THE CALCULATION OF THE SECOND VIRIAL COEFFICIENT
FOR DIPOLAR AND QUADRUPOLEAR POLYATOMIC GASES

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The calculation of the second virial coefficient
for dipolar and quadrupolar polyatomic gases^{*}

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The classical statistical mechanical development of the equation of state for polyatomic gases is reviewed and a historical background of work of interest to the present study is given. Equations for the second virial coefficient for dipolar and quadrupolar gases are derived from an assumed model of interaction. The model consists of two rigid cores interacting via a soft potential which is a sum of valence repulsion, dispersion and electrostatic interaction potentials and which is parameterized by the shortest distance between the hard cores. This parameterization is accomplished by expanding the electrostatic potential about multipole centers which "float" on the surfaces of the hard cores, and by assuming the valence repulsion and dispersion potentials to be of a Kihara type.

Model parameters for this potential are given for CO, N₂O, HCl, propyne, SO₂, H₂O, H₂S, fluorobenzene, pyridine, CH₃F, CH₃Cl, CF₃Cl, CCl₃H, CCl₃F and CO₂. A comparison of the present work is made to that of several other investigators.

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CHAPTER I. INTRODUCTION

The first equation of state of gases developed was, of course, the ideal gas equation. It adequately describes real gases at low density and at high temperatures. From a statistical viewpoint it is derived by assuming noninteraction between molecules. However, at moderate or high density and low temperatures all real gases deviate significantly from the ideal gas equation due to molecular interactions, and thus deviation from ideality provides information concerning these interactions.

The modern study of the equation of state for fluids dates back to the pioneering work of van der Waals. He proposed the equation of state

$$\left(P + \frac{an^2}{V^2}\right)\left(\frac{V}{n} - b\right) = RT \quad (1.1)$$

on the basis of physical arguments which utilized the concept of molecules and molecular forces. In Equation (1.1) P is the pressure, V is volume, n is the number of moles, T is the temperature, and R is the gas constant. Here " a " accounts for the attractive forces between molecules in the gas, and " b " accounts for the fact that the molecules have volume (i.e., that molecules interact via short range repulsive forces). If the constants a and b are both set to zero, then the ideal gas law is, of course, regained.

By making a density expansion it can be simply shown how a and b relate to the second virial coefficient. Thus we find that

$$P = \frac{nRT}{V} \left(1 + \frac{n}{V} \left(b - \frac{a}{RT}\right) + \cdots\right) \quad (1.2)$$

The volume of the molecule represented by b changes very little with temperature, however a/RT , the attractive force term, is much greater at lower temperatures than at higher temperatures. Thus one might expect the second virial coefficient, $B(T)$, to be negative at low temperatures and positive at high temperatures. This is the case as can be seen for N_2 in Figure 1. Thus we see qualitatively from van der Waal's equation that $B(T)$ is intimately related to the intermolecular forces. The goal of our work is to better quantify the relationship between $B(T)$ and intermolecular forces.

In Chapter II a well-known solution is given to what is known as the direct problem. That is, an explicit expression for the virial equation of state is derived from which $B(T)$ (and higher virial coefficients) can be determined if the molecular interaction model is specified. The indirect problem, the converse of the direct problem, poses the question: Given a macroscopic thermodynamic property as a function of temperature (in our case $B(T)$), to what extent is the intermolecular potential determined? Since it would be very useful to deduce the law of force from $B(T)$, the indirect problem is of some interest. It has been shown by Keller and Zumino (1) that a monotonic, central potential (i.e., one which is everywhere repulsive or everywhere attractive and is only a function of the distance between molecular centers) is uniquely determined by the second virial coefficient. However, for a realistic potential, which is not monotonic, the interaction law cannot be uniquely determined from $B(T)$. A brief discussion of their proof is given in Appendix A.

In Chapter III we discuss the work of previous investigators who have

theoretically calculated $B(T)$ for various models. In Chapter IV the concept of effective intermolecular distance is carefully discussed, and a form for the intermolecular potential is derived. We develop an expression for the second virial coefficient in Chapter V with the use of results from Chapters II and IV. The experimental techniques for determining the dipole and quadrupole moments, and $B(T)$ are outlined in Chapter VI. We present in Chapter VII the numerical results of the equations derived in Chapter V. Finally, Chapter VIII gives some of the conclusions which have been reached as a result of our work.

Figure 1. Comparison of vander Waal's $B(T)$ to the experimental $B(T)$ for N_2 . T is in $^{\circ}\text{K}$ and $B(T)$ is in cm^3/mole

CHAPTER II. THE VIRIAL EQUATION OF STATE

The equation of state of a fluid is intimately related to the forces between its constituent molecules. The statistical mechanical theory which relates bulk fluid properties to the intermolecular forces is highly developed for dilute gases. Once the law of force is given (or assumed), it is possible to calculate the partition function, Z_N , and hence the equation of state

$$P = P(V/n, T) \quad (2.1)$$

and all other thermodynamic properties.

It is well known from statistical mechanics that the equation of state can be expressed in terms of the partition function, Z_N , as follows:

$$P = kT \left(\frac{\partial \ln Z_N}{\partial V} \right)_T \quad (2.2)$$

where

$$Z_N = \sum_i e^{-\beta E_i} \quad (2.3)$$

Here E_i is the energy of the i^{th} quantum state of a N particle system, and k is Boltzmann's constant. At low and moderate densities, Equation (2.2) can be converted to the virial expansion

$$\frac{PV}{nRT} = 1 + \frac{n}{V} B(T) + \left(\frac{n}{V}\right)^2 C(T) + \left(\frac{n}{V}\right)^3 D(T) + \dots \quad (2.4)$$

The coefficients $B(T)$, $C(T)$, $D(T)$, ... are called, respectively, the second, third, fourth, etc. virial coefficients. In this chapter we develop the full virial expansion by use of a standard technique. (To obtain only an

expression for $B(T)$ the complete argument is not really necessary.)

By means of Equation (2.2) the virial coefficients can be expressed in terms of the intermolecular potential functions. The expression for Z_N in Equation (2.3) is of quantum mechanical origin. However, we chose to use the classical statistical treatment instead of the quantum mechanical one because it is simpler and because quantum mechanical effects at the temperatures and densities which we consider are negligible. In general quantum mechanical effects are only significant when the thermal de Broglie wavelength of the molecules is of the order of magnitude of the average distance between the molecules in the gas. For example at $T = 273^\circ\text{K}$ the thermal de Broglie wavelength for N_2 is $0.094 \text{ \AA}$ which is much smaller than the average molecular separation of $33.3 \text{ \AA}$ at STP.

The classical partition function for a system of N identical molecules is

$$Z_N = \frac{1}{N! h^{6N}} \int \cdots \int e^{-H(\mathbf{q}^N, \mathbf{p}^N)/kT} d\mathbf{p}^N d\mathbf{q}^N \quad (2.5)$$

where $H(\mathbf{q}^N, \mathbf{p}^N)$ is the classical Hamiltonian of the N particle system, and where h is Planck's constant. Here $\mathbf{q}^N$ represents the set of position coordinates of the system and $\mathbf{p}^N$ is the corresponding set of conjugate momenta. We consider a system of N molecules which have only translational and rotational degrees of freedom since excited electronic and vibrational energy states are not likely to be populated at the temperatures of interest. The Hamiltonian, $H(\mathbf{q}^N, \mathbf{p}^N)$, for a gas composed of N nonlinear rigid tops each with mass, m , and principal moments of inertia, I_a , I_b , I_c , is

$$\begin{aligned}
H(\mathbf{q}^N, \mathbf{p}^N) = & \sum_i \frac{1}{2m} p_i^2 + \sum_i \left(\frac{\sin^2 \Psi_i}{2I_a} \left\{ p_{\theta_i} - \frac{\cos \Psi_i}{\sin \theta_i \sin \Psi_i} (p_{\phi_i} - \cos \theta_i p_{\psi_i}) \right\}^2 \right. \\
& + \left. \frac{\cos^2 \Psi_i}{2I_b} \left\{ p_{\phi_i} + \frac{\sin \Psi_i}{\sin \theta_i \cos \Psi_i} (p_{\theta_i} - \cos \theta_i p_{\psi_i}) \right\}^2 + \frac{p_{\psi_i}^2}{2I_c} \right) \\
& + \Phi(\mathbf{q}^N)
\end{aligned}$$

(A different expression is required for linear molecules but the method of development is the same.) The symbol $\mathbf{q}$ represents the collection of six coordinates $x, y, z, \theta, \phi, \psi$ (where θ, ϕ, ψ are the usual Eulerian angles (2)) necessary to specify the location and orientation of a single molecule and $\mathbf{p}$ represents the six momenta, $p_x, p_y, p_z, p_\theta, p_\phi, p_\psi$, conjugate to the coordinates. Here $\Phi(\mathbf{q}^N)$ is the potential energy of the system. Integration over the momenta in Equation (2.5) leads to the expression

$$Z_N = \frac{1}{N! \lambda^N} \int \dots \int e^{-\Phi(\mathbf{q}^N)/kT} \prod_{i=1}^N (\sin \theta_i dx_i dy_i dz_i d\theta_i d\phi_i d\psi_i) = \frac{Q_N}{\lambda^N} \quad (2.6)$$

in which $\lambda = \lambda_x \lambda_y \lambda_z$ where

$$\lambda_x^2 = \frac{h^2}{2\pi m kT}$$

and

$$\lambda_\alpha^2 = \frac{h^2}{2\pi kT I_\alpha}$$

By defining the Boltzmann factor, $W_N(\mathbf{q}^N)$, as

$$W_N(\mathbf{q}^N) = e^{-\Phi(\mathbf{q}^N)/kT} \quad (2.7)$$

we see that

$$Q_N = \frac{1}{N!} \int \cdots \int W_N(\mathbf{q}^N) \prod_{i=1}^N (\sin \theta_i \, dx_i \, dy_i \, dz_i \, d\theta_i \, d\phi_i \, d\psi_i) \quad (2.8)$$

The following development of Q_N is due to Ursell (3), who expressed the Boltzmann factor, $W_N(\mathbf{q}^N)$, as

$$W_N(\mathbf{q}^N) = \sum_{(\sum l m_l = N)} \pi \, U_l(\mathbf{q}^{[l]}) \quad (2.9)$$

where the Ursell functions, U_l , are defined by this relation. Here $[l]$ represents a particular labelled set of l molecules. The sum is over all possible divisions of N molecules and the product is over all groups of a given division. For example,

$$W_1(\mathbf{q}_i) = U_1(\mathbf{q}_i) = 1,$$

$$W_2(\mathbf{q}_i, \mathbf{q}_j) = U_2(\mathbf{q}_i, \mathbf{q}_j) + U_1(\mathbf{q}_i) U_1(\mathbf{q}_j),$$

$$\begin{aligned} W_3(\mathbf{q}_i, \mathbf{q}_j, \mathbf{q}_k) = & U_3(\mathbf{q}_i, \mathbf{q}_j, \mathbf{q}_k) + U_2(\mathbf{q}_i, \mathbf{q}_j) U_1(\mathbf{q}_k) \\ & + U_2(\mathbf{q}_i, \mathbf{q}_k) U_1(\mathbf{q}_j) + U_2(\mathbf{q}_j, \mathbf{q}_k) U_1(\mathbf{q}_i) \\ & + U_1(\mathbf{q}_i) U_1(\mathbf{q}_j) U_1(\mathbf{q}_k), \end{aligned}$$

etc. By reverting the above relations, one can see that the U -functions are given in terms of various combinations of Boltzmann factors. For example,

$$\begin{aligned} U_1(\mathbf{q}_i) &= W_1(\mathbf{q}_i), \\ U_2(\mathbf{q}_i, \mathbf{q}_j) &= W_2(\mathbf{q}_i, \mathbf{q}_j) - W_1(\mathbf{q}_i) W_1(\mathbf{q}_j), \end{aligned} \quad (2.10)$$

$$\begin{aligned}
 u_3(q_i, q_j, q_k) = & \omega_3(q_i, q_j, q_k) - \omega_2(q_i, q_j) \omega_1(q_k) \\
 & - \omega_2(q_j, q_k) \omega_1(q_i) - \omega_2(q_k, q_i) \omega_1(q_j) \\
 & + 2 \omega_1(q_i) \omega_1(q_j) \omega_1(q_k),
 \end{aligned}$$

etc. It is apparent from the Equations (2.10) that the U-functions have the following very important property: The function $u_x(q_f^{(x)})$ approaches zero for a "separated" configuration in which the molecules in the set $\{l\}$ are divided into two or more groups which are separated from one another by a distance sufficiently great such that there is negligible interaction between the groups. This results from the fact that, if $\{N\}$ and $\{M\}$ represent two noninteracting groups, then

$$\phi_{N+M}(q_f^{(N+M)}) = \phi_N(q_f^{(N)}) + \phi_M(q_f^{(M)})$$

which yields

$$W_{N+M}(q_f^{(N+M)}) = W_N(q_f^{(N)}) W_M(q_f^{(M)})$$

from Equation (2.6).

The reason for employing these U-functions may be indicated by citing an example. For a dilute gas, where two-body collisions are relatively frequent but collisions involving three molecules are rare, the functions u_3 are of little importance and can be set to zero. All U-functions of higher order are even less important.

Having expressed the Boltzmann factor as a sum of products of U-functions, we now formally integrate the configurational integral, Equation (2.8). The result is

$$Q_N = \frac{1}{N!} \int W_N(\mathbf{q}^N) d\mathbf{q}^N = \sum_{(\sum l m_l = N)} \prod_{l=1}^N \frac{(V b_l)^{m_l}}{m_l!} \quad (2.11)$$

The factor $N! \prod_{l=1}^N \frac{1}{(m_l)! (l!)^{m_l}}$

gives the number of ways that the N molecules can be divided for a given set of numbers $\{m_l\}$ satisfying the requirement that $\sum_l l m_l = N$. The quantities, b_l , are known as cluster integrals and are defined by

$$b_l = \frac{1}{V l!} \int U_l(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_l) d\mathbf{q}_1 d\mathbf{q}_2 \dots d\mathbf{q}_l \quad (2.12)$$

The limits of integration are such that the molecules are confined to the container of volume, V . If the ratio V/l is considerably larger than the volume of a single molecule and if external forces are ignored, then the value of the integral over $l-1$ of the molecules is effectively independent of the position of the l^{th} molecule, since the integrand drops rapidly to zero when the molecules are not in a single cluster. The integral over the l^{th} molecule yields a factor of V , which cancels the volume in the denominator of Equation (2.12). Thus the cluster integrals for small l are very nearly independent of the volume.

The evaluation of the configurational integral given in Equation (2.11) can be completed by the method of "steepest descents" which was first applied to this problem by Born and Fuchs (4). For the application of this method the generating function

$$g(\mathcal{T}) = \exp\left(\sum_{l=1}^{\infty} V b_l \mathcal{T}^l\right)$$

is introduced. Here $\mathcal{T}$ is taken to be a complex variable. When this function

is expanded in a power series in $\mathcal{J}$, the coefficient of $\mathcal{J}^N$ is equal to Q_N . From this fact it is seen that the generating function, $g(\mathcal{J})$, is closely related to the grand canonical ensemble partition function with $\mathcal{J}$ playing the role of the absolute activity. After the generating function is multiplied by $\mathcal{J}^{-N-1}$, Cauchy's residue theorem may be used to obtain

$$Q_N = \frac{1}{2\pi i} \oint_C \mathcal{J}^{-N-1} e^{\sum V b_k \mathcal{J}^k} d\mathcal{J}, \quad (2.13)$$

which provides an integral expression for the configurational integral.

The contour C is taken to be a circle around the origin in the $\mathcal{J}$ -plane.

Now we introduce $\mathcal{J} = r \exp(i\phi)$ and $d\mathcal{J} = i r d\phi$ into Equation (2.13) to obtain

$$Q_N = \frac{1}{2\pi} \int_{-\pi}^{\pi} e^{\left\{ \sum V b_k (r e^{i\phi})^k - N i \phi - N \ln r \right\}} d\phi \quad (2.14)$$

The integrand has a minimum on the positive real axis (i.e., $\phi = 0$) for a value of $r = \omega$ given by

$$\frac{d}{dr} \left\{ r^{-N} e^{\sum V b_k r^k} \right\} = 0$$

that is

$$N = \sum V b_k \omega^k. \quad (2.15)$$

This minimum is extremely sharp since high powers of r occur in the integrand and just balance each other at $r = \omega$. According to the theory of complex variables the integrand (and hence its modulus) has a sharp maximum in a direction perpendicular to the positive real axis at $r = \omega$. That is, the point, $|\mathcal{J}| = \omega$, is a "saddle point."

The exponent of the integrand in Equation (2.14) may now be expanded in a power series in ϕ on the contour $|\gamma| = \omega$ yielding

$$\sum_l V b_l (\omega e^{i\phi})^l - N \ln(\omega e^{i\phi}) = \sum_l V b_l \omega^l - N \ln \omega - \frac{1}{2} \phi^2 \sum_l V l^2 b_l \omega^l + O(\phi^3).$$

Because of the steep maximum in the modulus a good approximation is obtained if the Taylor's series is truncated after the term in ϕ^2 . The integration domain of ϕ in Equation (2.14) can be extended with negligible error to go from $-\infty$ to ∞ , giving

$$Q_N = \frac{\exp(\sum_l V b_l \omega^l)}{2\pi \omega^N} \int_{-\infty}^{\infty} \exp\left(-\frac{1}{2} \phi^2 \sum_l V l^2 b_l \omega^l\right) d\phi$$

or finally

$$Q_N = \frac{\exp\left(\sum_{l=1}^{\infty} V b_l \omega^l\right)}{\omega^N \sqrt{2\pi \sum_l V l^2 b_l \omega^l}} \quad (2.16)$$

From Equations (2.6) and (2.16) the partition function, Z_N , is then given by

$$\ln Z_N = -N \ln \omega \lambda^3 + \sum_{l=1}^{\infty} V b_l \omega^l \quad (2.17)$$

In this equation the terms in $\ln Z_N$ resulting from the square root in the denominator of Equation (2.16) have been neglected. This may be done since both $\sum V b_l \omega^l$ and $\sum l^2 V b_l \omega^l$ are proportional to N whereas the neglected term contributes a term of order $\ln N$. Substituting $\ln Z_N$ into Equation (2.2) for P yields

$$PV = kT \sum_l V b_l \omega^l \quad (2.18)$$

which expresses the equation of state in terms of the variable ω .

To this point the parameter ω is simply a quantity defined in Equation (2.15). Its physical meaning is shown when the expression for the partition function in Equation (2.17) is used to obtain the expression

$$G = NkT \ln \lambda^3 + NkT \ln \omega \quad (2.19)$$

for the Gibbs free energy. But from thermodynamics we know that the quantity G is related to the activity, a , of the gas by

$$G = G^\circ + NkT \ln a.$$

Here G° is the Gibbs free energy of some standard state. If we choose the standard state to be the ideal gas at the same temperature and volume, then

$$G^\circ = NkT \ln \{ \lambda^3 (N/V) \}$$

and

$$G = NkT \ln \lambda^3 + NkT \ln \frac{aN}{V}. \quad (2.20)$$

Comparing Equation (2.20) and (2.19) we find that

$$\omega = a \frac{N}{V}.$$

Thus we may think of the parameter ω as the "active number density", which is in accord with our previous remarks concerning the relationship between the generating function, $g(J)$ and the partition function of the grand canonical ensemble.

To express P as a power series in the number density, $n = N/V$, it is necessary to know ω in terms of n . We can see by reverting Equation (2.15) that

$$\omega = n - 2b_2 n^2 + (8b_2^2 - 3b_3) n^3 + \dots$$

Alternately ω can be written as

$$\omega = n \exp \left(- \sum_{k=1}^{\infty} \beta_k n^k \right), \quad (2.21)$$

in which the β_k are various combinations of the cluster integrals. The first two are

$$\begin{aligned} \beta_1 &= 2 b_2, \\ \beta_2 &= 3 b_3 - 6 b_2^2. \end{aligned}$$

The quantity β_k for any k may be obtained by expanding ω from Equation (2.15) in powers of n , and equating the coefficients of equal powers of n in Equation (2.21).

Substitution of the expression for ω into the formula for PV of Equation (2.4) gives the equation of state in the virial form

$$\frac{PV}{NkT} = 1 - \sum_{k=1}^{\infty} \frac{k \beta_k}{k+1} \left(\frac{N}{V} \right)^k. \quad (2.22)$$

From Equation (2.22) and Equation (2.4), the $(k+1)^{\text{st}}$ virial coefficient is then given by $-k/(k+1) \beta_k N^k$ where N is Avogadro's number. In particular, we have that

$$B(T) = -\frac{1}{2} N \beta_1 = -N b_2 \quad (2.23)$$

and

$$C(T) = -\frac{2}{3} N^2 \beta_2 = -2N^2 (b_3 - 2b_2^2).$$

In the rest of the treatment we will need only $B(T)$. Using Equations (2.23) and (2.12)

$$B(T) = -\frac{N}{2V} \iint d\mathbf{q}_1 d\mathbf{q}_2 U_2(\mathbf{q}_1, \mathbf{q}_2). \quad (2.24)$$

Equation (2.24) will be used in Chapter V as a starting point for the development of specific formulae of interest.

CHAPTER III. ASSUMED POTENTIAL FORMS AND THEIR RELATIONSHIP TO THEORY

As we have seen, in order to calculate $B(T)$ (or any other thermodynamic property) from statistical mechanical considerations a form for the intermolecular potential must be available. Although for a few very simple cases it is possible to obtain an intermolecular potential from an ab initio calculation, in general this is not yet possible. For all of the previous investigations, which are of interest to our present study the form of the potential has been assumed.

One of the earliest and most important calculations of $B(T)$ using statistical methods was that of Lennard-Jones (5). Using London's dispersion force (6) as a basis for his potential, Lennard-Jones assumed the well-known 6-12 potential form

$$\phi_{LJ} = \epsilon \left\{ \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right\} ,$$

where r is the distance between molecular centers, and σ and ϵ are adjustable potential parameters. It can easily be seen that σ is the distance at which $\phi(r) = 0$ and ϵ is the minimum energy in the potential as shown in Figure 2. This potential has been applied by many investigators to the interaction between spherically symmetric or approximately spherically symmetric molecules with success.

However, when the molecule is particularly nonspherical or when the electrostatic energy makes a significant contribution, a potential which accounts for these factors is needed to calculate $B(T)$. A number of

investigations have been concerned with the effect of noncentral interaction potentials in the determination of $B(T)$. Several of these are important to the present study.

Isihara (7) has developed an expression for the second virial coefficient of a gas of rigid convex bodies in terms of their volume, surface area, and mean curvature. This treatment has been generalized by Kihara (8) by assuming that the two rigid molecular "cores" also interact via a soft interaction potential. Specifically, Kihara has assumed the soft interaction to be of the form

$$\phi_K = \phi_{LJ}(\ell)$$

where ϕ_{LJ} is the Lennard-Jones potential and where ℓ is the minimum distance between the cores. This distance is determined by the separation of the molecular centers and the relative configuration of the cores. It is apparent that such a model takes into account nonspherical interactions arising from steric considerations and hence is appropriate for modeling of nonspherical valence repulsion or dispersive interactions but not, for example, interactions between fixed dipoles. In Chapters IV and V we discuss the Kihara potential in some detail.

In order to consider interaction between permanent dipoles Stockmayer (9) added a dipole-dipole interaction term to a Lennard-Jones central potential. Stockmayer's potential is given by

$$\phi = \phi_{LJ}(r) - \mu_1 \mu_2 : \frac{(3\hat{r}\hat{r} - \underline{U})}{r^3}$$

Here μ_i is the permanent dipole moment, $\hat{r}$ is a unit vector along $\underline{r}$, the vector between centers, and $\underline{U}$ is the unit tensor. The nonspherical term is

simply the interaction energy between two fixed, point dipoles separated by the vector, $\underline{r}$.

Models which include nonspherical valence repulsion and dispersion-induction potential terms as well as electrostatic interactions have received less attention. Pople (10) has developed a first-order perturbation technique for computing the second virial coefficient for axially symmetric molecules of this type. Pople assumes a total potential of the form $\phi = \phi_0 + \phi'$ where ϕ_0 is the spherical part and ϕ' is a sum of the "small" nonspherical effects arising from permanent electric multipoles, angular dependence of dispersion, induction and repulsion. While it is certainly true that these terms are small in some molecules, the number of molecules for which this is the case is limited. A model consisting of a spherical hard core with an imbedded off-center dipole and a soft, central interaction between the core centers has been considered by Smith and coworkers (11). Spurling and Mason (12) have pointed out that this model can be conveniently treated by shifting the dipole to the core center, thereby introducing higher multipole interactions. The Kihara potential with an imbedded point dipole has been treated approximately by Storvick and coworkers (13). Their method in essence consists of replacing certain difficult integrals of an exact treatment by integrals using an approximate, spherical Kihara potential and utilizing a Pople first order perturbation term for the dipole term. Datta and Singh (14) using Pople's perturbation expansion have incorporated a Kihara type potential as the "central potential term" in the calculations of the second virial coefficient for quadrupolar molecules.

We present a model consisting of a Kihara potential to describe

dispersion and valence repulsion and a floating center multipole potential parameterized by λ to describe the electrostatic interaction. In those investigations presented above, in which Pople's multipole term from first order perturbation technique is used, only the first term of the multiple term which we propose in Chapter V appears.

Figure 2. The Lennard-Jones potential

CHAPTER IV. THE NATURE OF INTERMOLECULAR POTENTIALS

Intermolecular forces are of two types, short range force and long range forces. The short range, valence repulsion force, can be seen to arise from the interpenetration of the electron clouds of two molecules. Although intuitively one expects that this repulsive force increases sharply as the molecular separation distance decreases, no specific form for it has yet been demonstrated theoretically (as opposed to the case for the long range forces). Therefore, we somewhat arbitrarily chose a form for $\phi^{(sr)}$, the potential from which the short range force is derived.

Let us now consider the long range interaction energy between two molecules having permanent electric moments. It can be written as the sum of three potential terms as follows:

$$\phi^{(lr)} = \phi^{(es)} + \phi^{(ind)} + \phi^{(dis)}$$

The contribution, $\phi^{(es)}$, represents the purely electrostatic interaction between the permanent charge distributions of the two molecules. The term, $\phi^{(ind)}$, is the energy of induction and represents the interaction energy between the permanent charge distribution of one molecule and the moments induced in the other molecule. The term, $\phi^{(dis)}$, is the London dispersion energy and represents the interaction between two induced charge distributions. The electrostatic forces and the induction forces can be understood classically; however, the London dispersion forces are strictly quantum mechanical in origin. All three of these terms can be shown to arise from a second order perturbation treatment of the molecular interaction energy.

The magnitude of the dispersion forces between asymmetric molecules

depends upon the relative orientations of the molecules as opposed to the case for spherical molecules. In both cases at large separations the energy of dispersion varies as the reciprocal of the sixth power of the internuclear separation. Although none of the various forces which act between nonspherical molecules are central, the electrostatic forces differ from those of valence repulsion and dispersion in that the nonsphericity of the latter is "steric" in nature, as has been previously mentioned. From a crude point of view, steric forces depend only on the distance separating the molecules.

Knowing that a molecule is a charge distribution in space, not a point, the question arises: what is meant by separation distance between two molecules? If the separation of the distributions is large compared with the dimensions of the distributions, it is satisfactory to take the distance between the molecules as the distance between fixed origins imbedded in the molecules. However, when the separation distance becomes comparable to molecular dimensions this is no longer acceptable if the distributions are nonspherical. In particular the "effective" separation distance will depend on the relative orientation of the distributions. Such an "effective" separation distance will determine the interaction strength for interaction terms which are noncentral from only steric considerations. For instance, the "distance" between two molecules close together might be determined by the contours of equal charge density that are just in contact. Such a choice would take into account the steric features of the molecule (i.e., the separation parameter would have a parameteric angle dependence). This is clearly not a rigorous concept, many choices of parameterization are

possible.

The manner in which we characterize the intermolecular potential is a generalization of the method of Kihara which is based on the theory of convex surfaces. We consider each molecule in the gas to be surrounded by a family of body fixed, convex surfaces which are centered about some fixed origin within the molecule. The surfaces for molecule i are of the general shape of the molecule and are parameterized by a continuous variable ρ_i which has the dimensions of length. An arbitrary point in space, with radius vector $\underline{r}_i$ from the origin, is assumed to lie on only one surface and is uniquely specified by the value of ρ_i of that surface and the outward unit surface normal, $\hat{k}_i$, at that point. In the limit that ρ_i becomes large, the surfaces are assumed to become spherical in the sense that

$$\lim_{\rho_i \rightarrow \infty} (\rho_i / |\underline{r}_i|) = 1$$

For two molecules (1 and 2) in a given configuration there exists a unique value of $\rho = \rho_1 = \rho_2$ such that the contours of the two molecules with this ρ value touch at a single point. At this point the surface normal, $\hat{k}_1$, for molecule 1 is antiparallel to the surface normal for molecule 2, $\hat{k}_2$. A discussion of the geometry of these surfaces is given in Chapter V. In this model the parameter ρ determines the effective separation distance in a manner that takes into account steric dependence. We define a distance variable $d(\rho)$ (as yet unspecified) which determines the effective distance between the molecules. Further, we define the vector quantity $\underline{d} = d(\rho) \hat{k}$, where $\hat{k} = \hat{k}_1 = -\hat{k}_2$.

We now provide a heuristic justification for the use of a generalized

Kihara type potential. The treatment we give follows the original treatment of London as modified by Buckingham (15) to include angle dependent forces. Our treatment differs from Buckingham's in that we seek to express the angle dependent valence repulsion and dispersion terms by a generalized Kihara potential.

When molecules 1 and 2 are far apart electron exchange can be neglected and the interaction Hamiltonian, $\mathcal{H}'$, can be treated as a perturbation to the noninteracting system (16,17) whose Hamiltonian is $\mathcal{H}^{(1)} + \mathcal{H}^{(2)}$, with eigenvalues $\omega_r^{(1)} + \omega_s^{(2)}$ and eigenfunctions $\psi_r^{(1)} \psi_s^{(2)}$. The interaction Hamiltonian, $\mathcal{H}'$, can be conveniently written in a multipole expansion about the points $\underline{r}_1 - \frac{1}{2}\underline{d}$ in molecule 1 and $\underline{r}_2 + \frac{1}{2}\underline{d}$ in molecule 2 (see Figure 3). It has the general Cartesian tensor form

$$\mathcal{H}' = \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} \frac{(-1)^j}{k! j!} Q_2^{(k)} \odot^k \underline{A}^{(k+j)}(\underline{d}) \odot^j Q_1^{(j)} \quad (4.1)$$

where $\odot^m$ denotes a contraction on m indices, $Q_i^{(\alpha)}$ is the α^{th} multipole moment operator of the i^{th} molecule, and

$$\underline{A}^{(m)}(\underline{d}) = \frac{\partial^m}{\partial \underline{d}^m} \frac{1}{d} = \frac{(-1)^m (2m)!}{2^m m!} \frac{[(\hat{k})^m]}{d^{m+1}} \quad (4.2)$$

Here the square bracket $[]$ about the m^{th} rank polyad, $(\hat{k})^m = \hat{k} \cdots \hat{k}$, represents the irreducible part of the tensor (i.e., the part which is traceless and symmetric on all its indices). As shown in Appendix B the multipole moment operators, $Q_i^{(\alpha)}$, are easily established to be

$$\underline{Q}_1^{(s)} = \sum_{j=0}^s \binom{s}{j} \left[\left(\frac{1}{2} \underline{Q} - \underline{I}_1 \right)^{s-j} \underline{q}_1^{(j)} \right] \quad (4.3)$$

and

$$\underline{Q}_2^{(s)} = \sum_{j=0}^s \binom{s}{j} \left[\left(\frac{1}{2} \underline{Q} + \underline{I}_2 \right)^{s-j} \underline{q}_2^{(j)} \right] \quad (4.4)$$

where $\underline{q}_1^{(j)}$ and $\underline{q}_2^{(j)}$ are the multipole moment operators about the fixed origins (e.g., center of mass) in molecules 1 and 2, respectively. As before, the square brackets indicate the irreducible part of the enclosed tensor.

The energy of the pair 1,2 in their ground state is

$$\omega_0^{12} = \omega_0^{(1)} + \omega_0^{(2)} + \underline{\mathcal{H}}' \quad (4.5)$$

where the perturbation Hamiltonian matrix, $\underline{\mathcal{H}}'$ to second order is defined by

$$\underline{\mathcal{H}}' = \langle \psi_0^{(1)} \psi_0^{(2)} | \underline{\mathcal{H}}' | \psi_0^{(1)} \psi_0^{(2)} \rangle - \sum_{r,s}' \frac{\langle \psi_0^{(1)} \psi_0^{(2)} | \underline{\mathcal{H}}' | \psi_r^{(1)} \psi_s^{(2)} \rangle^2}{\omega_r^{(1)} - \omega_0^{(1)} + \omega_s^{(2)} - \omega_0^{(2)}}.$$

Here $\sum_{r,s}'$ denotes a summation over all unperturbed states except the ground state, $r=s=0$. We now define

$$\Delta \underline{\mathcal{H}} = \underline{\mathcal{H}}' - \underline{\mathcal{H}}_{\text{ave}}$$

where $\underline{\mathcal{H}}_{\text{ave}}$ is the average of the perturbation Hamiltonian matrix, $\underline{\mathcal{H}}'$.

We chose to average in such a way as to keep $\underline{Q}$ fixed while bodies 1 and 2, which represent molecules 1 and 2, are rotated through all orientation angles. (Note that the origins do not remain fixed in this averaging process.) Since the first nonzero multipole moment operator is independent

of origin, this first term of $\mathcal{H}'$, when averaged as above, will be zero (except for charged species, i.e., $q_1 \neq 0$ and $q_2 \neq 0$, which is a case we do not consider). Thus the first term in ΔH is equal to the first term (i.e., the term which arises from the first nonzero multipole moment operator) in $\mathcal{H}'$. The second, third, etc. terms in ΔH will be much smaller than the first for two reasons. First, they are of higher order (in one of two ways--the perturbation, the multipole expansion or both) and second, they are the difference between $\mathcal{H}'$ and $\mathcal{H}_{ave}$ terms which partially cancel. Thus we keep only the first term in ΔH (which is the first term in $\mathcal{H}'$) and neglect all terms of higher order.

Now identifying the lowest order term in ΔH as $\phi^{(es)}$ to lowest order, we obtain

$$\phi^{(es)} = \langle \psi_0^{(1)} \psi_0^{(2)} | \mathcal{H}_1 | \psi_0^{(1)} \psi_0^{(2)} \rangle$$

where $\mathcal{H}_1$ is the first nonzero multipole moment operator in Equation (4.1).

Substituting in for $\mathcal{H}_1$ yields

$$\phi^{(es)} = \frac{(-1)^\beta}{\alpha! \beta!} Q_2^{(\alpha)} \odot^\alpha A(\underline{Q}) \odot^\beta Q_1^{(\beta)} \quad (4.6)$$

where $Q_2^{(\alpha)}$ and $Q_1^{(\beta)}$ are the "permanent" moments of the unperturbed molecules, e.g.,

$$Q_i^{(\alpha)} = \langle \psi_0^{(i)} | Q_i^{(\alpha)} | \psi_0^{(i)} \rangle.$$

For the case $\mu_1 \neq 0$ and $\mu_2 \neq 0$

$$\phi^{(es)} = \mu_2 \cdot A^{(2)}(\underline{Q}) \cdot \mu_1 \quad (4.7)$$

As previously discussed the first term in $\underline{H}_{ave}$ goes to zero, yielding

$$\underline{H}_{ave} = - \left[\sum_{r,s} \frac{\langle \psi_r^{(1)} \psi_s^{(2)} | \mathcal{H}_1 | \psi_r^{(1)} \psi_s^{(2)} \rangle^2}{\omega_r^{(1)} - \omega_0^{(1)} + \omega_s^{(2)} - \omega_0^{(2)}} \right]_{ave} + \left[\text{higher order terms} \right]_{ave}$$

where $[]_{ave}$ denotes the averaging procedure over all angles about the multipole expansion center of each molecule as previously described and where higher multipoles of the first and second order perturbation are the higher order terms. Again, we only consider the lowest order terms in $\underline{H}_{ave}$. By identifying $\phi^{(ind)}$ and $\phi^{(dis)}$ as the lowest order terms in $\underline{H}_{ave}$, we obtain

$$\phi^{(ind)} = - \left[\sum_{r \neq 0} \frac{\langle \psi_r^{(1)} \psi_0^{(2)} | \mathcal{H}_1 | \psi_r^{(1)} \psi_0^{(2)} \rangle^2}{\omega_r^{(1)} - \omega_0^{(1)}} \right]_{ave} - \left[\sum_{s \neq 0} \frac{\langle \psi_0^{(1)} \psi_s^{(2)} | \mathcal{H}_1 | \psi_0^{(1)} \psi_s^{(2)} \rangle^2}{\omega_s^{(2)} - \omega_0^{(2)}} \right]_{ave} \quad (4.8)$$

and

$$\phi^{(dis)} = - \left[\sum_{\substack{r \neq 0 \\ s \neq 0}} \frac{\langle \psi_r^{(1)} \psi_s^{(2)} | \mathcal{H}_1 | \psi_r^{(1)} \psi_s^{(2)} \rangle^2}{\omega_r^{(1)} - \omega_0^{(1)} + \omega_s^{(2)} - \omega_0^{(2)}} \right]_{ave} \quad (4.9)$$

Recalling that

$$\underline{A}^{(2)}(\underline{d}) = \frac{3\hat{d}\hat{d} - U}{d^3}$$

we see that Equation (4.8) becomes

$$\phi^{(ind)} = - \frac{\omega_{2,1} + \omega_{1,2}}{d^6}$$

where

$$\omega_{i,j} = \left[\mu_i \cdot (3\hat{d}\hat{d} - U) \mu_i \cdot (3\hat{d}\hat{d} - U) \right]_{ave} \otimes_j^2$$

and ω_{ij} is thus independent of orientation. Now considering Equation (4.9) and proceeding as above, we obtain

$$\phi^{(dis)} = - \left[\underline{A}^{(2)}(\underline{Q}) \underline{A}^{(2)}(\underline{Q}) \odot^y \sum_{\substack{r \neq 0 \\ s \neq 0}} \frac{\langle \Psi_0^{(1)} \Psi_0^{(2)} | \underline{\mu} \underline{\mu} | \Psi_r^{(1)} \Psi_s^{(2)} \rangle \langle \Psi_r^{(1)} \Psi_s^{(2)} | \underline{\mu} \underline{\mu} | \Psi_0^{(1)} \Psi_0^{(2)} \rangle}{\omega_r^{(1)} - \omega_0^{(1)} + \omega_s^{(2)} - \omega_0^{(2)}} \right]_{ave} \quad (4.10)$$

It is possible to simplify Equation (4.10) in terms of the polarisability, α ; however, it is not to our advantage to do this since it can be easily seen, as with $\phi^{(ind)}$, that

$$\phi^{(dis)} = - \frac{\omega^{(d)}}{\underline{Q}^6}$$

where $\omega^{(d)}$ is a scalar independent of orientation by virtue of averaging as previously discussed.

Thus our results are similar to Buckingham's results in that $\phi^{(ind)}$ and $\phi^{(dis)}$ are proportional to the inverse sixth power of a separation parameter in both derivations. However, we have removed all explicit angle dependence in $\phi^{(ind)}$ and $\phi^{(dis)}$. These interaction energies depend implicitly on orientation through $\underline{Q}$.

Figure 3. Origins of the multipole expansions in molecules 1 and 2

CHAPTER V. DEVELOPMENT OF THE SECOND VIRIAL COEFFICIENT FOR POLAR, NONSPHERICAL MOLECULES

In this chapter we first discuss the family of surfaces originally introduced in Chapter IV. We then show how the second virial coefficient is derived for various polyhedral models for molecules with either a dipole or quadrupole moment as the first nonzero multipole moment.

The family of surface contours surrounding molecule i is conveniently described by a corresponding family of supporting functions, $H(\hat{\mathbf{r}}, \rho)$. The supporting functions are defined by the relation

$$H_i(\hat{\mathbf{r}}_i, \rho_i) = \underline{\mathcal{I}}_i \cdot \hat{\mathbf{r}}_i. \quad (5.1)$$

where as before, $\underline{\mathcal{I}}_i$ is the radius vector from the origin to only one surface. If we follow Cooper and Hoffman (13) and define $\partial/\partial\hat{\mathbf{r}}_i$ by the relation

$$\frac{\partial}{\partial\hat{\mathbf{r}}_i} = \hat{\Theta}_i \left(\frac{\partial}{\partial\Theta_i} \right) + \frac{\hat{\Phi}_i}{\sin\Theta_i} \left(\frac{\partial}{\partial\Phi_i} \right),$$

where Θ_i and Φ_i are the polar angles of $\hat{\mathbf{r}}_i$, then it is apparent the $\partial/\partial\hat{\mathbf{r}}_i$ transforms like a vector and that

$$\frac{\partial\hat{\mathbf{r}}_i}{\partial\hat{\mathbf{r}}_i} = \hat{\Theta}_i \hat{\Theta}_i + \hat{\Phi}_i \hat{\Phi}_i = \underline{\underline{U}} - \hat{\mathbf{r}}_i \hat{\mathbf{r}}_i \equiv \underline{\underline{U}}_{\hat{\mathbf{r}}_i}^{(2)} \quad (5.2)$$

where $\underline{\underline{U}}$ is the unit tensor and $\underline{\underline{U}}_{\hat{\mathbf{r}}_i}^{(2)}$ is the unit tensor in the subspace normal to $\hat{\mathbf{r}}_i$. Now

$$\frac{\partial H_i}{\partial\hat{\mathbf{r}}_i} = \left(\frac{\partial \underline{\mathcal{I}}_i}{\partial\hat{\mathbf{r}}_i} \right) \cdot \hat{\mathbf{r}}_i + \underline{\mathcal{I}}_i \cdot \underline{\underline{U}}_{\hat{\mathbf{r}}_i}^{(2)}$$

but since $\hat{\mathbf{r}}_i$ is normal to the i th surface, any differential change in $\underline{\mathcal{I}}_i$

must be perpendicular to $\hat{k}_i$. Thus

$$\frac{\partial H_i}{\partial \hat{k}_i} = \underline{J}_i \cdot \underline{U}_{\hat{k}_i}^{(2)}$$

and from Equations (5.1) and (5.2)

$$\underline{J}_i = H_i \hat{k}_i + \left(\frac{\partial H_i}{\partial \hat{k}_i} \right)$$

For two molecules in a given configuration there exists a unique value of $\rho = \rho'$ such that the contours of the two molecules with this ρ value touch at a single point. At this point the surface normal, $\hat{k}_1$, for molecule 1 is antiparallel to the surface normal for molecule 2, $\hat{k}_2$. If molecule 2 is allowed to pass about 1 at constant ρ (both molecules being held at fixed orientation), the origin of 2 traces out a new convex surface with surface normal $\hat{k} = \hat{k}_1 = -\hat{k}_2$. The vector $\underline{r}$ from the origin in molecule 1 to the origin in molecule 2 is given by

$$\underline{r} = \underline{J}_1 - \underline{J}_2$$

where $\underline{J}_1$ and $\underline{J}_2$ are the vectors from the respective origins to the contact point. The supporting function of the surface formed when molecule 2 passes around 1 is

$$H(\hat{k}, \rho) = \hat{k} \cdot \underline{r} = H_1(\hat{k}_1, \rho) + H_2(\hat{k}_2, \rho).$$

The element of surface area per unit solid angle on the contour, S , is given by the determinant of $(\partial \underline{r} / \partial \hat{k})_\rho$ in the subspace normal to $\hat{k}$. This quantity can be conveniently expressed as follows:

$$S = -\frac{1}{2} \underline{G} : \underline{G}$$

where

$$\underline{G} = H \underline{V} + \left(\frac{\partial^2 H}{\partial \hat{k}^2} \right) \cdot \underline{V} = \underline{G}_1 + \underline{G}_2 \quad (5.3)$$

and

$$\underline{G}_i = H_i \underline{V}_i + \frac{\partial^2 H_i}{\partial \hat{k}_i^2} \cdot \underline{V}_i$$

Here $\underline{V} = \underline{V}_1 = -\underline{V}_2$ where $\underline{V}_i$ is the antisymmetric tensor $-\hat{k}_i \times \underline{U}$.

The criterion for convexity is that $\mathcal{S}$ be nonzero.

It is easily established that the volume element $d\mathbf{r}$ is given by

$$d\mathbf{r} = -1/2 \underline{G} : \underline{G} \frac{\partial H}{\partial \rho} d\rho d\hat{k} \quad (5.4)$$

In this equation $(\partial H / \partial \rho) d\rho$ is the normal component of the displacement of a surface point by the infinitesimal transformation $\rho \rightarrow \rho + d\rho$ at fixed $\hat{k}$.

Having established these basic geometric relationships for convex surfaces, we now derive an expression for $B(T)$. Substituting Equations (2.7), (2.10) and (5.4) into Equation (2.24) and using the fact that $d\mathbf{r}_i = d\alpha_i d\mathbf{r}_i$, we have that

$$B(T) = - \frac{N}{128\pi^4} \int d\alpha_1 \int d\alpha_2 \int d\rho \int d\hat{k} \left(-1/2 \underline{G} : \underline{G} \right) \left(\frac{\partial H}{\partial \rho} \right) \times (\exp(-\beta\phi) - 1) \quad (5.5)$$

where $d\alpha_i = d\phi_i d\psi_i \sin\theta_i d\theta_i$ is the differential Eulerian angle element of the i th molecule.

Now we assume the intermolecular potential to be of the form

$$\phi = \phi^{(sr)} + \phi^{(dis)} + \phi^{(ind)} + \phi^{(es)} \equiv \phi^{(d)} + \phi^{(es)} \quad (5.6)$$

for which we provided justification earlier.

Here

$$\phi^{(d)} = \phi^{(sr)} + \phi^{(dis)} + \phi^{(ind)}.$$

We complete the specification of our model of interaction as follows:

$$\begin{aligned} \underline{d} &= l \hat{h} \quad \text{at } l = 0, & \rho &= \rho_m \\ H_i &= h_i + \frac{1}{2} l & \rho &\geq \rho_m \\ H_i &= \rho / \rho_m h_i & \rho &\leq \rho_m \\ \phi^{(d)} &= 4U_0 \left\{ \left(\frac{l_0}{l} \right)^{12} - \left(\frac{l_0}{l} \right)^6 \right\} & \rho &\geq \rho_m \\ \phi^{(d)} &= \infty & \rho &\leq \rho_m \\ \phi^{(es)} &= P/l^a \end{aligned} \quad (5.7)$$

Here h_i is the supporting function of the core of molecule i , and U_0 and l_0 are the usual adjustable parameters of the Lennard-Jones potential.

The quantity P is a function of the orientation of molecules 1 and 2 as given in Equation (4.6) and a is the appropriate exponent depending on the nature of the lowest nonzero multipole. Note that our model places the origin of the multipole expansion on the core.

Making use of Equation (5.6), we have that

$$\begin{aligned} (\exp(-\beta\phi) - 1) &= (\exp(-\beta\phi^{(d)}) - 1) \\ &+ \sum_{n=1}^{\infty} \frac{1}{n!} (-\beta\phi^{(es)})^n \exp(-\beta\phi^{(d)}). \end{aligned} \quad (5.8)$$

Using the model given in Equation (5.7), i.e. a convex core model, we can see that Equation (5.3) becomes

$$\underline{G} = \underline{g} + \sum l \quad (5.9)$$

Here

$$\underline{g} = \underline{g}_1 + \underline{g}_2,$$

where

$$\underline{g}_i = h_i \underline{V}_i + \frac{\partial^2 h_i}{\partial h_i^2} \cdot \underline{V}_i. \quad (5.10)$$

Now substituting Equations (5.7), (5.8), and (5.9) into Equation (5.5), we obtain

$$B(T) = I + II + III,$$

where we have defined

$$I = \frac{N}{128\pi^4} \int d\hat{k} \int d\alpha_1 \int d\alpha_2 \int_0^{\beta_m} d\rho \left(-\frac{1}{2} \underline{G} : \underline{G} \right) \frac{\partial H}{\partial \rho}, \quad (5.11)$$

$$II = -\frac{N}{128\pi^4} \int d\hat{k} \int d\alpha_1 \int d\alpha_2 \int_0^\infty dl \left\{ -\frac{1}{2} (\underline{g} : \underline{g} + 2l \underline{g} : \underline{V} + l^2 \underline{V} : \underline{V}) \right\} \\ \times \left\{ \exp \left(-t^* \left[\left(\frac{l_0}{l} \right)^{12} - \left(\frac{l_0}{l} \right)^6 \right] \right) - 1 \right\}, \quad (5.12)$$

and

$$III = -\frac{N}{128\pi^4} \int d\hat{k} \int d\alpha_1 \int d\alpha_2 \int_0^\infty dl \left\{ -\frac{1}{2} (\underline{g} : \underline{g} + 2l \underline{g} : \underline{V} + l^2 \underline{V} : \underline{V}) \right\} \\ \times \exp \left(-t^* \left[\left(\frac{l_0}{l} \right)^{12} - \left(\frac{l_0}{l} \right)^6 \right] \right) \sum_{n=1}^\infty \frac{1}{n!} \left\{ -\beta P(l)^{-n} \right\}^n. \quad (5.13)$$

Here t^* is equal to $4\beta u_0$. In Appendix C, I is shown to equal $B_{H.C.}$, the hard core second virial coefficient as given by Isihara (7).

Now in general Equations (5.12) and (5.13) can be integrated exactly over l . Following Lennard-Jones we obtain by integrating by parts over l , and after some algebraic manipulation

$$\begin{aligned}
\text{II} = & + \frac{N}{128\pi^4} \frac{1}{12} \int d\alpha_1 \int d\alpha_2 \int d\hat{k} \sum_{m=0}^{\infty} \frac{(t^* l_0^6)^m}{m!} \\
& \times \left\{ E_{-1}^{\text{II}}(m) \frac{q}{2} : \frac{q}{2} / 2 + E_{-2}^{\text{II}}(m) \frac{q}{2} : \underline{V} + E_{-3}^{\text{II}}(m) \underline{V} : \underline{V} / 2 \right\} \quad (5.14)
\end{aligned}$$

where

$$E_i^{\text{II}}(m) = \Gamma\left(\frac{6m+i}{12}\right) \left\{ \frac{1}{t^* l_0^{1/2}} \right\}^{\frac{6m+i}{12}}$$

Here $\Gamma()$ is the ordinary gamma function. If we now integrate Equation (5.13) over l by expanding the exponential,

$$\exp\left(-4u_0\beta\left\{\frac{l_0}{2}\right\}^6\right)$$

and apply the relation

$$\int_0^{\infty} x^{-t} e^{-bx^{-q}} dx = \frac{1}{q} \left(\frac{1}{b}\right)^{\frac{t-1}{q}} \Gamma\left(\frac{t-1}{q}\right),$$

we obtain

$$\begin{aligned}
\text{III} = & \frac{N^{1/2}}{128\pi^4} \int d\alpha_1 \int d\alpha_2 \int d\hat{k} \sum_{m=0}^{\infty} \frac{(t^* l_0^6)^m}{m!} \sum_{n=1}^{\infty} \frac{(-\beta p)^n}{n!} \\
& \times \left\{ E_{-1}^{\text{III}}(m,n) \frac{q}{2} : \frac{q}{2} / 2 + E_{-2}^{\text{III}}(m,n) \frac{q}{2} : \underline{V} + E_{-3}^{\text{III}}(m,n) \underline{V} : \underline{V} / 2 \right\} \quad (5.15)
\end{aligned}$$

where, analogous to E_i^{II} ,

$$E_i^{\text{III}}(m,n) = \Gamma\left(\frac{6m+6n+i}{12}\right) \left\{ \frac{1}{t^* l_0^{1/2}} \right\}^{\frac{6m+6n+i}{12}} \quad (5.16)$$

For the case $n = 0$

$$E_i^{II}(m) = E_i^{III}(m, 0)$$

therefore we can see by combining Equations (5.14) and (5.15) that

$$B(T) = I + IV, \quad (5.17)$$

where

$$IV = \frac{N}{128\pi^4} \frac{1}{12} \int d\alpha_1 \int d\alpha_2 \int d\hat{k} \sum_{m=0}^{\infty} \frac{(t^* l_0^m)^m}{m!} \sum_{n=0}^{\infty} \frac{(-\beta P)^n}{n!} \\ \times \left\{ E_{-1}^{III}(m, n) \frac{1}{2} + E_{-2}^{III}(m, n) \frac{1}{2} + E_{-3}^{III}(m, n) \frac{1}{2} \right\} \quad (5.18)$$

Before the orientation integrals can be performed, we must specify the angular dependence of P . We will consider two cases. In case a.) the dipole moment is the first nonzero multipole moment and in case b.) it is the quadrupole moment.

For a.) using Equation (4.7), we obtain

$$P^n = (-\mu^2 \hat{e}_1 \hat{e}_2 : [3\hat{k}\hat{k} - \underline{1}])^n. \quad (5.19)$$

Here $\mu \hat{e}_i = \mu_i$ and, again, the square bracket $[\]$ denotes the irreducible part of the enclosed tensor. Performing the dot product in Equation (5.19), defining $x_i = \hat{k}_i \cdot \hat{e}_i$, $\tilde{e}_i = \hat{e}_i - x_i \hat{k}_i$ and $y_i = (1 - x_i^2)^{1/2}$ and expanding the result in a binomial series, we obtain

$$P^n = (\mu^2)^n \sum_{j=0}^n \binom{n}{j} (\tilde{e}_1 \cdot \tilde{e}_2)^j (2x_1 x_2)^{n-j} \quad (5.20)$$

where $\binom{n}{j}$ is the binomial coefficient. Using

$$\frac{1}{j} = \frac{1}{j_1} + \frac{1}{j_2} \quad (5.21)$$

and

$$\int d\alpha_1 f_1 = \int d\alpha_2 f_2, \quad (5.22)$$

and Equation (5.20), we obtain by performing all integrations

$$\begin{aligned} \text{IV} = & \frac{2N}{12} \sum_{m=0}^{\infty} \frac{(t^* l_0^*)^m}{m!} \sum_{n=0}^{\infty} (-\beta \mu^2)^n \sum_{\substack{j=0 \\ \text{even}}}^n \frac{2^{n-j}}{(n-j)! j!} B\left(\frac{1}{2}, \frac{j+1}{2}\right) \\ & \times \left\{ E_{-1}^{\text{III}}(m,n) A_d^{(1)}(n,j) + E_{-2}^{\text{III}}(m,n) A_d^{(2)}(n,j) + E_{-3}^{\text{III}}(m,n) A_d^{(3)}(n,j) \right\} \end{aligned} \quad (5.23)$$

(Note some of the integrations involve tensor integrals.) Here $B\left(\frac{1}{2}, \frac{j+1}{2}\right)$ is the ordinary beta function defined by

$$B(k, i) = \frac{\Gamma(k) \Gamma(i)}{\Gamma(k+i)}.$$

The coefficients $A_d^{(1)}$, $A_d^{(2)}$, and $A_d^{(3)}$ are

$$\begin{aligned} A_d^{(1)}(n, j) = & S_{n,j}^{(3)} S_{n,j}^{(0)} - 2 S_{n,j}^{(2)} S_{n,j}^{(2)} \left(\frac{j}{j+2} \right) - S_{n,j}^{(-1)} S_{n,j}^{(-1)} \left(\frac{1}{j+2} \right) \\ & + S_{n,j}^{(-1)} S_{n,j}^{(1)} \left(\frac{2j+2}{j+2} \right) - S_{n,j}^{(1)} S_{n,j}^{(1)} \left(\frac{1}{j+2} \right), \end{aligned} \quad (5.24)$$

$$A_d^{(2)}(n, j) = 2 S_{n,j}^{(0)} \left(S_{n,j}^{(1)} - S_{n,j}^{(-1)} \right), \quad (5.25)$$

and

$$A_d^{(3)}(n, j) = - S_{n,j}^{(0)} S_{n,j}^{(0)}. \quad (5.26)$$

In Equations (5.24), (5.25) and (5.26).

$$S_{n,j}^{(\lambda)} = \frac{1}{4\pi} \int d\hat{k}_i x_i^{n-j} y_i^{j-1} f_i^{(\lambda)} \quad (5.27)$$

where

$$\begin{aligned} f_i^{(0)} &= y_i^2 \\ f_i^{(2)} &= y_i^2 g_i g_i \\ f_i^{(1)} &= g_i : \tilde{e}_i \tilde{e}_{i\perp} \\ f_i^{(1)} &= g_i : \tilde{e}_{i\perp} \tilde{e}_i \\ f_i^{(2)} &= g_i : \tilde{e}_i \tilde{e}_i \end{aligned}$$

and

$$\tilde{e}_{i\perp} = \hat{e}_i \cdot \underline{V}_i.$$

Clearly $S_{n,j}^{(0)}$ is core independent and can be evaluated exactly. However, for $\lambda = 3, 1, -1$, or 2 , $S_{n,j}^{(\lambda)}$ is core dependent since it involves g_i , where g_i is the tensor quantity defined by Equation (5.10) for body i .

To this point our discussion has been applicable to arbitrary convex cores. We now limit our considerations to polyhedral cores. These are, of course, not strictly convex. However, the ideas we have developed can be applied to them since they can be thought of as a limit of a series of strictly convex cores.

Consider first the integrals $S_{n,j}^{(3)}$. We can replace $d\hat{k} g_i g_i$ in the integrand by $-2dS$ where dS is the differential amount of surface area. There are no contributions to $S_{n,j}^{(3)}$ from the edges and corners since these have no area. The contribution of the faces, however, will be nonzero in general. Since $\hat{k}$ is constant on a face then $x_f = \hat{k}_f \cdot \hat{e}$ is also a constant. Also, since

the integrand is constant along a face, the integral of $g_i \cdot g_j d\hat{n}$ over the face is just (-2) times the surface area of the face. Hence the contribution to $S_{n,j}^{(3)}$ from the faces is just

$$-2 \frac{1}{4\pi} \sum_f A_f x_f^{n-j} (1-x_f^2)^{j/2}$$

where $\sum_f$ means a sum over faces and A_f is the surface area of face f .

Next consider the integrals $S_{n,j}^{(-1)}$, $S_{n,j}^{(1)}$ and $S_{n,j}^{(2)}$. To evaluate these we need an explicit expression for g_i , which, with some difficulty, can be shown to be

$$g_i = \sum_e b_e \hat{b}_e \hat{b}_e \cdot \nabla \delta(\hat{b}_e \cdot \hat{n}) \Theta_e \quad (5.28)$$

where $\hat{b}_e$ is a unit vector in the direction of edge e , b_e is the length of edge e , and $\Theta_e = 1$ if ϕ is in the range C_e and is zero outside. Here ϕ is the dihedral angle between the faces which is, of course, determined by $\hat{n}$. It is very important to note that, C_e , the integration range for ϕ is not from 0 to 2π but instead is over the angle determined by the two neighboring faces. Substituting in g_i from Equation (5.28), integrating over $d\hat{n} = d(\hat{b}_e \cdot \hat{n}) d\phi$ and making use of the δ -function, we find that

$$S_{n,j}^{(s)} = \frac{1}{4\pi} \sum_e b_e \int_{C_e} d\phi F^{(s)} x^{n-j} (1-x^2)^{(j-2)/2},$$

where

$$F^{(1)} = (\hat{b}_e \cdot \hat{e})^2$$

$$F^{(-1)} = -(\hat{b}_{e\perp} \cdot \hat{e})^2$$

$$F^{(2)} = (\hat{b}_e \cdot \hat{e})(\hat{b}_{e\perp} \cdot \hat{e})$$

and

$$\hat{b}_{e\perp} = \hat{b}_e \cdot \nabla.$$

Now defining

$$\gamma_d^{(\infty-1)}(n) = \sum_{\substack{j=0 \\ \text{even}}}^n \frac{2^{n-j}}{(n-j)!j!} B\left(\frac{1}{2}, \frac{j+1}{2}\right) A_d^{(\infty)}(n, j)$$

we see that Equation (5.23) can be written

$$IV = \frac{2N}{12} \sum_{m=0}^{\infty} \frac{(t^* l_0^m)^m}{m!} \sum_{n=0}^{\infty} (-\beta \mu^2)^n \left\{ \gamma_d^{(0)}(n) E_{-1}^{III}(m, n) + \gamma_d^{(1)}(n) E_{-2}^{III}(m, n) + \gamma_d^{(2)}(n) E_{-3}^{III}(m, n) \right\} \quad (5.29)$$

in terms of the constants $\gamma_d^{(\alpha)}(n)$. We give these constants in Table 1 for the next six cores for which $B(T)$ is calculated using Equation (5.17).

Note that in the limit $b_e = 0$, the model reduces to Stockmayer's expression for $B(T)$ for a gas of polar molecules, and in the limit that $\mu = 0$ the expression for $B(T)$ becomes that of Kihara for a gas of nonspherical, nonpolar molecules.

We now consider case b.) where the quadrupole is the first nonzero multipole moment. If the molecule is a symmetric top, the quadrupole is a function of a constant times the irreducible part of the diad of the unit vector along the nondegenerate principal axis, i.e.

$$\underline{Q}_i = Q_i [\hat{e}_i \hat{e}_i] \quad (5.30)$$

Using Equations (4.6) and (5.30) we obtain

$$P_Q^n = \left(\frac{3Q_i Q_i}{4} \right)^n \left\{ 1 + 2 (\tilde{e}_1 \cdot \tilde{e}_2)^2 - 5 (\hat{e}_2 \cdot \hat{k})^2 - 5 (\hat{e}_1 \cdot \hat{k})^2 - 16 (\hat{e}_1 \cdot \hat{k}) (\hat{e}_2 \cdot \hat{k}) (\tilde{e}_1 \cdot \tilde{e}_2) + 17 (\hat{e}_1 \cdot \hat{k})^2 (\hat{e}_2 \cdot \hat{k})^2 \right\}^n \quad (5.31)$$

Here

$$\tilde{\epsilon}_i = \hat{\epsilon}_i - \chi_i^* \hat{k}_i$$

where

$$\chi_i^* = \hat{\epsilon}_i \cdot \hat{k}_i. \quad (5.32)$$

We define

$$\tilde{\epsilon}_1 \cdot \tilde{\epsilon}_2 = \gamma_1^* \gamma_2^* \cos \phi^* \quad (5.33)$$

where

$$\gamma_i^* = (1 - \chi_i^{*2})^{1/2}$$

and ϕ^* is the angle between $\tilde{\epsilon}_1$ and $\tilde{\epsilon}_2$. Now expanding Equation (5.31) in a multinomial series using Equations (5.32) and (5.33), we find that

$$P_Q^n = \left\{ \frac{3Q_1 Q_2}{4} \right\}^n n! \sum_{m_1=0}^n \sum_{m_2=0}^{m_1} \sum_{m_3=0}^{m_2} \sum_{m_4=0}^{m_3} \sum_{m_5=0}^{m_4} C(n, \{m_i\}) (\chi_1^*)^{l_1} \chi (\chi_2^*)^{l_2} (\gamma_1^* \gamma_2^* \cos \phi^*)^{l_2}. \quad (5.34)$$

Here

$$C(n, \{m_i\}) = \frac{(-5)^{m_2-m_4} 17^{n-m_1} 16^{m_1-m_2} 2^{m_4-m_5}}{(n-m_1)! (m_1-m_2)! (m_2-m_3)! (m_3-m_4)! (m_4-m_5)! m_5!}$$

and

$$l_1 = 2n - 2m_2 + 2m_3 - 2m_5,$$

$$l_2 = 2n - 2m_3 + 2m_4 - 2m_5,$$

and

$$l_2 = m_1 - m_2 + 2m_4 - 2m_5. \quad (5.35)$$

We consider only the case of linear, quadrupolar molecules for which

case $\hat{e}_i$ is the unit vector along the internuclear axis. If we substitute Equation (5.34) into Equation (5.18), use Equations (5.21) and (5.22) and integrate over all angles we obtain

$$\begin{aligned}
 \text{IV} = & \frac{2N}{12} \sum_{m=0}^{\infty} \frac{(t^* l_0^w)^m}{m!} \sum_{n=0}^{\infty} \left(\frac{-\beta 3 Q^2}{4} \right)^n \sum_{m_1=0}^n \sum_{m_2=0}^{m_1} \sum_{m_3=0}^{m_2} \sum_{m_4=0}^{m_3} \sum_{m_5=0}^{m_4} C(n, \{m_i\}) \\
 & \times B\left(\frac{1}{2}, \frac{k+1}{2}\right) \left\{ E_{-1}^{\text{III}}(m, n) A_g^{(1)}(l_1, l_2, k) + E_{-2}^{\text{III}}(m, n) A_g^{(2)}(l_1, l_2, k) \right. \\
 & \left. + E_{-3}^{\text{III}}(m, n) A_g^{(3)}(l_1, l_2, k) \right\} \quad (5.36)
 \end{aligned}$$

where

$$\begin{aligned}
 A_g^{(1)}(l_1, l_2, k) = & S_{l_1, k}^{(3)} S_{l_2, k}^{(0)} - 2 S_{l_2, k}^{(2)} S_{l_1, k}^{(2)} \left(\frac{k}{k+2} \right) \\
 & - S_{l_1, k}^{(-1)} S_{l_2, k}^{(-1)} \left(\frac{1}{k+2} \right) + S_{l_1, k}^{(-1)} S_{l_2, k}^{(0)} \left(\frac{k+1}{k+2} \right) + S_{l_2, k}^{(-1)} S_{l_1, k}^{(1)} \left(\frac{k+1}{k+2} \right) \\
 & - S_{l_1, k}^{(1)} S_{l_2, k}^{(1)} \left(\frac{1}{k+2} \right) , \\
 A_g^{(2)}(l_1, l_2, k) = & S_{l_2, k}^{(0)} \left(S_{l_1, k}^{(1)} - S_{l_1, k}^{(-1)} \right) , \\
 \text{and} \\
 A_g^{(3)}(l_1, l_2, k) = & - S_{l_1, k}^{(0)} S_{l_2, k}^{(0)} .
 \end{aligned}$$

Here $S_{n, i}^{(s)}$ is defined in Equation (5.27), $E_i^{\text{III}}(m, n)$ is defined in Equation (5.15), and k is defined in Equation (5.35).

Further, if we define

$$\gamma_f^{(\alpha-1)}(n) = \sum_{m_1=0}^n \sum_{m_2=0}^{m_1} \sum_{m_3=0}^{m_2} \sum_{m_4=0}^{m_3} \sum_{m_5=0}^{m_4} C(n, \{m_i\}) B\left(\frac{1}{2}, \frac{k+1}{2}\right) \\ \times A_f^{(\alpha)}(l_1, l_2, k),$$

$(m_1 - m_2 + 2m_4 - 2m_5) = \text{even}$

then Equation (5.36) becomes

$$IV = \frac{2N}{12} \sum_{m=0}^{\infty} \frac{(t^* l_0^6)^m}{m!} \sum_{n=0}^{\infty} \left(\frac{-\beta 3Q^2}{\gamma} \right)^n \left\{ E_{-1}^{III(m,n)} \gamma_f^{(0)}(n) + E_{-2}^{III(m,n)} \gamma_f^{(1)}(n) + E_{-3}^{III(m,n)} \gamma_f^{(2)}(n) \right\}$$

We give the quantities $\gamma_f^{(\alpha)}(n)$ in Table 2 for the line core.

Table 1. The $\gamma_d^{(n)}$'s for the six core shapes for which B(T) data are computed. The term $\gamma_d^{(2)}$ is a constant for each n independent of core

n	Line Core			Hexagon Core		Tetrahedral Core	
	$-\gamma_d^{(2)}$	$-\gamma_d^{(1)}$	$-\gamma_d^{(0)}$	$-\gamma_d^{(1)}$	$-\gamma_d^{(0)}$	$-\gamma_d^{(1)}$	$-\gamma_d^{(0)}$
1	1.257x10	1.257x10	1.571	3.770x10	2.453x10	2.293x10	5.379
2	0	0	0	0	3.810	0	0
3	8.378	4.189	3.927x10 ⁻¹	2.199x10	1.075x10	1.529x10	3.536
4	0	0	0	0	5.252	0	3.144x10 ⁻¹
5	1.206x10	2.513	1.963x10 ⁻¹	2.839x10	1.054x10	2.151x10	4.828
6	0	0	0	0	9.093	0	1.863
7	2.380x10	1.795	1.227x10 ⁻¹	5.073x10	1.527x10	4.190x10	9.257
8	0	0	0	0	1.793x10	0	7.545
9	5.617x10	1.396	8.590x10 ⁻²	1.079x10 ²	2.807x10	1.003x10 ²	2.251x10
10	0	0	0	0	3.837x10	0	2.753x10
11	1.481x10 ²	1.142	6.443x10 ⁻²	2.535x10 ²	5.904x10	2.742x10 ²	6.429x10
12	0	0	0	0	8.679x10 ²	0	9.738x10 ²
13	4.203x10 ²	9.666x10 ⁻¹	5.062x10 ⁻²	6.331x10 ²	1.340x10 ²	8.170x10 ²	2.027x10 ²
14	0	0	0	0	2.043x10 ²	0	3.429x10 ²
15	1.255x10 ³	8.378x10 ⁻¹	4.113x10 ⁻²	1.647x10 ³	3.184x10 ²	2.574x10 ³	6.777x10 ²
16	0	0	0	0	4.957x10 ²	0	1.214x10 ³
17	3.892x10 ³	7.392x10 ⁻¹	3.427x10 ⁻²	4.414x10 ³	7.802x10 ²	8.418x10 ³	2.347x10 ³
18	0	0	0	0	1.231x10 ³	0	4.334x10 ³
19	1.242x10 ⁴	6.614x10 ⁻¹	2.913x10 ⁻²	1.210x10 ⁴	1.955x10 ³	2.827x10 ⁴	8.314x10 ³
20	0	0	0	0	3.116x10 ³	0	1.562x10 ⁴
21	4.058x10 ⁴	5.984x10 ⁻¹	2.516x10 ⁻²	3.374x10 ⁴	4.988x10 ³	9.686x10 ⁴	2.991x10 ⁴
22	0	0	0	0	8.011x10 ³	0	5.675x10 ⁴
23	1.351x10 ⁵	5.464x10 ⁻¹	2.202x10 ⁻²	9.544x10 ⁴	1.291x10 ⁴	3.370x10 ⁵	1.088x10 ⁵
24	0	0	0	0	2.087x10 ⁴	0	2.079x10 ⁵
25	4.566x10 ⁵	5.027x10 ⁻¹	1.948x10 ⁻²	2.732x10 ⁵	3.383x10 ⁴	1.187x10 ⁶	3.994x10 ⁵
26	0	0	0	0	5.497x10 ⁴	0	7.665x10 ⁵
27	1.564x10 ⁶	4.654x10 ⁻¹	1.739x10 ⁻²	7.898x10 ⁵	8.955x10 ⁴	4.222x10 ⁶	1.476x10 ⁶
28	0	0	0	0	1.462x10 ⁵	0	2.843x10 ⁶
29	5.417x10 ⁶	4.333x10 ⁻¹	1.565x10 ⁻²	2.303x10 ⁶	2.392x10 ⁵	1.515x10 ³	5.489x10 ⁶
30	0	0	0	0	3.922x10 ⁵	0	1.060x10 ⁷

Table 1. (continued)

n	120° Triangle Core		109° Triangle Core		90° Triangle Core	
	$-\gamma_a^{(i)}(n)$	$-\gamma_a^{(e)}(n)$	$-\gamma_a^{(i)}(n)$	$-\gamma_a^{(e)}(n)$	$-\gamma_a^{(i)}(n)$	$-\gamma_a^{(e)}(n)$
1	2.345x10	5.607	2.283x10	5.333	2.145x10	4.737
2	0	3.820	0	3.395	0	2.546
3	1.797x10	4.905	1.693x10	4.347	1.474x10	3.294
4	0	6.114	0	5.166	0	3.501
5	2.899x10	8.846	2.644x10	7.322	2.151x10	4.827
6	0	1.304x10	0	1.046x10	0	6.472
7	6.188x10	2.033x10	5.502x10	1.600x10	4.282x10	9.654
8	0	3.236x10	0	2.496x10	0	1.465x10
9	1.538x10 ²	5.299x10	1.344x10 ²	4.034x10	1.026x10 ²	2.347x10
10	0	8.828x10 ²	0	6.648x10 ²	0	3.851x10
11	4.202x10 ²	1.497x10 ²	3.637x10 ²	1.120x10 ²	2.772x10 ²	6.520x10 ²
12	0	2.572x10 ²	0	1.916x10 ²	0	1.127x10 ²
13	1.224x10 ³	4.475x10 ²	1.056x10 ³	3.330x10 ²	8.129x10 ²	1.986x10 ²
14	0	7.869x10 ²	0	5.862x10 ²	0	3.553x10 ²
15	3.738x10 ³	1.397x10 ³	3.229x10 ³	1.044x10 ³	2.523x10 ³	6.440x10 ²
16	0	2.503x10 ³	0	1.878x10 ³	0	1.180x10 ³
17	1.183x10 ⁴	4.518x10 ³	1.026x10 ⁴	3.411x10 ³	8.153x10 ³	2.180x10 ³
18	0	8.213x10 ³	0	6.243x10 ³	0	4.059x10 ³
19	3.854x10 ⁴	1.503x10 ⁴	3.364x10 ⁴	1.151x10 ⁴	2.715x10 ⁴	7.603x10 ³
20	0	2.766x10 ⁴	0	2.135x10 ⁴	0	1.431x10 ⁴
21	1.284x10 ⁵	5.119x10 ⁴	1.129x10 ⁵	3.984x10 ⁴	9.242x10 ⁴	2.706x10 ⁴
22	0	9.519x10 ⁴	0	7.470x10 ⁴	0	5.137x10 ⁴
23	4.363x10 ⁵	1.770x10 ⁵	3.866x10 ⁵	1.407x10 ⁵	3.202x10 ⁵	9.780x10 ⁴
24	0	3.335x10 ⁵	0	2.660x10 ⁵	0	1.867x10 ⁵
25	1.506x10 ⁶	6.279x10 ⁵	1.344x10 ⁶	5.048x10 ⁵	1.124x10 ⁶	3.574x10 ⁵
26	0	1.186x10 ⁶	0	9.610x10 ⁵	0	6.855x10 ⁵
27	5.269x10 ⁶	2.248x10 ⁶	4.737x10 ⁶	1.834x10 ⁶	3.994x10 ⁶	1.317x10 ⁶
28	0	4.273x10 ⁶	0	3.510x10 ⁶	0	2.535x10 ⁶
29	1.864x10 ⁷	8.142x10 ⁶	1.687x10 ⁷	6.732x10 ⁶	1.431x10 ⁷	4.887x10 ⁶
30	0	1.555x10 ⁷	0	1.294x10 ⁷	0	9.434x10 ⁶

Table 2. The quantities $\gamma_g^{(\infty)}(n)$ for the line core

	$\gamma_g^{(2)}(n)$	$\gamma_g^{(1)}(n)$	$\gamma_g^{(0)}(n)$
1	-1.257 x 10	-1.257 x 10	-1.571
2	-9.326 x 10 ⁻¹⁴	-2.887 x 10 ⁻¹⁴	-2.356
3	-3.128 x 10	-2.178 x 10	-1.963
4	-8.754	5.745	-1.211
5	-3.453 x 10	-1.348 x 10	-6.136 x 10 ⁻¹
6	-1.921 x 10	4.526	-2.675 x 10 ⁻¹
7	-2.668 x 10	-4.407	-1.027 x 10 ⁻¹
8	-1.816 x 10	1.509	-3.517 x 10 ⁻²
9	-1.579 x 10	-8.929 x 10 ⁻¹	-1.087 x 10 ⁻²
10	-1.044 x 10	2.887 x 10 ⁻¹	-3.053 x 10 ⁻³
11	-7.043	-1.229 x 10 ⁻¹	-7.861 x 10 ⁻⁴
12	-4.173	3.632 x 10 ⁻²	-1.867 x 10 ⁻⁴
13	-2.371	-1.219 x 10 ⁻²	-4.113 x 10 ⁻⁵
14	-1.241	3.255 x 10 ⁻³	-8.448 x 10 ⁻⁶
15	-6.152 x 10 ⁻¹	-9.111 x 10 ⁻⁴	-1.625 x 10 ⁻⁶
16	-2.863 x 10 ⁻¹	2.191 x 10 ⁻⁴	-2.939 x 10 ⁻⁷
17	-1.262 x 10 ⁻¹	-5.296 x 10 ⁻⁵	-5.015 x 10 ⁻⁸
18	-5.272 x 10 ⁻²	1.151 x 10 ⁻⁵	-8.098 x 10 ⁻⁹
19	-2.095 x 10 ⁻²	-2.460 x 10 ⁻⁶	-1.241 x 10 ⁻⁹
20	-7.932 x 10 ⁻³	4.858 x 10 ⁻⁷	-1.811 x 10 ⁻¹⁰
21	-2.869 x 10 ⁻³	-9.327 x 10 ⁻⁸	-2.519 x 10 ⁻¹¹
22	-9.929 x 10 ⁻⁴	1.683 x 10 ⁻⁸	-3.350 x 10 ⁻¹²
23	-3.293 x 10 ⁻⁴	-2.940 x 10 ⁻⁹	-4.266 x 10 ⁻¹³
24	-1.049 x 10 ⁻⁴	4.879 x 10 ⁻¹⁰	-5.213 x 10 ⁻¹⁴
25	-3.222 x 10 ⁻⁵	-7.824 x 10 ⁻¹¹	-6.120 x 10 ⁻¹⁵
26	-9.718 x 10 ⁻⁶	1.201 x 10 ⁻¹¹	-6.916 x 10 ⁻¹⁶
27	-2.814 x 10 ⁻⁶	-1.781 x 10 ⁻¹²	-7.531 x 10 ⁻¹⁷
28	-1.028 x 10 ⁻⁶	2.540 x 10 ⁻¹³	-7.915 x 10 ⁻¹⁸
29	2.107 x 10 ⁻⁸	-3.504 x 10 ⁻¹⁴	-8.038 x 10 ⁻¹⁹
30	9.011 x 10 ⁻⁸	4.668 x 10 ⁻¹⁵	-7.895 x 10 ⁻²⁰

CHAPTER VI. EXPERIMENTAL MEASUREMENTS

In this chapter we briefly discuss the experimental techniques used to measure dipole and quadrupole moments and second virial coefficients. Some comments about the accuracy of the methods are also given. We first discuss three techniques for measuring dipole moments in the gas phase.

The first reliable measurements of dipole moments were all based upon the application of the Debye equation to measurements of the low frequency permittivity (dielectric constant). Since measurements of the dielectric constant to determine the dipole moment involve bulk property measurements, substances of high purity and chemical stability are required and the experimental variables, density and temperature, must be accurately known. In addition the derived moments represent averages over the various molecular states of the system.

The second method for the measurement of dipole moments is the use of microwave spectroscopy to observe the Stark effect on the rotational energy levels of the molecule. When a polar molecule is placed in an external electric field of magnitude E , the rotational energy levels of the molecule are split through the Stark effect. If the total angular momentum of the molecule in the absence of the field is described by the quantum number J , application of the field results in partially removing the degeneracy of the $2J + 1$ associated angular momentum states. Measurement of the splittings of the spectral lines as a function of the applied field allows an accurate determination of the "splitting coefficients." A complete analysis of the microwave spectrum provides enough information to extract the dipole moment components along the principal inertial axes from the experimentally

determined splitting coefficients.

Measurements using microwave spectroscopy can, in principle, yield the value of a dipole moment to within an uncertainty of one percent or less. The purity of the sample is unimportant. In spite of these advantages a number of dipole moments measured by microwave spectroscopy are not accurate to within one percent. There are several reasons for this. Many spectra are complicated by nuclear quadrupole hyperfine structure, which introduces another perturbation which may be comparable in magnitude to the Stark effect. Another difficulty sometimes arises when the Stark effects of all accessible transitions are sensitive to one dipole component but quite insensitive to the others. Thus only one component can be determined with high accuracy, and the total moment is subject to a sizable uncertainty.

The last method of experimentally determining dipole moments which we discuss is a method very similar in principle to that of the previous method, since it makes use of the Stark effect on rotational levels. However, in this case, the measurement is carried out on a molecular beam. This procedure has several advantages. When the Stark effect is measured from the molecular beam the accuracy of the measurements is greatly improved since the spectral line widths are much smaller. Furthermore, the apparatus can be designed so that the electric field is more uniform and its absolute value more accurately measurable than is possible in the normal microwave absorption cell. The molecular beam technique offers the highest inherent accuracy of any known method of dipole moment determination. Uncertainties approaching 0.02 percent have been claimed by some investigators, and the

precision is an order of magnitude higher than this. The chief limitation of the molecular beam technique is the very restricted class of molecules to which it can be applied. This limitation results from the fact that the population is distributed over a large number of states except for diatomic or triatomic molecules. This results in a loss of sensitivity for the more complicated molecules.

There are a number of techniques which have been used to determine molecular quadrupole moments. However, we will discuss only two of the most recently developed methods. The earliest of these two techniques was suggested and implemented by Buckingham (19). The experiment is to measure the birefringence induced in a gas through the orientation of molecular electric quadrupole moments by an inhomogeneous electric field. The results lead to a determination of the magnitude and sign of the molecular quadrupole moment. The second technique of interest is that suggested and implemented by Flygare and Benson (20). It is the measurement of individual components in the molecular magnetic susceptibility and nuclear magnetic shielding tensors from microwave Zeeman effect in diamagnetic molecules under high magnetic fields. The measured components can be then directly related to the molecular electric quadrupole moment.

The second technique (Flygare) for measuring quadrupole moments has been used in the measurement of many molecules and is considered the most reliable method currently available for measuring molecular quadrupole moments.

The second virial coefficient may be obtained from experimental p - V - T data in several different ways. We discuss only the most commonly used

method. The second virial coefficient is determined experimentally from gas-compressibility data by curve fitting the results at a given temperature by a polynomial in reciprocal volume. The coefficients of this finite polynomial are then identified with the coefficients of the infinite virial series. Values for the virial coefficients obtained in this way depend on the degree of the polynomial used and on the density range of the compressibility data.

The resulting uncertainty in the second virial coefficient should theoretically be small (usually less than one percent); however, in many cases the uncertainty is only less than ten percent. This results from the dependence of $B(T)$ on the pressure range of the measurements and upon the degree of the polynomial used in the curve-fit process. Hence, unless the data extend to sufficiently low pressures, the 1st coefficient of the fitting polynomial is not necessarily the second virial coefficient. Most of the careful measurements of compressibilities of gases have been made at moderate and high pressures so that it is difficult to obtain reliable values of $B(T)$.

CHAPTER VII. NUMERICAL RESULTS

In this chapter we use the core models mentioned in Chapter V to test the numerical consequences of our theory. For simplicity we have confined our model studies to a limited number of polyhedral shapes although it certainly would be possible to design a core specifically for each molecule. For example, a tetrahedron has been used as a core for all five of the methane derivatives we consider even though trigonal pyramids of various shapes would be more appropriate. In most cases the accuracy of the experimental data does not warrant such refinements. We consider four basic core shapes. These are the line, the isosceles triangle, the regular hexagon and the regular tetrahedron. For H_2S , H_2O and SO_2 , respectively, we use the isosceles triangle cores with a bond angle of 90° , 109° and 120° . A more critical discussion of suitable core shapes and results is given in the conclusions.

It is easy to show that $B(T)/Nl_0^3$ can be expressed as a function of the three dimensionless quantities kT/u_0 , b_e/l_0 , and either $\mu^2/u_0 l_0^3$ or $Q^2/u_0 l_0^5$ depending upon whether we consider the dipolar or quadrupolar cases. In Tables 3 through 17 we give numerical values for u_0 , σ_r and b_e for each molecule we consider. The σ_r parameter is the sum of the average core size, $\langle h \rangle$, and l_0 . As seen in Figure 4 this number gives an estimate of the size of the molecules.

One can readily generate $B_T(T)$ for any given set of parameters for molecules with a dipole or quadrupole moment from the quantities $\gamma_i^{(\infty)}(n)$ given in Table 1 and 2 and Equations (T.17), (C-4), and (5.29) or (5.37), respectively.

The parameters U_0 , σ_T , and b_e were obtained by fitting the theoretical second virial coefficient given by Equation (5.17) to the experimental second virial coefficient, $B_{\text{exp}}(T)$. For each data set, two theoretical virial coefficients are fitted to the data: these are derived from the Stockmayer model (9), ($B_s(T)$), and from the model of the present work, ($B_T(T)$).

The fitting procedure involves the use of a program known as CURFIT, which is given by Bevington (21). This program adjusts the parameters U_0 , σ_T and b_e simultaneously until χ^2 or Δ^2 is minimized. The χ^2 and Δ^2 functions are defined by

$$\chi^2 = \sum_i \left\{ \frac{B_{\text{calc.}}(T_i) - B_{\text{exp}}(T_i)}{E_{\text{exp}}(T_i)} \right\}^2$$

and

$$\Delta^2 = \sum \left\{ B_{\text{calc.}}(T_i) - B_{\text{exp}}(T_i) \right\}^2$$

where $B_{\text{calc.}}$ is B_s or B_T and where $E_{\text{exp}}(T_i)$ is the experimental error in $B_{\text{exp}}(T_i)$, and where T_i is the i^{th} experimental temperature. The sum is over the available experimental points. The quantity Δ^2 is used when no experimental errors are available, or when the available experimental errors are so large that no statistical discrimination between the Stockmayer model and the present model is possible.

In Tables 3 through 16 we give for molecules with a nonzero dipole moment, the quantities $B_{\text{exp}}(T)$, $B_T(T)$, and $B_s(T)$, the χ^2 or Δ^2 values, the potential parameters, and the dipole moment value, μ . Only in the cases of CO and propyne (Tables 3 and 6, respectively) are the errors small enough to warrant calculating χ^2 ; in all other cases Δ^2 is reported.

In Tables 3 and 6, χ^2 probabilities, $P(\chi^2)$, are also given.

In Table 17 we give $B_{\text{exp}}(T)$ and $B_T(T)$ for CO_2 (a linear, quadrupolar molecule), calculated using Equations (5.17) and (5.37). The parameters obtained from CURFIT, the Δ^z value and the value for the quadrupole moment are also given.

Analysis and comparisons of this data to other published data are made in Chapter VIII.

One can readily generate $B_T(T)$ for any given set of parameters for molecules with a dipole or quadrupole moment from the quantities given in Table 1 or 2 and Equations (5.17), (C-4), and (5.29) or (5.37), respectively.

Table 3. Comparison of experimental (B_{exp}) (22), present work (B_T) and Stockmayer's (B_S) values of the second virial coefficients in cm^3/mole for CO as a function of temperature

$T(^{\circ}\text{K})$	B_{exp}^a	B_T^b	B_S
90.67	-233.0	-233.0	-232.2
273.2	- 13.65	- 14.01	- 16.93
298.2	- 7.95	- 7.95	- 10.04
323.2	- 3.29	- 2.97	- 4.36
348.2	1.06	1.17	.393
373.2	4.57	4.67	4.43
398.2	7.67	7.66	7.88
423.2	10.16	10.25	10.87
473.2	14.50	14.47	15.77
513.2	17.30	17.17	18.90
573.2	20.50	20.41	22.66

$\mu = .13$ Debye (23)	$u_o \times 10^{14} = 2.117$ ergs	1.397 ergs
	$\sigma = 2.709$ Å	3.913 Å
	$b_e = .987$ Å	0 Å ^c
	$\chi^2 = 0.2$	26.8
	$P(x) \approx 99\%$	$\approx 0.1\%$
	Present Work	Stockmayer

^aAccuracy of $B_{\text{exp}} \pm 1$.

^bLine core.

^cFixed.

Table 4. Comparison of experimental (B_{exp}) (24), present work (B_T) and Stockmayer's (B_S) values of the second virial coefficients in cm^3/mole for N_2O as a function of temperature

$T(^{\circ}\text{K})$	B_{exp}	B_T^a	B_S
200.0	-346.	-346.	-340.
225.0	-268.	-269.	-273.
250.0	-218.	-217.	-222.
275.0	-181.	-181.	-181.
300.0	-153.	-153.	-149.

$\mu = 0.18$ Debye (23)	$U_0 \times 10^{14} = 6.783$ ergs	2.249 ergs
	$\sigma_r = 2.621 \text{ \AA}$	5.353 $\text{\AA}$
	$b_e = .267 \text{ \AA}$	0 $\text{\AA}^b$
	$\Delta^z = 1.4$	86.8
	Present Work	Stockmayer

^aLine Core.

^bFixed.

Table 5. Comparison of experimental (B_{exp}) (25), present work (B_T) and Stockmayer's (B_S) values of the second virial coefficients in cm^3/mole for HCl as a function of temperature

$T(^{\circ}\text{K})$	B_{exp}	B_T^a	B_S
373	-102.5	-102.9	-98.5
423	- 66.43	- 65.67	-70.3
473	- 44.90	- 44.98	-48.9
523	- 32.30	- 32.10	-32.2
573	- 22.60	- 23.43	-18.9

$\mu = 1.03$ Debye (23)	$U_0 \times 10^{14} = 2.56$ ergs	2.67 ergs
	$\sigma_r = 2.50$ Å	4.80 Å
	$b_e = 1.30$ Å	0.0 Å ^b
	$\Delta^z = 1.5$	61.5
	Present Work	Stockmayer

^aLine Core.

^bFixed.

Table 6. Comparison of experimental (B_{exp}) (26), present work (B_T) and Stockmayer's (B_S) values of the second virial coefficients in cm^3/mole for $\text{H}_3\text{C} - \text{C} \equiv \text{C} - \text{H}$ as a function of temperature

$T(^{\circ}\text{K})$	B_{exp}^a	B_T^b	B_S
348.2	-287.8	-287.9	-288.4
373.2	-244.0	-243.8	-243.3
398.2	-210.0	-209.8	-209.3
423.2	-182.8	-183.1	-182.8
448.2	-161.3	-161.5	-161.7
473.2	-144.0	-143.8	-144.5

$\mu = .781$ Debye (23)	$U_0 \times 10^{14} = 11.1$ ergs	12.8 ergs
	$\sigma_r = 3.06 \text{ \AA}$	2.33 $\text{ \AA}$
	$b_e = 1.70 \text{ \AA}$	0.0 $\text{ \AA}^c$
	$\chi^2 = 0.3$	1.5
	$P(\chi^2) \approx 95\%$	$\approx 80\%$
	Present Work	Stockmayer

^aAccuracy of $B_{\text{exp}} \pm 1$.

^bLine core.

^cFixed.

Table 7. Comparison of experimental (B_{exp}) (26), present work (B_T) and Stockmayer's (B_S) values of the second virial coefficients in cm^3/mole for SO_2 as a function of temperature

$T(^{\circ}\text{K})$	B_{exp}	B_T^a	B_S
280.0	-494.0	-493.5	-496.6
330.0	-318.0	-320.1	-312.3
380.0	-225.0	-223.3	-219.6
430.0	-164.0	-162.4	-165.1
480.0	-119.0	-120.8	-129.7

$\mu = 1.01$ Debye (23)	$U_0 \times 10^{14} = 4.93$ ergs	6.38 ergs
	$\sigma_r = 4.50$ Å	2.98 Å
	$b_e = 1.35$ Å	0.0 Å ^b
	$\Delta^z = 13.2$	184.8
	Present Work	Stockmayer

^a120° isosceles triangle core.

^bFixed.

Table 8. Comparison of experimental (B_{exp}) (26), present work (B_T) and Stockmayer's (B_S) values of the second virial coefficients in cm^3/mole for H_2O as a function of temperature

$T(^{\circ}\text{K})$	B_{exp}	B_T^a	B_S
423.1	-334.0	-334.0	-334.1
573.1	-117.1	-117.5	-116.4
873.2	- 35.2	- 34.1	- 34.8
1173.	- 11.6	- 12.4	- 13.8

$\mu = 1.83$ Debye (23)

$u_0 \times 10^{14} = 3.61$ ergs

3.74 ergs

$\sigma_r = 2.67 \text{ \AA}$

2.53 $\text{\AA}$

$b_s = .117 \text{ \AA}$

0.0 $\text{\AA}^b$

$\Delta^+ = 1.8$

5.4

Present Work

Stockmayer

^a_{109°} isosceles triangle core.

^bFixed.

Table 9. Comparison of experimental (B_{exp}) (26) present work (B_T) and Stockmayer's (B_S) values of the second virial coefficients in cm^3/mole for H_2S as a function of temperature

$T(^{\circ}\text{K})$	B_{exp}	B_T^a	B_S
283.2	-500.0	-498.0	-500.0
318.2	-347.0	-354.0	-350.0
368.2	-245.0	-239.0	-236.7
423.2	-171.0	-169.0	-170.2
473.2	-125.8	-128.1	-135.5

$\mu = .97$ Debye (23)	$u_0 \times 10^{14} = 8.59$ ergs	11.49 ergs
	$\sigma_r = 3.58$ Å	2.34 Å
	$b_e = 1.51$ Å	0.0 Å ^b
	$\Delta^z = 1.8$	137.7
	Present Work	Stockmayer

^a90° isosceles triangle core.

^bFixed.

Table 10. Comparison of experimental (B_{exp}) (26) present work (B_T) and Stockmayer's (B_S) values of the second virial coefficients in cm^3/mole for fluorobenzene as a function of temperature

$T(^{\circ}\text{K})$	B_{exp}	B_T^a	B_S
318.4	-1446	-1450	-1458
336.8	-1275	-1264	-1257
357.9	-1086	-1084	-1080
382.4	- 909	- 911	- 922
<hr/>			
$\mu = 1.60$ Debye (23)		$U_0 \times 10^{14} = 6.36$ ergs	12.60 ergs
		$\sigma_T = 7.81 \text{ \AA}$	3.74 $\text{\AA}$
		$b_e = 2.30 \text{ \AA}$	0.0 $\text{\AA}^b$
		$\Delta^z = 16.2$	678.3
		<hr/>	
		Present Work	Stockmayer

^aRegular hexagon core.

^bFixed.

Table 11. Comparison of experimental (B_{exp}) (26) present work (B_T) and Stockmayer's (B_S) values of the second virial coefficients in cm^3/mole for pyridine as a function of temperature

$T(^{\circ}\text{K})$	B_{exp}	B_T^a	B_S
349.1	-1263	-1266	-1281
363.0	-1132	-1149	-1143
376.9	-1052	-1043	-1029
393.1	- 973	- 931	- 918
409.0	- 823	- 831	- 828
424.0	- 759	- 746	- 757
437.8	- 650	- 673	- 700

$$\mu = 2.19 \text{ Debye (23)}$$

$$U_e \times 10^{14} = 3.67 \text{ ergs}$$

$$11.45 \text{ ergs}$$

$$\sigma_T = 10.42 \text{ \AA}$$

$$3.67 \text{ \AA}$$

$$b_e = 1.27 \text{ \AA}$$

$$0.0 \text{ \AA}^b$$

$$\Delta^L = 2908$$

$$6476$$

Present Work

Stockmayer

^aRegular hexagon core.

^bFixed.

Table 12. Comparison of experimental (B_{exp}) (26) present work (B_T) and Stockmayer's (B_S) values of the second virial coefficients in cm^3/mole for CH_3F as a function of temperature

$T(^{\circ}\text{K})$	B_{exp}	B_T^a	B_S
280	-244	-244	-245
300	-206	-205	-205
320	-174	-174	-174
340	-150	-150	-149
360	-129	-129	-129
380	-112	-113	-113
400	- 99	- 99	- 99
420	- 87	- 87	- 88

$\mu = 1.85$ Debye (23)	$U_0 \times 10^{14} = 2.79$ ergs	2.73 ergs
	$\sigma_r = 3.79 \text{ \AA}$	2.52 $\text{\AA}$
	$b_e = .253 \text{ \AA}$	0.0 $\text{\AA}^b$
	$\Delta^2 = 2.3$	5.7
	Present Work	Stockmayer

^aRegular tetrahedron core.

^bFixed.

Table 13. Comparison of experimental (B_{exp}) (26) present work (B_T) and Stockmayer's (B_S) values of the second virial coefficients in cm^3/mole for CH_3Cl as a function of temperature

$T(^{\circ}\text{K})$	B_{exp}	B_T^a	B_S
280	-465	-464	-455
320	-345	-347	-350
360	-264	-266	-272
400	-212	-208	-214
460	-146	-144	-148
500	-111	-113	-114
540	- 85	- 87	- 86
580	- 66	- 66	- 63
623	- 47	- 47	- 41

$\mu = 1.87$ Debye (23)	$U_0 \times 10^{14} = 4.08$ ergs	2.91 ergs
	$\sigma_r = 5.28 \text{ \AA}$	6.07 $\text{\AA}$
	$b_e = .882 \text{ \AA}$	0.0 $\text{\AA}^b$
	$\Delta^z = 42.2$	254.4
	Present Work	Stockmayer

^aRegular tetrahedron core.

^bFixed.

Table 14. Comparison of experimental (B_{exp}) (26) present work (B_T) and Stockmayer's (B_S) values of the second virial coefficients in cm^3/mole for CF_3Cl as a function of temperature

$T(^{\circ}\text{K})$	B_{exp}	B_T^a	B_S
298.2	-225.5	-226.8	-228.9
303.2	-220.4	-218.2	-218.8
323.2	-186.5	-187.8	-185.2
348.2	-157.3	-157.2	-154.1
373.2	-132.9	-132.6	-131.1
398.2	-112.8	-112.4	-113.5
423.2	- 95.20	- 95.57	- 99.7
<hr/>			
$\mu = 0.50$ Debye (23)	$U_0 \times 10^{14} = 6.86$ ergs		12.70 ergs
	$\sigma_T = 4.00 \text{ \AA}$		1.94 $\text{\AA}$
	$b_e = 1.68 \text{ \AA}$		0.0 $\text{\AA}^b$
	$\Delta^2 = 8.7$		50.1
	<hr/>		<hr/>
	Present Work		Stockmayer

^aRegular tetrahedron core.

^bFixed.

Table 15. Comparison of experimental (B_{exp}) (26) present work (B_T) and Stockmayer's (B_S) values of the second virial coefficients in cm^3/mole for CCl_3H as a function of temperature

$T(^{\circ}\text{K})$	B_{exp}	B_T^a	B_S
320	-1000	-1002	-1007
340	- 860	- 857	- 852
360	- 740	- 739	- 734
380	- 640	- 642	- 641
400	- 560	- 560	- 567

$\mu = 1.01$ Debye (23)	$U_0 \times 10^{14} = 8.42$ ergs	14.30 ergs
	$\sigma_r = 6.31$ Å	3.06 Å
	$b_e = 3.32$ Å	0.0 Å ^b
	$\Delta^z = 14.3$	207.9
	Present Work	Stockmayer

^aRegular tetrahedron core.

^bFixed.

Table 16. Comparison of experimental (B_{exp}) (26) present work (B_T) and Stockmayer's (B_S) values of the second virial coefficients in cm^3/mole for CCl_3F as a function of temperature

$T(^{\circ}\text{K})$	B_{exp}	B_T^a	B_S
238.7	-1150	-1158	-1158
249.8	-1070	-1069	-1069
283.2	- 862	- 855	- 855
310.9	- 720	- 720	- 720
338.7	- 617	- 612	- 612
366.5	- 523	- 523	- 523
394.3	- 459	- 450	- 450
422.0	- 381	- 387	- 387
449.8	- 328	- 334	- 334

$\mu = .45$ Debye (23)	$U_0 \times 10^{14} = 3.3$ ergs	3.32 ergs
	$\sigma_T = 7.10 \text{ \AA}$	7.10 $\text{\AA}$
	$b_e = 0.0 \text{ \AA}$	0.0 $\text{\AA}^b$
	$\Delta^* = 298$	298
	Present Work	Stockmayer

^aRegular tetrahedron core.

^bFixed.

Table 17. Comparison of experimental (B_{exp}) (19) and present work (B_T) values of the second virial coefficient in cm^3/mole for CO_2 as a function of temperature

T	$B_{\text{exp}}(T)$	$B(T)^a$
203.8	-330.0	-330.6
223.8	-226.0	-244.1
273.2	-148.0	-144.9
323.2	-102.1	-95.7
373.2	-71.3	-66.6
423.2	-50.4	-47.4
473.2	-33.3	-33.8
523.2	-25.1	-23.7
573.2	-14.9	-15.9
623.2	-9.4	-9.7
673.2	-2.6	-4.7
723.2	.9	.5
773.2	5.4	2.9
873.2	12.1	8.4

$$U_0 = 2.585 \times 10^{-14} \text{ ergs}$$

$$\sigma_T = 3.611 \text{ A}$$

$$b_e = .160 \text{ A}$$

$$\Delta^* = 525$$

$$Q = 4.3 \times 10^{-25} \text{ esu} \cdot \text{cm}^2 \text{ (19)}$$

Present Work

^aLine Core.

Figure 4. A plot of the valence repulsion and dispersion terms of the present model

CHAPTER VIII. CONCLUSIONS

In this chapter we make comparisons between the present model and several other models. We also discuss the significance of the potential parameters of the molecules.

In Figure 5 we show a difference plot for comparison of the second virial coefficients calculated from the present model ($B_T(T)$), the Stockmayer model ($B_S(T)$), and the Kihara model ($B_K(T)$) to the Lennard-Jones model ($B_{LJ}(T)$) for CH_3Cl using a single set of parameters. Using the difference $B_K(T) - B_{LJ}(T)$ we see from Figure 5 that including the non-spherical valence repulsion and dispersion terms of Kihara causes the second virial coefficient values to increase; the increase is much greater at lower temperatures. Thus one can see from the much lower $B(T)$ values at low temperatures for the Lennard-Jones and Stockmayer models that they tend to underestimate the $B(T)$ due to the fact they do not include the nonspherical valence repulsion and dispersion terms.

By considering the difference $B_S(T) - B_{LJ}(T)$ one can see from Figure 5 that the effect of the electrostatic potential is to decrease the value of the second virial coefficient at all temperatures and, moreover, the decrease is larger at lower temperatures. Thus one can see that the Kihara model overestimates $B(T)$, particularly at low temperatures, because it does not take into account the electrostatic interaction. The present model gives a larger electrostatic contribution than the Stockmayer model, particularly at low temperatures, since the "floating" dipole is located on the surface of the core. This can be seen from

Figure 5 by comparing the difference between $(B_T(T) - B_{LJ}(T))$ and $(B_K(T) - B_{LJ}(T))$ to $(B_S(T) - B_{LJ}(T))$.

In Table 3 the χ^2 probabilities, $P(\chi^2)$, for the two fits show that the present model fit is clearly superior to that for the Stockmayer model. However, in Table 6, the $P(\chi^2)$ values show the present model and the Stockmayer model fits to be essentially equivalent statistically. This can be understood from the fact that propyne has a fairly large dipole whereas CO has a very small dipole. Thus one would expect that the nonspherical potential for propyne is dominated by the dipole-dipole interaction. Thus the second virial coefficient is much more like that for the Stockmayer model. For CO the nonspherical interaction is dominated by the nonspherical valence repulsion and dispersion terms.

As shown in Tables 3 through 16, the optimum σ_T parameters for the Stockmayer model have almost no correlation to molecular size. For our model, however, the optimum σ_T parameters increase in accord with our concept of molecular size. However, it should be pointed out that for the nonpolar molecules CH_4 , CF_4 and CCl_4 , we find σ_T values of 3.62 Å, 4.18 Å, and 4.74 Å, respectively, whereas σ_T for CCl_3F is 7.10 Å. We would expect CCl_4 to be larger based on physical arguments. Part of the reason for this anomaly can perhaps be attributed to the use of the tetrahedral core instead of a trigonal pyramid shape for CCl_3F . We have not attempted to refine the calculation by such alterations of core shape, first, because the experimental uncertainty for the most part does not warrant it and, second, because our purpose is mainly to show in general,

how calculations for the present potential model can be made. Future work could include modification of the shapes and sizes of the cores and a change of the soft potential function.

Figure 5. A difference plot for comparison of the second virial coefficients calculated from the present model ($B_T(T)$), the Stockmayer model ($B_S(T)$), and the Kihara model ($B_K(T)$) to the Lennard-Jones model ($B_{\text{LJ}}(T)$)

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APPENDIX A

The second virial coefficient as a functional of the intermolecular potential is given by

$$B(kT) = 2\pi N \int_0^\infty \{1 - \exp(-\phi(r)/kT)\} r^2 dr$$

Introducing the new variables $\beta = 1/kT$ and $\omega = r^3$, we see that B is a function of β and ϕ can be considered a function of ω . Rewriting $B(kT)$ as

$$B(\beta) = \frac{2\pi N}{3} \int_0^\infty \{1 - \exp(-\beta\phi)\} d\omega \quad (A-1)$$

and differentiating Equation (A-1) with respect to β we obtain

$$B'(\beta) = \frac{2\pi N}{3} \int_0^\infty \phi \exp(-\beta\phi) d\omega \quad (A-2)$$

Now suppose that ϕ is monotonic and repulsive so that $\phi' < 0$. Then ϕ and ω are monotonic functions of each other, so we may introduce ϕ as the integration variable in Equation (A-2) and obtain

$$B'(\beta) = -\frac{2\pi N}{3} \int_0^\infty \left(\frac{\phi}{\phi'}\right) \exp(-\beta\phi) d\phi \quad (A-3)$$

We have chosen the lower limit as zero in Equation (A-3) since ϕ must vanish as r (or ω) becomes infinite. The upper limit is chosen as infinity since ϕ may become infinite when r or ω is zero. (If $\phi(\omega)$ has a maximum value $\phi(0)$ we will define ϕ/ϕ' to be zero for $\phi > \phi(0)$.) From Equation (A-3) we see that $-3/2 N B'(\beta)$ is the Laplace transform of ϕ/ϕ' . Therefore ϕ/ϕ' is the inverse Laplace transform, L^{-1} of $-3/2 N B'(\beta)$ i.e.,

$$\left(\frac{\phi}{\phi'}\right) = -\frac{3}{2\pi N} L^{-1}[B'(\beta)] \quad (A-4)$$

Equation (A-4) is an ordinary differential equation for ϕ as a function of ω . Its solution is given by

$$\omega = \frac{3}{2\pi N} \int_{\phi}^{\infty} \frac{L^{-1}[B'(\beta)]}{\phi} d\phi \quad (A-5)$$

The upper limit is infinity in Equation (A-5) since ϕ may become infinite at $\omega = 0$. However, if $\phi(\omega)$ is finite then $L^{-1}(B'(\beta))$ must be zero for $\phi > \phi(\omega)$ and the upper limit is effectively $\phi(\omega)$. Equation (A-5) determines the repulsive potential, ϕ , as a function of ω or of r , since $\omega = r^3$.

If ϕ is monotonic and attractive we obtain, instead of Equation (A-5)

$$\omega = \frac{3}{2\pi N} \int_{-\infty}^{\phi} \frac{L^{-1}[B'(\beta)]}{\phi} d\phi$$

Now if we wish to look at potentials which are nonmonotonic we start at Equation (A-2). Now we introduce ϕ as a new integration variable separately in each range of ω in which ϕ is monotonic. If, for example, we look at a potential which has two such ranges (e.g., a Lennard-Jones type curve as in Figure 2.). We define ϕ_0 as the minimum value of ϕ , and ϕ'_- and ϕ'_+ as the derivative of ϕ in the decreasing and increasing ranges, respectively. Then from Equation (A-2) we obtain

$$\begin{aligned} B'(\beta) &= -\frac{2\pi N}{3} \int_{\phi_0}^{\infty} \left(\frac{\phi}{\phi'} \right) \exp(-\beta\phi) d\phi + \frac{2\pi N}{3} \int_{\phi_0}^{\phi_0} \left(\frac{\phi}{\phi'} \right) \exp(-\beta\phi) d\phi \\ &= \frac{2\pi N}{3} \int_{\phi_0}^{\infty} \left[\left(-1/\phi'_- \right) + \left(1/\phi'_+ \right) \right] \phi \exp(-\beta\phi) d\phi \end{aligned} \quad (A-6)$$

Here $(1/\phi'_+)$ is zero for $\phi > 0$. From Equation (A-6) we obtain

$$\left[(-1/\phi_-') + (1/\phi_+') \right] \phi = - \frac{3}{2\pi N} L^{-1} [B'(\beta)] \quad (\text{A-7})$$

If $\phi > 0$, $1/\phi_+$ is zero and Equation (A-7) coincides with Equation (A-4) which has the solution Equation (A-5). In the region $\phi < 0$ we define two inverse functions $\omega_-(\phi)$ and $\omega_+(\phi)$ which give the two values of ω at which ϕ has a given value. Again the subscript indicates whether the function $\omega_-(\phi)$ or $\omega_+(\phi)$ refers to the decreasing or increasing part of $\phi(\omega)$. Thus $1/\phi_- = \omega_-'$ and $1/\phi_+ = \omega_+'$. Substituting these variables into Equation (A-7) yields

$$(\omega_+' - \omega_-') = \frac{3}{2\pi N \phi} L^{-1} [B'(\beta)] . \quad (\text{A-8})$$

Integrating Equation (A-8) we obtain

$$\omega_+ - \omega_- = \frac{3}{2\pi N} \int_{\phi_0}^{\phi} \frac{L^{-1} [B'(\beta)]}{\phi} d\phi . \quad (\text{A-9})$$

The lower limit ϕ_0 was chosen in Equation (A-9) because at it $\omega_+ = \omega_-$ so $\omega_+ - \omega_- = 0$. Thus Equation (A-9) gives the width $\omega_+ - \omega_-$ of the potential well at any depth $\phi_1 = \phi$. Since $\omega = r^3$, Equation (A-9) gives the physical volume of space in which the potential is less than or equal to ϕ_1 , apart from a constant factor.

Equation (A-5) uniquely determines $\phi(r)$ in the range where ϕ is positive, while where $\phi < 0$, only the width of the well of any potential which yields the second virial coefficient $B(\beta)$ is determined, and it is given by Equation (A-9).

APPENDIX B

In general, one can write the multipole moment $\underline{Q}_i^{(s)}$ as

$$\underline{Q}_i^{(s)} = \int d\mathbf{x}_i \rho(\mathbf{x}_i) [(\mathbf{x}_i)^{(s)}]$$

where the square brackets $[]$ represent the irreducible part of the enclosed tensor, (note, in general for a system of point particles $\rho(\mathbf{x}_i)$ will be a sum of δ -functions) and one obtains

$$q_i = q$$

$$\mu_i = \mu,$$

etc. If we now consider the moments about a translated center

$$\underline{x}' = \underline{x} - \underline{a} \quad (\text{B-1})$$

we obtain

$$\underline{Q}_i^{(s)} = \int d\mathbf{x}_i' \rho'(\mathbf{x}_i') [(\mathbf{x}_i')^{(s)}] \quad (\text{B-2})$$

where

$$\rho'(\mathbf{x}_i') = \rho(\mathbf{x}_i).$$

Now substituting Equation (B-1) into Equation (B-2) we obtain

$$\underline{Q}_i^{(s)} = \int d\mathbf{x}_i \rho(\mathbf{x}_i) [(\mathbf{x}_i - \underline{a})^{(s)}] \quad (\text{B-3})$$

From Equation (B-3) we then obtain by means of a binomial expansion

$$\underline{Q}_i^{(s)} = \int d\mathbf{x}_i \rho(\mathbf{x}_i) \sum_{j=0}^s (-1)^{s-j} \binom{s}{j} \left[\underline{a}^{(s-j)} \underline{x}_i^{(j)} \right]. \quad (\text{B-4})$$

Integrating Equation (B-4) over $d\mathbf{x}_i$ we obtain

$$\underline{Q}_i^{(s)} = \sum_{j=0}^s (-1)^{s-j} \binom{s}{j} \left[\underline{Q}^{(s-j)} \underline{f}_i^{(j)} \right].$$

Identifying $\underline{Q}$ as the vector between the expansion centers we obtain Equations (4.3) and (4.4) in the text.

APPENDIX C

We now show that the hard core integral of Equation (5.11)

$$B_{H.C.} = \frac{N}{128\pi^4} \int d\hat{h} \int d\alpha_1 \int d\alpha_2 \int_0^{p_m} d\rho \left(-\frac{1}{2} \underline{G} : \underline{G} \right) \frac{\partial H}{\partial \rho} \equiv -\frac{N}{2} \int_0^{p_m} d\rho K_0(\rho) \quad (C-1)$$

yields Isihara's expression for the second virial coefficient for rigid convex molecules. From Equations (5-9), and (5-10) we have that

$$K_0(\rho) = 4\pi \frac{\rho^2}{\rho_m^3} \left\{ \langle \underline{g}_1 : \underline{g}_1, h_1 \rangle + \langle h_1 \rangle \langle \underline{g}_1 : \underline{g}_1 \rangle - \langle \underline{g}_1 : V_1 \rangle \langle \underline{g}_1 : V_1, h_1 \rangle \right\} \quad (C-2)$$

where h_1 is the supporting function of the core,

$$\underline{g}_1 = h_1 \underline{V}_1 + \frac{\partial^2 h_1}{\partial \hat{h}_1^2} \cdot \underline{V}_1,$$

and the symbol $\langle \rangle$ means $\frac{1}{8\pi^2} \int d\alpha_1$.

It is easily established from Equation (5.3) and the subsequent discussion that

$$K_0(\rho) = -4\pi \frac{\rho^2}{\rho_m^3} \left\{ \frac{6}{4\pi} (V + MS) - 2M \langle \underline{g}_1 : \frac{\partial^2 h_1}{\partial \hat{h}_1^2} \cdot \underline{V}_1 \rangle \right\} \quad (C-3)$$

where V is the volume of the core, S is the core surface area and

$M = \langle h_1 \rangle$. The integral

$$\langle \underline{g}_1 : \frac{\partial^2 h_1}{\partial \hat{h}_1^2} \cdot \underline{V}_1 \rangle$$

can be shown to vanish by the following manipulations:

$$\begin{aligned}
\left\langle \underline{f}_1 : \frac{\partial^2 h_1}{\partial \hat{k}_1^2} \cdot \underline{V}_1 \right\rangle &= \left\langle \left(h_1 \underline{V}_1 + \frac{\partial^2 h_1}{\partial \hat{k}_1^2} \cdot \underline{V}_1 \right) : \frac{\partial^2 h_1}{\partial \hat{k}_1^2} \cdot \underline{V}_1 \right\rangle \\
&= - \left\langle h_1 \frac{\partial}{\partial \hat{k}_1} \cdot \frac{\partial}{\partial \hat{k}_1} h_1 \right\rangle + \left\langle \frac{\partial^2 h_1}{\partial \hat{k}_1^2} : \frac{\partial^2 h_1}{\partial \hat{k}_1^2} - \left(\frac{\partial}{\partial \hat{k}_1} \cdot \frac{\partial}{\partial \hat{k}_1} h_1 \right)^2 \right\rangle \\
&= -\frac{1}{2} \frac{\partial}{\partial \hat{k}_1} \cdot \frac{\partial}{\partial \hat{k}_1} \langle h_1^2 \rangle + \left\langle \frac{\partial h_1}{\partial \hat{k}_1} \cdot \frac{\partial h_1}{\partial \hat{k}_1} \right\rangle \\
&\quad + \frac{\partial}{\partial \hat{k}_1} \cdot \left\{ \frac{\partial}{\partial \hat{k}_1} \left\langle \frac{\partial h_1}{\partial \hat{k}_1} \cdot \frac{\partial h_1}{\partial \hat{k}_1} \right\rangle - 2 \hat{k}_1 \left\langle \frac{\partial h_1}{\partial \hat{k}_1} \cdot \frac{\partial h_1}{\partial \hat{k}_1} \right\rangle \right. \\
&\quad \left. - \frac{\partial}{\partial \hat{k}_1} \cdot \left\langle \frac{\partial h_1}{\partial \hat{k}_1} \right\rangle \right\}
\end{aligned}$$

Since the integrals $\langle \rangle_1$ are integrated over all orientations at fixed $\hat{k}$, they must be isotropic in the subspace normal to $\hat{k}$. Hence

$$\left\langle \underline{f}_1 : \frac{\partial^2 h_1}{\partial \hat{k}_1^2} \cdot \underline{V}_1 \right\rangle = \left[\frac{\partial}{\partial \hat{k}_1} \cdot \left\{ -2 \hat{k}_1 + \frac{1}{2} \frac{\partial}{\partial \hat{k}_1} \cdot (\hat{k}_1 \hat{k}_1) \right\} + 2 \right] \left\langle \frac{\partial h_1}{\partial \hat{k}_1} \cdot \frac{\partial h_1}{\partial \hat{k}_1} \right\rangle = 0.$$

Finally by substituting Equation (C-3) into Equation (C-1) and integrating we obtain

$$B_{H.C.} = N(V + MS) \tag{C-4}$$

which is Isihara's result.