CHAPTER - 1

THE LIQUID STATE AND ITS CHARACTERISTIC

CONTENTS

1.1 INTRODUCTION

1.2 LIQUID STRUCTURE

1.3 PERTURBATION THEORIES OF SPHERICAL MOLECULES

1.4 THERMODYNAMIC PERTURBATION THEORY OF NON-SPHERICAL MOLECULAR FLUIDS

1.5 THE EQUATION OF STATE – THE VIRIAL COEFFICIENTS
   The Second Virial Coefficient For Non-Spherical Molecules

1.6 KIHARA’S GENERALIZED SPHEROCYLINDRICAL MOLECULES

1.7 EXAMPLES OF SPHERICAL AND NON-SPHERICAL MOLECULES

1.8 REFERENCES
1.1 INTRODUCTION

The equation of state and the transport properties of gases and liquids are intimately related to the forces between the molecules. The statistical mechanical theories which relate the bulk properties to the intermolecular forces are highly developed for dilute gases and developed to a lesser extent for dense gases and liquids. From measurements of any of these macroscopic properties it is in principle possible to determine the law of force between the molecules. Furthermore, once the law of force has been determined, it is possible to calculate the equation of state or the transport properties. In this manner one reduces the description of a great number of equilibrium and non-equilibrium phenomena to a common basis and understands their interrelation from a molecular viewpoint.

Since the existence of liquids depends on intermolecular forces, we might expect that studies of the liquid state would provide much information about molecular interactions. This was not generally true in the past, as a consequence of the complex connection between the properties of liquids and the forces between molecules. This connection is provided by statistical mechanics and it is only quite recently that adequate theories of the liquid state have been developed. However, the deficiencies in statistical mechanics may be substantially by-pass by the use of a technique that has become increasingly important in recent years, the direct simulation of systems containing many molecules using computers.

These computer simulation procedures make it possible to determine
the structural and thermodynamic properties of assemblies of molecules that interact with a known form of intermolecular potential, without introducing statistical mechanical approximations. They have produced essentially exact results for model systems with well-defined intermolecular forces, which are valuable in testing other approaches to the liquid state. Unfortunately, computer simulations are relatively costly, and they have not been widely used in the characterization of accurate intermolecular potentials from studies of liquid state properties. Indeed, almost all studies of liquids have adopted simplified representations of the intermolecular pair potential, and have generally made the further assumption that the intermolecular energy is pairwise additive.

Despite these limitations, computer simulations have provided invaluable evidence to support the belief that it is the repulsive intermolecular forces that determine the way in which the molecules pack together in the liquid, in the absence of strongly directional attractive forces such as hydrogen bonds. This simple picture of liquid structure provides the basis for the very successful perturbation theories of liquids, which probably provide the most reliable economical route to liquid-state properties at the present time.

1.2 LIQUID STRUCTURE

In spite of the high densities which characterize the liquid state, liquids do not show the regular periodic structure that is characteristic of solids, whose density is similar. The structure of liquids is characterized by a certain degree of molecular ordering at short separations, but no long-range order.
The description of the structure may conveniently be carried out for spherical molecules using the radial distribution function, \( g(r) \), which measures the probability of finding another molecule at a distance \( r \) from a central reference molecule. For a system of \( N \) molecules in a total volume, \( V \), the number of molecules, \( n(r) \), in the volume element, \( 4\pi r^2 \, dr \), at a distance \( r \) from a central molecule is given by

\[
n(r) = \frac{N}{V} g(r) 4\pi r^2 \, dr. \tag{1.1}
\]

The total number of pairs of molecules whose separations lie in the range \( r \) to \( r + dr \), is then related to \( g(r) \) by the expression

\[
n'(r) = \frac{N^2}{2V} g(r) 4\pi r^2 \, dr. \tag{1.2}
\]

For a system in which the molecules interact only through a pair-wise additive intermolecular potential, \( U(r) \), the total intermolecular energy may be readily calculated.

\[
U_n = \frac{2\pi N^2}{V} \int_0^\infty U(r) g(r) r^2 \, dr \tag{1.3}
\]

and the pressure may then be obtained in terms of the forces between the molecules using the virial theorem of Clausius

\[
P V = N k T - \frac{1}{3} \sum_{i<j} r_{ij} F(r_{ij})
\]
or, in this case,

\[
\frac{PV}{NkT} = 1 - \frac{2\pi N}{3kTV} \int_0^\infty g(r) \frac{dU(r)}{dr} r^3 dr
\]  

(1.4)

other properties may be obtained from these by standard thermodynamic manipulations.

The above expressions are valid only if the total intermolecular potential energy can be written as a sum of pair interactions. If non-additive many-body interactions are present, then higher order distribution functions must also be considered. The most important of these is the triple distribution function, \( g_3(r_1, r_2, r_3) \), which measures the probability that a molecule will be found at a position \( r_3 \), when two other molecules are at \( r_1 \) and \( r_2 \). If the only important non-additive interactions are the three-body terms (as seems usually to be the case), then a knowledge of the triplet function, together with the radial distribution function, is sufficient to determine the equilibrium properties of the system.

However, the principal structural information is contained in the radial distribution function, and the typical appearance of \( g(r) \) for a simple liquid is shown in fig. 1.1. It is seen that for a liquid, \( g(r) \) is zero for small values of \( r \), where owing to the large positive values of the intermolecular energy the molecules do not overlap. At a value of \( r \) near to the molecular collision diameter, \( \sigma \), \( g(r) \) increases rapidly, and reaches a maximum value of 2-3 near to \( r = r_m \). Hence the probability of finding a molecule at such a distance from
Fig. 1.1: Radial distribution functions for monoatomic substances. (i) Liquid; (ii) Solid; (iii) Dilute gas.
a central molecule is several times larger than for a random distribution. At larger separations, \( g(r) \) then falls away to a minimum, followed by a smaller maximum, and then oscillates about the limiting long-range value of unity, showing that at long distances the influence of the central molecule has died away and that there is no long-range order. Also shown in Fig. 1.1 are the corresponding results for a simple solid, and for a gas at a moderate density. The regular long-range order of the solid is clearly shown, in contrast to the short-range order characteristic of the liquid. For the gas, \( g(r) \) has a value of unity at almost all separations, with deviations at smaller \( r \) determined chiefly by the Boltzmann factor, \( \exp \left( -\frac{U(r)}{kT} \right) \), based on the energy of a pair of molecules.

For diatomic and polyatomic molecules, some structural information may again be conveyed by the radial distribution function for the centers of mass of the molecules. However, it is clear that such information is incomplete, and a fuller description of the structure requires a radial distribution function, \( g(r,\omega) \) which is also a function of the relative orientation of the molecules, \( \omega \), as well as their separation. Even for a pair of diatomic molecules, the specification of the orientation requires three regular variables, and it is clear that the representation of such an orientation-dependent function presents difficulties. An alternative representation of the structure of molecular liquids uses sets of distribution functions based on the positions of the atoms, rather than of the centers of mass of the molecules. Atom-atom distribution functions, \( g_{AB}(r_{AB}) \) may be defined in a manner
analogous to that used for \( g(r) \), and describe the probability of finding an atom of type B at a distance \( r_{AB} \) from an atom of type A. Such a distribution function may have contributions from atoms that are in the same or different molecules. In order to describe the structure as completely as possible it is necessary to specify as many atom-atom distribution functions as there are different types of atom pairs. For example, in liquid H\(_2\)O (fig. 1.2), we would need to know \( g_{HH}(r_{HH}) \), \( g_{OO}(r_{OO}) \), and \( g_{OH}(r_{OH}) \). However, in spite of the increased number of functions we observe that each separate function depends only on a single distance variable, and this representation of the structure is probably simpler than that using orientation-dependent functions. Nevertheless, both types of function are valuable.

Experimental values of \( g(r) \) for liquids may be obtained from studies of X-ray or neutron diffraction. When monochromatic incident radiation is used, interference patterns arise in the diffracted radiation owing to correlation's between the positions of the atoms. This effect is similar to, though less sharply defined than, the diffraction effects produced by solids, where the atoms on their lattice sites behave in a manner resembling a three-dimensional diffraction grating. Interference occurs between components of the diffracted beam that have been scattered by different atoms, and this results in the almost total cancellation of intensity, except at a very few scattering angles, which are related to the wavelength of the radiation and the dimensions of the lattice. In practice, the perfect regularity of the solid crystal is modified by the vibrations of the atoms about their sites, and the diffraction pattern is less sharp than would be expected from the simple picture given above. In the
Fig. 1.2: Atom-atom distribution functions for water. Only the intermolecular contributions are shown.
liquid, this blurring of the pattern is carried further, since long-range structural correlation's are absent, but the intensity variations nevertheless allow the recovery of the distribution function.

### 1.3 PERTURBATION THEORIES OF SPHERICAL MOLECULES

One of the most successful approaches to the study of liquids in recent years has been through the development of perturbation theories. These may be thought of as modern versions of Vander Waals theory, and their essential physical basis is the separation of the roles of attractive and repulsive intermolecular forces. It is proposed that the structure of simple liquids, as revealed by their radial distribution functions, is chiefly determined by the packing requirements of the molecules, which in turn reflect the repulsive intermolecular forces. The attractive forces are thought to serve essentially as the 'glue' that holds the molecules together, maintaining the high density, but otherwise playing no major structural role.

When the structures of hard-sphere liquids are compared with those of real monatomic liquids, close similarities are seen. This suggests that the effects of the soft repulsive forces of real molecules may be modeled with reasonable accuracy using a hard-sphere system. The properties of hard-sphere system are well known from computer simulations and from statistical mechanical theories.

In the formal development of perturbation theories, the effects of changes in the form of the intermolecular potential on the properties of a
system of molecules are studied. For pair-wise-additive systems the pair potential energy function is written as a sum of terms, a reference potential, \( U_0(r) \), plus a perturbation, \( U_1(r) \):

\[
U(r) = U_0(r) + U_1(r) \tag{1.5}
\]

The properties of the system of molecules interacting through \( U_0(r) \) are assumed to be known, and those of the perturbed system are expressed in terms of \( U_1(r) \) and the properties of the reference system. For example, the configurational energy, \( U_N \), for a system of \( N \) molecules interacting through \( U(r) \) may be written, to first order in the perturbation theory

\[
U_N = U_N^0 + \frac{N^2}{2V} \int_0^\infty 4\pi r^2 g^0(r)U_1(r)dr, \tag{1.6}
\]

where \( U_N^0 \) is the configurational energy of the reference system, whose radial distribution function is \( g^0(r) \). (This equation should be compared with equ. (1.3). Similar expressions for other properties may also be written, and these are also quite easily calculated if \( g^0(r) \) is known. Higher-order perturbation terms may also be added, but their calculation is much more demanding, and the successful application of this theory depends on the rapid convergence of the expansion. This in turn will depend on the choice of a reference system whose structure faithfully mimics that of the system under study. The success of this approach has thus rested on the correct choice of the division of \( U(r) \) into reference and perturbation potentials. By a suitable division of \( U(r) \), the magnitude of the higher-order terms can be made very small, and rapid convergence achieved even at low temperatures.
Fig. 1.3: Division of the total intermolecular potential into reference and perturbation components.

1. \( U_0(r) \), the reference potential
2. \( U_1(r) \), the perturbation

(a) Baker-Henderson, (b) Weeks-Chandler-Andersen
Most perturbation theories have attempted to calculate the properties of a liquid whose molecules interacted through a model pair potential, usually the Lennard-Jones function. In the earliest studies, $U_0(r)$ was taken to be hard-sphere potential, with the hard-sphere diameter, $d$, slightly less than the Lennard-Jones collision diameter, $\sigma$, but with its value chosen in a slightly arbitrary manner. For all values of $r$ greater than $\sigma$, $U_1(r)$ was taken to be the Lennard-Jones potential. This division of the potential is illustrated in fig. 1.3(a) and may be written

$$
U_0(r) = \begin{cases} 
\infty, & r < d \\
0, & r > d 
\end{cases}
$$

$$
U_1(r) = \begin{cases} 
0, & r < \sigma \\
4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right], & r > \sigma.
\end{cases}
$$

The results of the first-order perturbation theory are found to be quite sensitive to the choice of the hard-sphere diameter, $d$. Significant progress in the application of perturbation theory to liquids was only made after reliable and well-founded methods for choosing $d$ were established. In the first successful theory, due to Barker and Henderson [1], the effective hard-sphere diameter was defined by the equation

$$
d = -\int_0^\sigma \left[\exp\left(-\frac{U(r)}{kT}\right) - 1\right] dr
$$

which gives a hard sphere diameter that is a function of temperature but not of density, and that decreases as the temperature is raised. Barker and
Henderson [1] were able to calculate the first- and second-order perturbation terms, using computer simulation results for the distribution functions of the reference system. Calculations of the properties of Lennard-Jones liquids were found to be in very good agreement with those obtained from direct computer simulation. The second-order term, though small, was found to be necessary to achieve the excellent level of agreement.

An alternative, very successful, perturbation theory was proposed by Weeks, Chandler, and Andersen [2], and is based on a novel choice of reference and perturbation potentials. This is illustrated in fig. 1.3(b), and may be written

\[
\begin{align*}
U_0(r) &= U(r) + \varepsilon & r \leq r_m \\
U_0(r) &= 0, & r > r_m \\
U_1(r) &= -\varepsilon, & r \leq r_m \\
U_1(r) &= U(r), & r > r_m.
\end{align*}
\]

This division of potentials assigns the whole of the repulsive region of \( U(r) \) to the role of reference potential and determinant of structure, rather than just the positive portion of \( U(r) \), as in the Barker-Henderson theory. A consequence of this division is that the perturbation energy, \( U_1(r) \), is now a very smoothly varying function of \( r \), and this seems to have the useful effect of reducing the higher-order fluctuation terms, giving a very accurate equation of state even when restricted to a first-order treatment. However, a penalty is incurred also, in that the properties of the reference fluid are not now so simple as those of the hard-sphere fluid nor as well established.
Weeks and co-workers were able to propose a relation between their reference fluid and a hard-sphere fluid, and used this to make calculations for the Lennard-Jones fluid that proved to be approximately as accurate in first order as those based on the second-order Barker-Henderson perturbation treatment.

Both of these perturbation theories provide remarkably accurate and reasonably simple procedures by which the properties of fluids of spherical molecules may be calculated. They have been extended in recent years to the study of more complex systems with non-spherical molecules. The wide range of successful applications of perturbation theories in the study of the liquid state has displayed with remarkable force the primary role of repulsive intermolecular interactions in determining the structural properties of liquids.

1.4 THERMODYNAMIC PERTURBATION THEORY OF NONSPHERICAL MOLECULAR FLUIDS

Beginning with the pioneering work of Zwanzig in 1954, [3] thermodynamic perturbation theory has been developed into a powerful tool for predicting the equilibrium properties of simple fluids. [2,4] This is particularly true if high-density states are considered and if the division of the pair potential into a repulsive and an attractive branch is performed according to the prescription of Weeks et al. [5–8]. For the treatment of spherical particles, a properly chosen hard-sphere fluid will usually serve as a reference system [7–10]. With accurate pair correlation functions available from the analytical solution of the Percus–Yevick integral equation, [11–14] together with the correction proposed by Verlet and Weis, [7] first-order perturbation
calculations (and sometimes even higher order ones) [9,10] are readily feasible today even on the smallest computers.

The straightforward generalization of these ideas to the case of particles interacting via noncentral potentials, such as interaction site [15,16] or Kihara-type [17] molecules, necessitates the consideration of anisotropic reference system [18–23]. This requirement, however, causes severe problems, as the properties of these reference fluids are not yet generally well known. Despite the considerable amount of computer simulation data already available for hard interaction site molecules, especially for homonuclear and heteronuclear hard dumbbells, [24–29] and to a smaller extent also for hard convex bodies, [30–35] this research is still in its exploratory stage. Nevertheless, the theoretical progress achieved so far [36–38, 16] justifies the assumption that at least for dense fluids it will be much easier to determine the hard-core reference properties in a first step and to account for the attractive contributions in a second step employing the methods of perturbation theory than to treat the complete system in a more or less direct manner. Once the necessary data on structure and thermodynamics of hard-body fluids can be evaluated readily with sufficient accuracy, the exploration of systems with realistic interactions will be greatly facilitated. We believe that this should be a strong motivation for continued efforts toward a better understanding of fluids composed of hard molecules.

A seemingly more convenient way to consider molecular anisotropy within the framework of perturbation theory is the separation of the full
potential function into a spherical reference part and a non-spherical perturbation. The expansion of Pople [39] and Gubbins and Gray, [40, 41] for example, starts with

\[ \nu_{12}(r_{12}, \Omega_1, \Omega_2, \lambda) = \nu_{12}^0(r_{12}) + \lambda \nu_{12}^a(r_{12}, \Omega_1, \Omega_2) \]  

(1.8)

where \( \nu_{12}^0(r_{12}) \) is obtained by unweighted averaging over the molecular orientations:

\[ \nu_{12}^0(r_{12}) = \langle \nu_{12}(r_{12}, \Omega_1, \Omega_2)_{\Omega_1, \Omega_2} \rangle \]  

(1.9)

Here \( r_{12} \) denotes the center-to-center distance, and \( \Omega_1 \) and \( \Omega_2 \) are the orientations of molecules 1 and 2, respectively. Setting the coupling parameter \( \lambda \) to zero yields the reference potential, while with \( \lambda = 1 \) the full interaction is recovered. This method works well, if \( \nu_{12}^a(r_{12}, \Omega_1, \Omega_2) \) consists mainly of idealized polar interaction terms (interactions of point dipoles, point quadrupoles, etc.), particularly in the Pade approximant version suggested by Stell et al., [10] which partially overcomes the sometimes insufficient convergence behavior of the perturbation series. For cases of strong geometric anisotropy, however, rather poor results are obtained, especially at high densities [42].

Despite its merits, the Pople expansion suffers from an inherent weakness, since the anisotropic perturbation cannot be small whenever the particle geometry (as characterized by the harshly repulsive portions of the intermolecular potential) deviates significantly from sphericity. As an
example, consider a fluid composed of hard dumbbell molecules. From Eq. (1.9) we obtain a reference system that consists of hard spheres just enveloping the dumbbell bodies. Clearly, with increasing particle anisotropy (i.e. with growing elongation of the dumbbells) this choice will become an increasingly poor one. Thus, it appears to be desirable to introduce as much in formation about molecular shape as possible into the properties of the reference fluid.

The exponentially averaged effective potential function represents an important step in this direction. [43–50, 22, 37] Equation (1.10) leads to a nonlinear coupling between the reference potential and the perturbation term,

\[ \nu_{12}^0 (r_{12}) = -kT \ln \left( \exp \left[ -\frac{\nu_{12} (r_{12}, \Omega_1, \Omega_2)}{kT} \right] \right) \]  

(1.10)

The exponentially averaged effective potential function represents an important step in this direction. [43–50, 22, 37] Equation (1.10) leads to a nonlinear coupling between the reference potential and the perturbation term,

\[ \nu_{12} (r_{12}, \Omega_1, \Omega_2, \lambda) = \nu_{12}^0 (r_{12}) - kT \ln \left[ 1 + \lambda s_\lambda (r_{12}, \Omega_1, \Omega_2) \right] \]  

(1.11)

where

\[ s_\lambda (r_{12}, \Omega_1, \Omega_2) = \exp \left\{ -\frac{\nu_{12} (r_{12}, \Omega_1, \Omega_2) - \nu_{12}^0 (r_{12})}{kT} \right\} - 1 \]  

(1.12)

Equivalently to Eq. (1.11) the Mayer function

\[ f_{12} (r_{12}, \Omega_1, \Omega_2) = \exp \left[ -\frac{\nu_{12} (r_{12}, \Omega_1, \Omega_2)}{kT} \right] - 1 \]  

(1.13)

may be used as an expansion functional: [45]
where

$$f^0_{i_2}(r_{i_2}) = \langle f_{i_2}(r_{i_2}, \Omega_1, \Omega_2) \rangle_{\Omega_1, \Omega_2}$$  (1.15)

Therefore, this method is often referred to as the RAM (reference system average Mayer function) theory [44,49,50].

To first order the molecular pair distribution function is given by

$$g_{12}(r_{12}, \Omega_1, \Omega_2) = g^0_{12}(r_{12}) [1 + s_\lambda(r_{12}, \Omega_1, \Omega_2)] + \rho W^{-1} \int g^0_{123}(r_{12}, r_{13}, r_{23})$$

$$\times [s_\lambda(r_{13}, \Omega_1, \Omega_3) + s_\lambda(r_{23}, \Omega_2, \Omega_3)] dr_3 d\Omega_3$$  (1.16)

where $g^0_{12}$ and $g^0_{123}$ denote the reference pair and triplet correlation functions, respectively, and

$$W = \begin{cases} 4\pi & \text{for linear molecules} \\ 8\pi^2 & \text{for nonlinear molecules} \end{cases}$$  (1.17)

The zeroth-order RAM theory is exact in the low-density limit, $\rho \to 0$, in that it predicts the second virial coefficient $B_2$ correctly. Note that the first-order correction term to Eq. (1.16) vanishes on integrating over $\Omega_1$ and $\Omega_2$. Thus, the zeroth-order orientationally averaged center-to-center correlation function as obtained from the reference pair potential remains correct within a first-order approximation, independent of density.
For liquids composed of hard dumbbell molecules, recent investigations have shown good agreement between $g_{12}^0(r_{12})$ and $<g_{12}(r_{12}, \Omega_1, \Omega_2)\rangle_{\Omega_1, \Omega_2}$ as evaluated from computer simulation data [22, 45, 46]. More important, the reproduction of angular correlations is quite satisfactory in most cases considered so far [49, 50]. But despite these encouraging results, some deficiencies still remain [46, 48, 49]. Obviously, the price to be paid for circumventing the treatment of anisotropic reference systems in a certain limitation of the range of applicability. For particles with distinctly nonspherical shape the RAM predictions are likely to become less reliable, especially at high densities [46, 49]. Nevertheless the investigations conducted so far do suggest that the RAM perturbation series converges much faster than the Pople expansion. Thus it appears to be worthwhile to keep the concept of Boltzmann averaging as a valuable guideline when looking for more elaborate and yet numerically tractable reference systems.

Once $g_{12}(r_{12}, \Omega_1, \Omega_2)$ is known, most of the structural and thermodynamic fluid properties may be evaluated. The configurational part of the internal energy, for example, is given by

$$U_c = 2\pi p N \int <g_{12}(r_{12}, \Omega_1, \Omega_2)\nu_{12}(r_{12}, \Omega_1, \Omega_2)\rangle_{\Omega_1, \Omega_2} r_{12}^2 dr_{12} \quad (1.18)$$

and the virial equation of state reads

$$\frac{P}{\rho kT} = 1 - \frac{2\pi p}{3kT} \int <g_{12}(r_{12}, \Omega_1, \Omega_2)\frac{\partial}{\partial r_{12}}\nu_{12}(r_{12}, \Omega_1, \Omega_2)\rangle_{\Omega_1, \Omega_2} r_{12}^3 dr_{12} \quad (1.19)$$
Alternatively, the equation of state may be obtained via the compressibility equation

$$\rho k T_k = 1 + 4\pi \rho \int < g_{12}(r_{12}, \Omega_1, \Omega_2) - 1 >_{\Omega_1, \Omega_2} r_{12}^2 dr_{12}$$  \hspace{1cm} (1.20)$$

where

$$k = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$  \hspace{1cm} (1.21)$$

denotes the isothermal compressibility.

Inspecting Eqs. (1.9) and (1.10) we note that no specific assumptions are made concerning the nature of the intermolecular interactions, except that they are reasonably described by pair potentials. On principal, this generality might be considered a highly expedient feature. For practical applications, however, it can be very rewarding to carefully examine the analytical structure as well as the physical implications of the potential model under consideration. Utilizing special symmetry properties or employing appropriate coordinate transforms, for instance, may not only result in more efficient or more convenient formalisms but will sometimes even lead to alternative physical descriptions of the liquid system of interest.

In order to exemplify this statement, we shall now consider a model fluid, where the orientation-dependent molecular pair potential is represented by a sum over contributions from interacting atoms, groups of atoms, point charge centers, etc. (so-called interaction sites [15, 51]):
Fig. 1.4: Example of an interaction site molecule ($\alpha = 1; \gamma = 2$). The location of site $\alpha$ of molecule 1 is given by $r_\alpha = r_1 + l_\alpha$, where $l_\alpha = l_\alpha(\Omega_1)$.

Fig. 1.5: Site-site interaction between two interaction site molecules ($\alpha = 1; \gamma = 2$).
The pair interaction between two particles with m and n interaction sites, respectively, is then described by a set of m.n spherically symmetric site-site potentials \( u_{\alpha \gamma}(r_{\alpha \gamma}) \), see figs. 1.4 and 1.5. By virtue of Eq. (1.22) the potential energy acting two molecules depends on the relative distance between their interaction sites. Thus, in dealing with interaction site systems it is often convenient to express structural and thermodynamic properties in terms of site-site distribution functions \( g_{\alpha \gamma}(r_{\alpha \gamma}) \). These are related to the molecular pair correlation function by [15].

\[
ge_{\alpha \gamma}(\mathbf{r} - \mathbf{r}') = W^{-2} \int dr_1 d\Omega_1 \int dr_2 d\Omega_2 g_{12}(r_{12}, \Omega_1, \Omega_2) \delta(r_{\alpha} - r) \delta(r_{\gamma}^2 - r')
\]

(1.23)

The configurational energy, for example, can now be written as

\[
U_c = 2\pi \rho N \sum_{\alpha \gamma} \int g_{\alpha \gamma}(r_{\alpha \gamma}) u_{\alpha \gamma}(r_{\alpha \gamma}) r_{\alpha \gamma}^2 dr_{\alpha \gamma}
\]

(1.24)

which should be compared to Eq. (1.18). The most general route to the equation of state proceeds from the compressibility theorem for interaction site molecules: [51]

\[
\rho kT_k = 1 + 4\pi \rho \int \left[ g_{\alpha \gamma}(r_{\alpha \gamma}) - 1 \right] r_{\alpha \gamma}^2 dr_{\alpha \gamma}
\]

(1.25)

Note that the integral on the right-hand side of Eqn. (1.25) does not depend on the particular choice of \( \alpha \) and \( \gamma \).
The Second Virial Coefficient For Non-Spherical Molecules

Just as the simplest model for a spherical molecule is a rigid impenetrable sphere, so also can non-spherical molecules be regarded as rigid impenetrable objects of various shapes. Hence this discussion begins with a summary of the work of Ishihara [52], who has shown how the second virial coefficient of any rigid convex molecule may be evaluated. Kihara [54] has extended the latter work to examine elongated and flat molecules which interact according to a Lennard-Jones potential in which the separation is taken to be the shortest distance between the “cores” of the molecules. The second virial coefficient for rigid spheres is just equal to four times the volume of the molecules in the gas. For rigid non-spherical molecules, the second virial coefficient may be written as

$$ B = 4 \tilde{N} v_m f \quad (1.26) $$

in which $v_m$ is the volume of a single molecule and $f$ is a factor (always greater than unity) which indicates deviation from rigid sphere behaviour. Ishihara [52, 53] has shown how this factor $f$ may be evaluated for any rigid convex molecule by the use of group theory and differential geometry. The result of his rigorous mathematical treatment is quite simple in form. For a gas containing molecules of a single kind the factor $f$ is given by

$$ f = 1 + \left[ \frac{R s_m}{4 v_m} - \frac{3}{4} \right] \quad (1.27) $$
in which $s_m$ is the surface area of a molecule and $\bar{R}$ is the average of the mean radius of curvature. The latter is given by

$$\bar{R} = \frac{1}{4\pi} \int \frac{1}{2} (R_1 + R_2) d\omega \quad (1.28)$$

**Table 1.1:** The factor $f$ for various non-spherical models

<table>
<thead>
<tr>
<th>Shape</th>
<th>Sphere</th>
<th>Cube</th>
<th>Regular Tetrahedron</th>
<th>Regular Octahedron</th>
<th>Cylinder</th>
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</thead>
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<td>Size</td>
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<td>Side=1</td>
<td>Side=1</td>
<td>Side=1</td>
<td>Lengths=1</td>
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<td>$4\pi/3$</td>
<td>1</td>
<td>$\sqrt{2}/12$</td>
<td>$\sqrt{2}/3$</td>
<td>$\pi a^2 l$</td>
</tr>
<tr>
<td>$s_m$</td>
<td>$4\pi$</td>
<td>6</td>
<td>$\sqrt{3}$</td>
<td>$2\sqrt{3}$</td>
<td>$2\pi a(a+1)$</td>
</tr>
<tr>
<td>$\bar{R}$</td>
<td>1</td>
<td>3/4</td>
<td>$\frac{3}{2\pi} \tan^{-1} \sqrt{2}$</td>
<td>$\frac{3}{\pi} \cot^{-1} \sqrt{2}$</td>
<td>$\frac{1}{4}(1+a\pi)$</td>
</tr>
<tr>
<td>$F$</td>
<td>1</td>
<td>11/8</td>
<td>1.926</td>
<td>1.330</td>
<td>$\frac{\pi a^2 + (\pi + 3)al + l^2}{8al}$</td>
</tr>
</tbody>
</table>

where $R_1$ and $R_2$ are the principal radii of curvature, and $d\omega$ is the surface element on a unit sphere. These results have been generalized for molecular models which are not smooth (for example, rigid tetrahedrons) and for mixtures of molecules of different shapes. The fact that $f$ is always greater than unity indicates that non-spherical molecules always have second virial coefficients which are larger than those for spherical molecules of the same volume. The second virial coefficients for all rigid molecules are temperature independent.
The factor $f$ for a number of non-spherical molecules are shown in table 1.1

1.6 KIHARA'S GENERALIZED SPHEROCYLINDRICAL MOLECULES

Kihara [54] has shown how the spherocylindrical model can be generalized to include attractive and repulsive forces according to a Lennard-Jones type interaction. The generalization has been performed in such a way as to preserve the integrability of the second virial coefficient. The results are applicable to both long and flat molecules.

First it is necessary to define what is meant by the core of the molecule. For a homopolar diatomic molecule the line segment between the nuclei is taken to be the core of the molecule. The core of other molecules of a prolonged shape may be specified in a similar way with respect to the basic molecular skeleton. For example, the O-O distance in CO$_2$ and the C-C distance in C$_2$H$_2$, C$_2$H$_4$, or C$_2$H$_6$ form cores. The energy of interaction $\varphi(\rho)$ between two such long molecules is then taken to be of the Lennard-Jones (6-12). However, the argument of the function, $\rho$, is not defined as the distance between the centers of the two molecules but rather as the shortest distance between their cores. The physical reality of such a potential is questionable, particularly in collisions in which both ends of both cores are within interaction distance of one another. Nevertheless, this approach introduces the principal notion of a non-spherical interaction, and good agreement is obtained between theory and experiment.
The core of flat molecules is taken to be thin circular disk. For benzene, for example, the core is chosen to be the circular disk ringed by the six carbon atoms. The intermolecular distance is then defined as the shortest distance between these cores. When it is necessary to distinguish between the cores of long molecules and those of flat molecules, the latter are referred to as disk cores and the former as rod cores. The length of the rod core and the diameter of the disk core are designated by \( l \). This quality is readily obtainable from information about intramolecular distances available in the literature.

The intermolecular potential is then characterized by three quantities: the length \( l \) and the parameters \( \sigma \) and \( \epsilon \) of the Lennard-Jones (6–12) potential. Actually Kihara chooses to use as one of his parameters the position of the potential minimum, \( \rho_m = 2^{1/6} \sigma \), in place of the collision diameter \( \sigma \). This distance, \( \rho_m \), is also identified with the shorter dimension ("minor axis") of the spherocylinder. When \( l = 0 \) the intermolecular potential reduces to the ordinary spherically symmetrical Lennard-Jones (6–12) potential. When \( \epsilon = 0 \) and the repulsive index 12 is replaced by \( \infty \), the model reduces to the rigid spherocylindrical molecules.

For spherically symmetrical molecules the second virial coefficient may be written in the form

\[
B(T) = \int_{r=0}^{r=\infty} \left[ 1 - e^{-q(r) kT} \right] db_0(r)
\]

(1.29)
in which \( b_0(r) \) is the second virial coefficient for rigid spheres with diameter \( r; b_0(r) = \frac{2\pi N r^3}{3} \). Similarly for the generalized spherocylindrical model, virial coefficient is given by

\[
B(T) = \int_{\rho=0}^{\rho=\infty} \left[ 1 - e^{-\frac{\phi}{kT}} \right] db_1(\rho) + b_1(0) \tag{1.30}
\]

In this expression \( b_1(\rho) \) is the second virial coefficient for rigid spherocylinders with core length \( l \) and minor axis \( \rho; b_1(\rho) = 4Nv_m(l, \rho)f(l, \rho) \) where \( f \) is a factor for prolate and oblate spherocylinders.

1.7. EXAMPLES OF SPHERICAL AND NON-SPHERICAL MOLECULES

The experimental and theoretical results for spherical molecules such as helium, neon, argon, and krypton are known. For each of these gases the experimental \( B(T) \) values are plotted and also the second virial coefficient calculated on the basis of several empirical potential functions.

Two examples are given of molecules which are somewhat asymmetrical, \( \text{N}_2 \) and \( \text{CO}_2 \). Because they are so nearly spherical, the dependence of the second virial coefficient on temperature is quite well represented by the Lennard-Jones (6–12) potential. Whereas the second virial coefficient is not sensitive to the shape of the molecules, the effect of asymmetry manifests itself in the temperature dependence of the third virial coefficient. However, it would be very difficult to distinguish between those
deviations in the third virial coefficient which are due to asymmetry and those which can be explained by the inaccuracy of the radial dependence of a spherical potential.

The factor $f$ has been computed for a number of non-spherical molecular models, (55) and the results of these calculations are given in table 1.1.

1.8 REFERENCES


