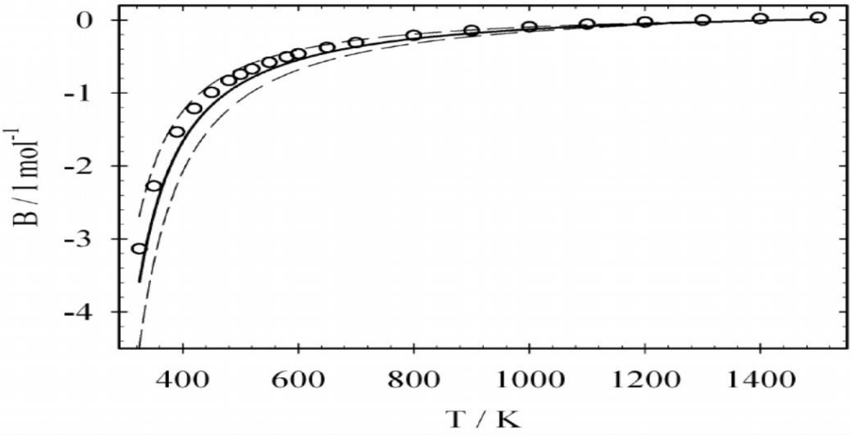


Figure 1

In equation (125), the negative sign now corresponds to the symmetric (Bose-Einsteins statistics) eigen functions. This is consistent with the motions of apparent attraction and repulsion. The expression (70) has been refined by taking the influence of the symmetry requirements into accounts i.e., for a quantum statistical ideal gas. Therefore, the second virial coefficient becomes

$$B = B_{CL} + B_1 + B_2 + B_{id} \tag{127}$$

The theoretical calculation of second virial coefficient involves the following steps: i. The "force constants" σ and ϵ/k for the molecules under consideration is determined. ii. We fit the experimental second virial coefficient to equation (109). This accomplished by successive approximation as:

a. First, values of the parameter σ and $/k$ are determined by using only the classical contribution to the second virial coefficient. With these a trial value of can be calculated.

b. This trial value of we may obtain new values of σ and ϵ/k from the experimental data and equation (109).

c. This process is repeated until a consistent set of values of σ and ϵ/k is obtained.

Once the parameters have been determined, the second virial coefficient may easily be calculated.

Chapter IV

1 The constant parameter

In order to make use of the theoretical expressions for the quantum statistical second virial coefficient for HCB it is necessary to know the constant parameters- the major axis a and minor axis b and E (the minimum energy) for the molecules under consideration. These constants parameters are determined by a process of successive approximations, which is as follows: First, values of the parameters are determined by using only the classical contribution of the second virial coefficient. The classical second virial coefficient may be written as

$$\mathrm{B}_{CL}(T) = -\frac{C}{48}L_{-1}K_3 \quad -\frac{C\epsilon}{48}\left[\frac{2}{\epsilon}L_0 + (L_1 - M_1)\right]K_2 - \frac{C\epsilon^2}{48}\left[\frac{1}{\epsilon^2}L_1 + \frac{1}{\epsilon}(L_2 - M_2) + \frac{1}{4}\left(\frac{L_3}{2} - M_3 + \frac{N_3}{2}\right)\right]K_1 \qquad (1)$$

which can also be written as

$$\mathrm{B}_{CL}(T) = -\frac{C}{48}\epsilon^2\left[\frac{1}{\epsilon^2}L_{-1}K_3 + \left[\frac{2}{\epsilon^2}L_0 + \frac{1}{\epsilon}(L_1 - M_1)\right]K_2 + \left[\frac{1}{\epsilon^2}L_1 + \frac{1}{\epsilon}(L_2 - M_2) + \frac{1}{4}\left(\frac{L_3}{2} - M_3 + \frac{N_3}{2}\right)\right]\right]K_1 \qquad (2)$$

$$= \frac{c}{48} \times K(Y) \text{ where, } K(Y) = \epsilon^2\left[\frac{1}{\epsilon^2}L_{-1}K_3 + \left[\frac{2}{\epsilon^2}L_0 + \frac{1}{\epsilon}(L_1 - M_1)\right]K_2 + \left[\frac{1}{\epsilon^2}L_1 + \frac{1}{\epsilon}(L_2 - M_2) + \frac{1}{4}\left(\frac{L_3}{2} - M_3 + \frac{N_3}{2}\right)\right]\right]K_1$$

Taking log, we can write,

$$\log B_{CL} = \log\frac{c}{48} + \log K(Y) \tag{3}$$

and

$$logY = log\frac{(kT)}{(4E)} = logk + logT - \log(4E)$$

or

$$logT = logY + \log(4E) - logk$$

The equation (3) and (4) are used for calculating the constant parameters. A graph of $logK(Y)$ versus $log(Y)$ and another graph of $logB$ and $logT$of experimental data are plotted. The curve of $logK(Y)$ versus $logY$is matched with curve of $logB$ versus $logT$of experimental data. The values of $logK(Y)$ versus $log(Y)$ and $logB$ versus $logT$ are taken for the best fit. These values have been used for calculating the constant parameters from equation (3) and equation (4).

The values of a, b and E at 71.5K^0C from the available experimental data have been calculated. These values have been used for computation of the first approximation of B_1, B_2 and B_{id} and quantum parameters Δ^*. These known quantum corrections have been used for determination of new values of parameter in B_{CL} from the equation (3). This process has been repeated till a consistent set of values of parameters is obtained. The values of parameter are tabulated in Table 1.

The classical and quantum mechanical theoretical second virial coefficient have been calculated with these known parameters and given in Table 2. The behaviour of the second virial coefficient for helium obtained with these parameters are presented together with the experimental data (Table 3) in Figure 2. The agreement between the theory and experiment is as good as can be expected, for the ratio of major and minor axis equal to 2. The quantum deviations of second virial coefficientas in Figure 2 depend on the magnitude of the quantity Δ^*. The equation in powers of Δ^* in equation (11) converges less rapidly as deviation from classical behaviour becomes greater. The larger the value of Δ^*, the greater will be the quantum deviations. At lower temperatures, the quantum deviations are quite appreciable for helium. The values of quantum second virial coefficient computed with these parameters fitted well with the experimental data. So we may safely conclude that the parameters for the potential best fit experimental values of the second virial coefficient of the helium for the hard convex fluid.

Chapter V

The quantum mechanical calculation of the transport phenomenon, the major problem is the evaluation of the evaluation of the phase shifts, $\eta_l(K)$ which is obtained by solving the radial wave equation for a collision for many values of the angular momentum $\hbar\sqrt{\,} l(l+1)$and the relative kinetic energy$\frac{h^2 j^2}{2\mu}$.The cross sections are obtained by performing the summation over l by the quantum formulae. μ is the reduced mass of the colliding pair of molecules and j may be defined by the relation $\frac{\mu g}{\hbar}$. g is the initial relative velocity.

1 Numerical calculation of the phase-shifts

The calculation of the phase shifts η_l needs the radial eigen functions of the relative motion of a pair of molecules for the case that there is an interaction potential $\Phi(K)$ and for the case that the interaction potential is zero. For HCB fluid, the isotropic symmetric part of pair, behaves much like that of a hard sphere fluid. So the Schrodingers equation for the radial eigen functions is taken as for a given intermolecular potential $\Phi(K)$, as

$$\frac{d^2\left(K^*\psi\right)}{dK^{*2}} + \left[J^* - \frac{l(l+1)}{K^*2} + \frac{16\pi^2}{\Delta^{*2}}\left(K^{*-12} - K^{*-6}\right)\right]K^*\psi = 0 \qquad (1)$$

$$\frac{d^2(K^*\psi)}{dK^{*2}} + \left[J^* - \frac{l(l+1)}{K^{*2}}\right]K^*\psi = 0 \qquad (2)$$

and for $\phi(K) = 0$
where the variable

$$\mathrm{K}^* = K/h(x), J^* = Jh(x)$$

and

$$\Delta^* = \frac{h}{\sqrt{h(x)(mE)}}$$

The reduced quantum mechanical parameter

$$\Delta^* = \frac{h}{\sqrt{a}(mE)}$$

. when $x = \cos\ \theta = 1$, i.e., when the orientation is along semi-major axis a and

$$\Delta^* = \frac{h}{\sqrt{b}(mE)}$$

when $x = \cos\ \theta = 0$, i.e., when the orientation is along semi minor axis b.

The asymptotic solutions for real (interacting) and ideal (non-interacting) pairs of molecules are sinusoidal and differed only in the phase of the sine functions, the difference being phase shifts η_l. The expression for phase shift may be written from equation (1) as

$$\sin \eta_l = \left(\frac{\pi}{2J^*}\right)^{\frac{1}{2}} \int_0^\infty K^{*\frac{1}{2}} J_{l+\frac{1}{2}}(J^*K^*) \times \frac{16\pi^2}{J^{*2}\Delta^{*2}} (K^{*-12} - K^{*-6}) \left(\frac{2}{\pi K^* \cdot J^*}\right)^{\frac{1}{2}} [\sin(K^*J^*) \times \sum_{n=0}^{n\leq\frac{l}{2}} \frac{(-1)^n (l+2n)!}{(2n)!\,(1-2n)!\,(2K^*J^*)^{2n}} \sin\left(J^*K^* - \frac{l\pi}{2} + \eta_l\right) dK^* \qquad (3)$$

$$I = \frac{16\pi^{\frac{5}{2}}}{J^{*\frac{3}{2}}\Delta^{*2}\sqrt{2}} \int_0^\infty K^{*\frac{1}{2}} J_{1+\frac{1}{2}}(J^*K^*) \left[\frac{1}{K^{*12}} - \frac{1}{K^{*6}}\right] \times \left[\sin\ \left(J^*K^* - \frac{l\pi}{2}\right) \cot\ \eta_l + \cos\ \left(J^*K^* - \frac{l\pi}{2}\right)\right] \mathrm{d}K^* \qquad (4)$$

The phase shift depends upon the angular momentum quantum numbers *l*. It is in general not possible to give an exact expression for the phases. The expression (3) has been given by N.F. Mott. This expression has been applied by Helium to calculate η_l, which gives very satisfactory results.

$$\cot\ \eta_l = \frac{1 - \frac{16\pi^{\frac{5}{2}}}{J^{\frac{3}{2}}\Delta^{*2}\sqrt{2}} \int_0^\infty K^{*\frac{1}{2}} J_{1+\frac{1}{2}}(J^*K^*) \left[\frac{1}{K^{*12}} - \frac{1}{K^{*6}}\right] \times \cos\ \left(J^*K^* - \frac{l\pi}{2}\right) dK^*}{\frac{16\pi^{\frac{5}{2}}}{J^{*\frac{3}{2}}\Delta^{*2}\sqrt{2}} \int_0^\infty K^{*\frac{1}{2}} J_{1+\frac{1}{2}}(J^*K^*) \left[\frac{1}{K^{*12}} - \frac{1}{K^{*6}}\right] \times \sin\left(J^*K^* - \frac{l\pi}{2}\right) dK^*} \qquad (5)$$

$$\eta_l = \tan^{-1} \frac{\frac{16\pi^{\frac{5}{2}}}{J^{*\frac{3}{2}}\Delta^{*2}\sqrt{2}} \int_0^\infty K^{*\frac{1}{2}} J_{1+\frac{1}{2}}(J^*K^*) \left[\frac{1}{K^{*12}} - \frac{1}{K^{*6}}\right] \times \sin\left(J^*K^* - \frac{l\pi}{2}\right) dK^*}{1 - \frac{16\pi^{\frac{5}{2}}}{J^{\frac{3}{2}}\Delta^{*2}\sqrt{2}} \int_0^\infty K^{*\frac{1}{2}} J_{1+\frac{1}{2}}(J^*K^*) \left[\frac{1}{K^{\cdot 12}} - \frac{1}{K^{*6}}\right] \times \cos\left(J^*K^* - \frac{l\pi}{2}\right) dK^*} \tag{6}$$

where $J_{l+\frac{1}{2}}$ is a Bessel's function given by the expression

$$J_{l+\frac{1}{2}}(K^*J^*) = \left(\frac{2}{\pi K^* \cdot J^*}\right)^{\frac{1}{2}} \left[\sin\left(K^*J^* - \frac{l\pi}{2}\right) \times \sum_{n=0}^{n \le \frac{l}{2}} \frac{(-1)^n (l+2n)!}{(2n)!\,(l-2n)!\,(2K^* \cdot J^*)^{2n}} + \right.$$

$$\left. \cos(K^*J^*) \times \sum_{n=0}^{n \le \frac{l}{2}} \frac{(-1)^n (l+1+2n)!}{(2n+1)!\,(l-2n-1)!\,(2K^*J^*)^{2n+1}} \right] \tag{7}$$

In particular, we have for $l = 3$, the value of $J_{l+\frac{1}{2}}$

$$J_{3+\frac{1}{2}}(K^*J^*) = \left(\frac{2}{\pi K^*J^*}\right)^{\frac{1}{2}} \left[\sin\left(K^*J^* - \frac{3\pi}{2}\right) \times \right.$$

$$\left. \left(1 - \frac{15}{K^{*2}J^{*2}}\right) + \cos\left(K^*J^* - \frac{3\pi}{2}\right) \times \left[\frac{6}{K^*J^*} - \frac{15}{K^{*3}J^{*3}}\right] \right.$$

(8)

Phase shifts have been calculated for He^3 and for He^4 from computer. Since He^4 has an even number of nucleons and electrons and zero spin, phase shifts with even l (l = 0, 2, 4) have been calculated. For He^3, which has an odd number of nucleons and electrons and spin $\frac{1}{2}$ ħ, phase shifts with both for odd (l = 0,1,3,5..) and even l have been calculated. The phase shifts have been calculated for a series of values of J^* from 1 to 2.5. The interval of 0.1 has been taken. The calculated values of phase shifts have been given in Table 4 for He^4 and in Table 5 for He^3.

2 The cross section for HCB fluids

Since the gas we are considering is composed of impenetrable elastic molecules, a collision between two molecules is well defined. This makes it possible to introduce a quantity known as the mean free path. The mean free path is given by the relation.$\frac{KT}{p\zeta'\pi\sigma^2}$It should be noted that at constant pressure the mean free path is directly proportional to the temperature. Where $\zeta' = \frac{1}{3} + 2\frac{\sqrt{2}}{3}$and the quantity $\pi\sigma^2$which appears in the denominator of the expression for the mean free path is the collision cross section for rigid spherical molecule. In classical theory cross section $Q(g)$ is expressed as an integral of the deflections, caused by collision of a pair of atoms integrated over the collision parameter at a fixed value of the relative velocity g. The total collision probability per unit time in terms of deflection angle and g converges (so that there is a finite probability of collision), when volume tends to zero as $r \rightarrow \infty$. Thus when the field satisfies this condition there is a natural definition of a free path in quantum theory.

In quantum theory it has been shown by Massey and Mohr that the cross section for viscosity $Q(J*)$ can be expressed entirely in the phases ηlcharacterizing the asymptotic behaviours of the wave function of relative motion of two atoms. The formula given by Massey and Mohr is

$$\mathrm{Q(J^*)} = \frac{8\pi}{J^{*2}} \times$$

$$\sum_{l=0,1\ldots}\left[\frac{2l^2 - 3l^2 - l - 1}{(2l-1)(2l-3)}\sin^2\,\eta_l - \frac{(l+2)(l+1)}{(2l-3)}\cos\,(\eta_l - \eta_{l+2})\sin\,\eta_l \sin\,\eta_{(l+2)}\right] \tag{9}$$

Kramer's has shown that this formula can further be simplified to

$$Q(J^*) = \frac{8\pi}{J^{*2}}\sum_{l=0,1,2}\frac{(l+1)(l+2)}{2(2l+3)}\sin^2(\eta_{l+2} - \eta_l) \tag{10}$$

The sum $\sum$ being over even or odd values of l , that is for the corresponding expressions for Bose-Einstein and Fermi-Dirac statistics, respectively. This formula is easier to use from a computational standpoint and living out nicely the analogy with the classical formula. At high temperatures where the deviations from classical theory are negligible the quantum mechanical expression approaches the classical expression in accordance with the correspondence,

$$l = \frac{bg\mu}{\hbar} = bK$$

and

$$[\eta_{l+2}(K) - \eta_l(K)] \to \psi(b,g) \qquad (11)$$

where b is the collision parameter and $\psi(b,g)$the angle of deflection. It is necessary however to take into account the influence of the statistics, if He^3had no nuclear spin Fermi-Dirac statistics should have been applied and consequently the summation in equation (10) should have been replaced by twice this sum over the odd values of l only. As He^3has a spin $\frac{1}{2}\hbar$, however, one has to take a 3: 1 mixture of cross section according to Fermi-Dirac statistics and Bose- Einstein statistics respectively. Thus the effective molecular cross sections for all types of encounter in He^3 is

$$Q(J^*) = \frac{3}{4}Q(J^*)_{F.D} + \frac{1}{4}Q(J^*)_{B.E} \qquad (12)$$

$$Q(J^*)_{F.D} = \frac{8\pi}{J^{*2}} \sum_{l=\text{ odd}} \frac{(l+1)(l+2)}{2(2l+3)} \sin^2(\eta_{l+2} - \eta_l) \qquad (13)$$

$$Q(J^*)_{B.E} = \frac{8\pi}{J^{*2}} \sum_{l=\text{ even}} \frac{(l+1)(l+2)}{2(2l+3)} \sin^2(\eta_{l+2} - \eta_l) \qquad (14)$$

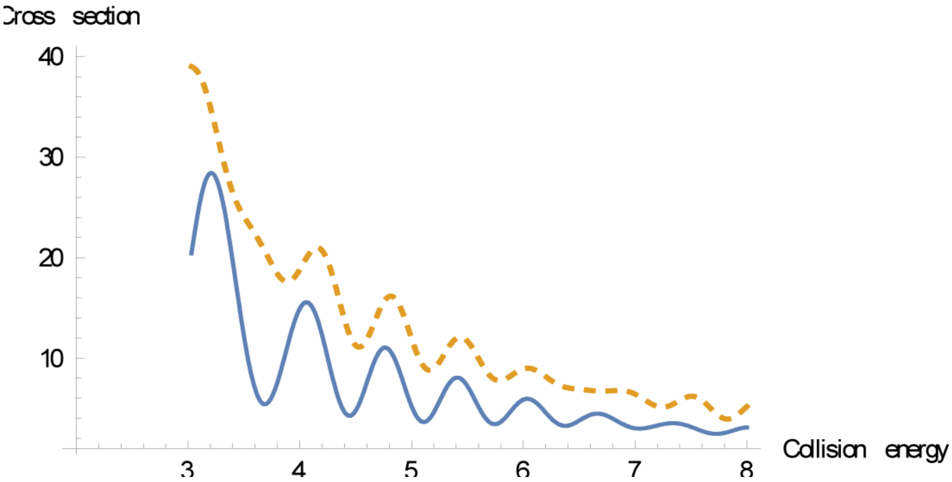


Figure 1

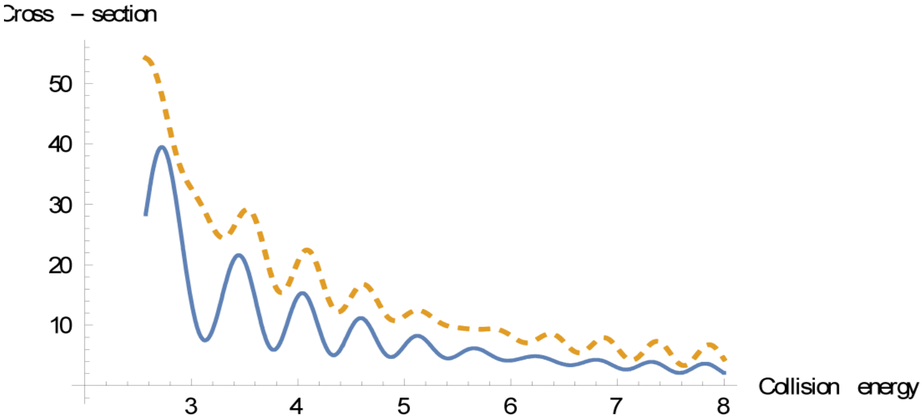


Figure 2

The two identical molecules lose their identity at an encounter. So, one has to consider the mutual encounter of two sets of similar, but distinguishable molecules. So the summation in equation (10) should be doubled. Since He^3 consists of Bose−Einsteins molecules without nuclear spin, the sum is taken over even values of l. The effective cross section for $He^4$is given by the expression (14) only. For $\frac{a}{b} = 2$, the calculated values of cross sections from equation (12) and (14) for helium molecules given in Table 6. The graphs for cross sections of helium illustrate the diffraction effects encountered in transport phenomena are shown in Figure 1,2 respectively.

Chapter VI

1 Calculation of viscosity of helium

The general expression for the coefficient of viscosity valid in quantum theory is in the notation of Chapmann and Cowling

$$\mu_i = \frac{5kT}{8\Omega_1^2(T)} \tag{1}$$

where the integral $\Omega^2{}_1$ is defined according to Chapman and Cowling as

$$\Omega_1^2 = \left[\frac{1}{2}\pi^{-\frac{1}{2}}\right]\left(\frac{\mu}{2kT}\right)^{\frac{7}{2}} \int \frac{-\hbar^2 J^* 2}{e^{2\mu K h^2(x) T}} \frac{\hbar^8 J^{*7}}{h^8(x)\mu^8} (QJ^*) h^2(x) dJ^* \tag{2}$$

where $Q(J*)$ is the cross section for viscosity and μ is the reduced mass. The unimportant correction facto of the second approximation an the density dependent correction terms which appear in quantum theory according to Uehling and Uhlenbeck are omitted because the detailed calculation by J.de Boer and Bird show that for other gases other than hydrogen and helium the correction do not in general exceed the experimental errors. Even for hydrogen and helium the correction to the viscosity do not exceed 0.6 percent for helium above200^0K.The value of coefficient of viscosity for helium have been calculated for major and minor is ratio $\frac{a}{b} = 2$ at temperature below 5K for temperature interval 0.2. These theoretical viscosities are given in Table 7, 8. These theoretical viscosities of He^4at very low temperature are compared with the available experimental data and calculated viscosities by Keller which is given in Table 7 for hard sphere model. The agreement with experiment and Keller viscosities for $He^4$is remarkably good. The theoretical viscosities of He^3 are compared with Keller and J. DeBoer results, Table 8 also presents viscosities of He^4 which is also for the hard-sphere model. The agreement for $He^3$is also remarkably good. The viscosity of He^3 actually exceeds that of He^4at very low temperatures. These values have been plotted in Figure 3 and 4.

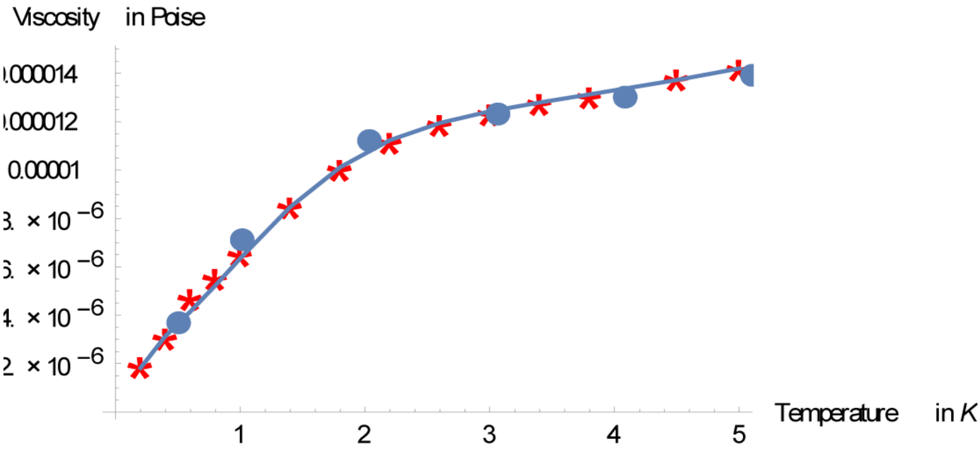


Figure 3

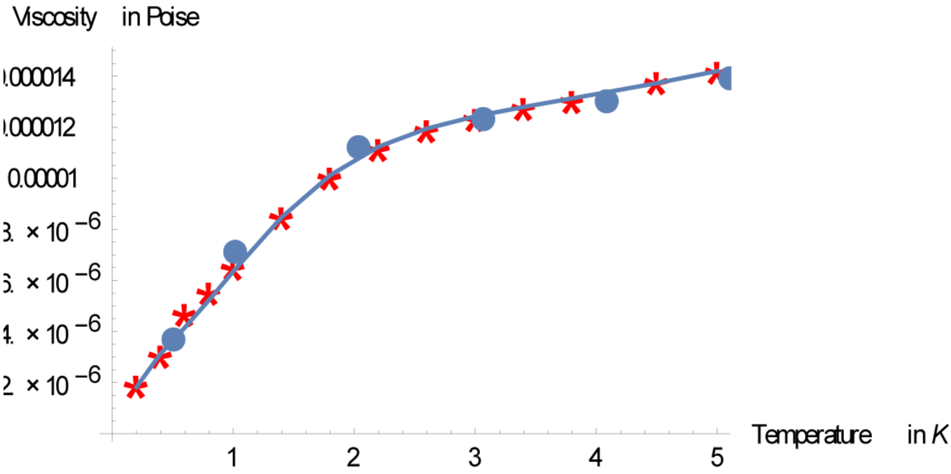


Figure 4

Conclusions

The theoretical values of the viscosities of He^4 and He^3 are based on the intermolecular potential $\Phi(K)$ for HCB'S model using values of the constant parameters a, b and E for ratio $\frac{a}{b} = 2$. So, we may safely conclude that the parameters for the potential best fit experimental values of the second virial coefficient of helium for the hard convex fluid. Thus, the proposed potential for HCB'S in term of support function simplifies the determination of constant parameters of the HCB'S model. Thus, this theoretical work supporting the concept that the HCB model would prove to be as valuable as hard sphere model as a reference fluid for real fluids.

It is clearly even more difficult to make predictions about the future developments in this area. However, it seems clear that certain works have received much more attention in the past than others. In particular, a vast amount of work has been reported on equations of state of pure HCB'S in the isotropic phase. It would be interesting to work with mixtures of non-spherical hard bodies because a less of it is known to us.

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TABLE-1

Constant Parameters of He^4 at ratio a/b = 2

$Y = kT/4E$	Major axis (a) in c.m.		Minor axis (b) in c.m.		$\Delta^* b$	E (In erg)
	Classical	Quantum	Classical	Quantum		
1.749	2.828×10^{-8}	2.729×10^{-8}	1.414×10^{-8}	1.396×10^{-8}	4.921	1.414×10^{-15}

TABLE- 2

THEORETICAL DATA

CLASSICAL VALUES		QUANTUM VALUES		CLASSICAL VALUES		QUANTUM VALUES	
Y	**SECOND VIRIAL CO-EFFICIENT**	**Y**	**SECOND VIRIAL CO-EFFICIENT**	**Y**	**SECOND VIRIAL CO-EFFICIENT**	**Y**	**SECOND VIRIAL CO-EFFICIENT**
0.05	-1206000	0.05	784	0.875	9.679	0.875	7.83
0.075	-59420	0.075	184.354	0.9	9.77	0.9	7.96
0.1	-10000	0.1	84.89	0.925	9.851	0.925	8.081
0.125	-2909	0.125	49.788	0.925	9.851	0.925	8.081
0.15	-1139	0.15	32.646	0.95	9.922	0.95	8.195
0.175	-535.794	0.175	22.667	0.975	9.986	0.975	8.301
0.2	-284.2	0.2	16.191	1	10.044	1	8.401
0.225	-163.657	0.225	11.671	1.025	10.095	1.025	8.496
0.25	-99.716	0.25	8.348	1.05	10.142	1.05	8.585
0.275	-63.065	0.275	5.806	1.15	10.288	1.15	8.893
0.3	-40.735	0.3	3.804	1.175	10.316	1.175	8.961
0.325	-26.443	0.325	2.187	1.2	10.342	1.2	9.024
0.35	-16.918	0.35	0.857	1.225	10.66	1.225	9.085
0.375	-10.35	0.375	0.256	1.25	10.389	1.25	9.142
0.4	-5.687	0.4	1.2	1.275	10.409	1.275	9.197

0.425	-2.295	0.425	2.01	1.3	10.427	1.3	9.249
0.45	-0.228	0.45	2.712	1.325	10.445	1.325	9.298
0.475	-2.41	0.475	3.326	1.35	10.46	1.35	9.345
0.5	-3.616	0.5	3.867	1.375	10.475	1.375	9.39
0.525	-4.77	0.525	4.346	1.4	10.488	1.4	9.433
0.55	5.686	0.55	4.774	1.425	10.501	1.425	9.474
0.575	6.422	0.575	5.158	1.45	10.513	1.45	9.513
0.6	7.02	0.6	5.505	1.475	10.523	1.475	9.551
0.625	7.51	0.625	5.818	1.5	10.533	1.5	9.586
0.65	7.917	0.65	6.104	1.525	10.542	1.525	9.621
0.675	8.256	0.675	6.364	1.55	10.551	1.55	9.653
0.7	8.542	0.7	6.602	1.8	10.608	1.8	9.916
0.725	8.785	0.725	6.821	2.05	10.32	2.05	10.092
0.75	8.992	0.75	7.023	2.3	10.639	2.3	10.213
0.775	9.171	0.775	7.209	2.55	10.634	2.55	10.298
0.8	9.325	0.8	7.382	2.8	10.623	2.8	10.357
0.825	9.459	0.825	7.542	3.05	10.607	3.05	10.397
0.85	9.76	0.85	7.691	3.3	10.588	3.3	10.424
CLASSICAL VALUES		**QUANTUM VALUES**		**CLASSICAL VALUES**		**QUANTUM VALUES**	

Y		**SECOND VIRIAL CO-EFFICIENT**		**Y**		**SECOND VIRIAL CO-EFFICIENT**	
3.8	10.544	3.8	10.45	11.5	9.893	11.5	10.01
4.05	10.521	4.05	10.453	11.6	9.886	11.6	10.004
4.3	10.497	4.3	10.452	11.7	9.88	11.7	9.998
4.55	10.472	4.55	10.447	11.8	9.873	11.8	9.991
4.8	10.448	4.8	10.439	11.9	9.867	11.9	9.985
5.05	10.424	5.05	10.43	12	9.86	12	9.979
5.3	10.399	5.3	10.418	12.1	9.854	12.1	9.973
5.55	10.375	5.55	10.405	12.2	9.847	12.2	9.967
5.8	10.51	5.8	10.391	12.3	9.841	12.3	9.961
6.05	10.327	6.05	10.376	12.4	9.835	12.4	9.955
6.3	10.304	6.3	10.36	12.5	9.828	12.5	9.949
6.55	10.281	6.55	10.344	12.6	9.822	12.6	9.943
6.8	10.258	6.8	10.327	12.7	9.816	12.7	9.937
7.05	10.236	7.05	10.31	12.8	9.81	12.8	9.931
7.3	10.214	7.3	10.293	12.9	9.803	12.9	9.925
7.55	10.192	7.55	10.276	13	9.797	13	9.919
7.8	10.171	7.8	10.259	13.175	9.787	13.175	9.908
8.05	10.15	8.05	10.241	13.325	9.778	13.325	9.9
8.3	10.129	8.3	10.224	13.425	9.772	13.425	9.894
8.55	10.109	8.55	10.206	13.525	9.766	13.525	9.888

8.8	10.089	8.8	10.189	13.55	9.764	1.355	9.887
9.05	10.069	9.05	10.172	13.575	9.763	13.575	9.885
9.3	10.05	9.3	10.155	13.6	9.761	13.6	9.884
9.55	10.31	9.55	10.155	13.625	9.76	13.625	9.882
9.8	10.012	9.8	10.121	13.65	9.758	13.65	9.881
9.9	10.012	9.9	10.121	13.675	9.757	13.675	9.88
10	9.998	10	10.108	13.7	9.755	13.7	9.878
10.2	9.983	10.2	10.094	13.725	9.754	13.725	9.877
10.4	9.969	10.4	10.081	13.775	9.751	13.775	9.874
10.55	9.958	10.55	10.071	13.8	9.75	13.8	9.872
10.6	9.955	10.6	10.068	13.825	9.748	13.825	9.871
10.8	9.941	10.8	10.055	13.85	9.747	13.85	9.887
10.9	9.934	10.9	10.048	13.875	9.745	13.875	9.868
11	9.927	11	10.042	13.9	9.744	13.9	9.867
11.2	9.913	11.2	10.029	13.925	9.742	13.925	9.865
11.3	9.906	11.3	10.023	13.975	9.739	13.975	9.863
11.4	9.9	11.4	10.016	14.00	9.738	14.00	9.861

TABLE -3

EXPERIMENTAL DATA

KILPATRIC AND KELLER		FLOWER AND GUGGENHEIM	
Y	**SECOND VIRIAL COEFFICIENT**	**Y**	**SECOND VIRIAL COEFFICIENT**
0.02445	-428.9	1.748209	10.2592
0.048901	-177.39	2.198582	10.7744
0.073351	-110.13	2.200543	10.5952
0.097802	-78.11	3.092985	12.3872
0.122252	-59.14	4.149246	13.1936
0.146703	-46.53	6.67498	11.6704
0.171153	-37.53	7.897504	11.7152
0.220054	-25.53	9.120027	11.424
0.293406	-15.04	11.56507	11.0432
0.391208	-7.2	14.01012	10.5056
0.415658	-5.82		
0.440109	-4.6		
0.464559	-3.51		
0.48901	-2.531		
0.51346	-1.651		
0.53791	-0.851		
0.562361	-0.12		

0.586811	0.54		
0.611262	1.15		
0.635712	1.71		
0.660163	2.23		
0.684613	2.71		
0.709064	3.15		
0.733514	3.57		
0.855767	5.25		
0.978019	6.49		
1.100271	7.43		
1.222524	8.16		
1.344776	8.74		
1.467029	9.2		

TABLE-4

Phase shift of He^4

J^*	$Tan^{-1}\eta$ $l = 0$	$Tan^{-1}\eta$ $l = 2$	$Tan^{-1}\eta$ $l = 4$	$Tan^{-1}\eta$ $l = 6$
1	0.038+1.5	-0.924+1.5711	-0.034	-0.065
1.1	0.032-1.5	-0.746+1.5711	-7.004.10^{-3}	-0.072
1.2	0.026+1.5	-0.816+1.5711	-0.171	-0.079
1.3	0.013-1.5	-0.569+1.5711	-0.352	-0.085
1.4	0.045-1.5	-0.542+1.5711	-0.32	-0.092
1.5	2.399 10^{-3}-1.5	-0.543+1.5711	-0.495	-0.098
1.6	0.057-1.5	-0.402+1.5711	-0.67	-0.105
1.7	0.058-1.5	-0.417+1.5711	-0.635	-0.112
1.8	0.042-1.5	-0.382+1.5711	-0.927	-0.118
1.9	0.095-1.5	-0.294+1.5711	-1.158	-0.125
2	0.078-1.5	-0.228+1.5711	-1.145	-0.132
2.1	0.088-1.5	-0.263+1.5711	-2.358+1.5711	-0.138
2.2	0.13-1.5	-0.212+1.5711	-1.675+1.5711	-0.155
2.3	0.108-1.5	-0.229+1.5711	-1.471+1.5711	-0.132
2.4	0.138-1.5	-0.166+1.5711	-0.942+1.5711	-0.159
2.5	0.164-1.5	-0.142+1.5711	-0.922+1.5711	-0.165

TABLE-5

Phase shift of He^3

J^*	$Tan^{-1}\eta$ $l = 0$	$Tan^{-1}\eta$ $l = 3$	$Tan^{-1}\eta$ $l = 0$	$Tan^{-1}\eta$ $l = 5$	$Tan^{-1}\eta$ $l = 2$	$Tan^{-1}\eta$ $l = 4$	$Tan^{-1}\eta$ $l = 6$
1	-0.171	-0.895+1.5	-0.4	0.01	-0.36	-1.9+1.5	-0.065
1.1	-0.14	-0.757+1.5	-0.5	$2.08.10^{-2}$	-0.339+1.5	-2.1+105	-0.072
1.2	-0.10	-0.614+1.5	-0.6	$8.825.10^{-2}$	-0.336+1.5	-1.842+1.5	-0.079
1.3	-0.09	-0.539+1.5	-0.9	$3.779.10^{-2}$	-0.307+1.5	-1.422+1.5	-0.036
1.4	-0.10	-0.518+1.5	-1.0	0.02	-0.258+1.5	-1.062+1.5	-0.092
1.5	-0.09	-0.495+1.5	-1.2	0.03	-0.226+1.5	-0.85+1.5	-0.098
1.6	-0.07	-0.44+1.5	-1.6	0.02	-0.219+1.5	-0.767+1.5	-0.003
1.7	-0.06	-0.382+1.5	-1.776+1.5	0.02	-0.216+1.5	-0.732+1.5	-0.112
1.8	-0.04	-0.353+1.5	-1.258+1.5	0.03	-0.193+1.5	-0.674+1.5	-0.118
1.9	-0.04	-0.343+1.5	-1.123+1.5	0.05	-0.16+1.5	-0.588+1.5	-0.125
2	-0.03	-0.325+1.5	-1.034+1.5	0.06	-0.14+1.5	-0.522+1.5	-0.132
2.1	-0.01	-0.289+1.5	-0.899+1.5	0.0	-0.135+1.5	-0.429+1.5	-0.138
2.2	1.419	-0.253+1.5	-0.767+1.5	0.06	-0.129+1.5	-0.474+1.5	-0.145

2.3	5.753.10^{-3}	-0.235+1.5	-0.69+1.5	0.70	-0.109+1.5	-0.437+1.5	-0.152
2.4	6.574.10^{-3}	-0.227+1.5	-0.656+1.5	.09	-0.083+1.5	-0.387+1.5	-0.159
2.5	.01	-0.618+1.5	-0.618+1.5	.10	-0.068+1.5	-0.35+1.5	-0.165

TABLE-6

J**	Cross-sections of He^{3}	***J****	Cross-section of He^{4}
1	46.919	1	41.127
1.1	38.609	1.1	18.51
1.2	33.029	1.2	32.183
1.3	25.27	1.3	22.768
1.4	21.151	1.4	19.071
1.5	18.31	1.5	18.67
1.6	15.907	1.6	18.902
1.7	13.646	1.7	16.236
1.8	11.761	1.8	15.821
1.9	10.388	1.9	15.236
2	9.327	2	13.455
2.1	8.347	2.1	13.13
2.2	5.15	2.2	12.346
2.3	4.651	2.3	11.2
2.4	4.258	2.4	10.909
2.5	3.925	2.5	10.15

TABLE–7

TEMPERATURE in °K	THEORETICAL VISCOSITY OF He^3 (IN POISE)	CALCULATED VISCOSITY OF He^3 BY KELLER (IN POISE)	TEMPERATURE °K	OBSERVRED VISCOSITY OF He^3 (IN POISE)
.2	1.684×10^{-6}	$.343 \times 10^{-6}$	1.29	3.4×10^{-6}
.4	2.381×10^{-6}	1.701×10^{-6}	2.68	4.6×10^{-6}
.6	2.916×10^{-6}	3.001×10^{-6}	4.20	5.7×10^{-6}
.8	3.367×10^{-6}	3.528×10^{-6}		7.4×10^{-6}
1	3.765×10^{-6}	3.624×10^{-6}		8.6×10^{-6}
1.4	4.455×10^{-6}	3.825×10^{-6}		10.78×10^{-6}
1.8	5.059×10^{-6}	4.459×10^{-6}		
2.2	5.631×10^{-6}	5.338×10^{-6}		
2.6	6.233×10^{-6}	6.382×10^{-6}		
3	6.918×10^{-6}	7.507×10^{-6}		
3.4	7.725×10^{-6}	8.648×10^{-6}		
3.8	8.685×10^{-6}	9.771×10^{-6}		
4.5	10.8×10^{-6}	11.636×10^{-6}		
5	12.71×10^{-6}	12.869×10^{-6}		

TABLE–8

TEMPERATURE °K	THEORETICAL VISCOSITY OF He^4 (IN POISE)	CALCULATED VISCOSITY OF He^4 BY KELLER (IN POISE)	TEMPERATURE °K	CALCULATED VISCOSITY OF He^4 By Je. De. Boer (IN POISE)
.2	2.662×10^{-6}	1.823×10^{-6}	.51	3.77×10^{-6}
.4	3.764×10^{-6}	3.139×10^{-6}	1.02	7.20×10^{-6}
.6	4.61×10^{-6}	4.162×10^{-6}	2.04	11.3×10^{-6}
.8	5.323×10^{-6}	5.234×10^{-6}	3.07	12.4×10^{-6}
1	5.951×10^{-6}	6.355×10^{-6}	4.09	13.1×10^{-6}
1.4	7.042×10^{-6}	8.475×10^{-6}	5.11	14.0×10^{-6}
1.8	7.958×10^{-6}	10.121×10^{-6}		
2.2	8.828×10^{-6}	11.236×10^{-6}		
2.6	9.6×10^{-6}	11.950×10^{-6}		
3	10.33×10^{-6}	12.429×10^{-6}		
3.4	11.03×10^{-6}	12.796×10^{-6}		
3.8	11.75×10^{-6}	13.128×10^{-6}		
4.5	13.11×10^{-6}	13.729×10^{-6}		
5	14.22×10^{-6}	14.204×10^{-6}		