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AN ACCURATE EQUATION OF STATE FOR RIGID-SPHERE FLUIDS AND ITS USE IN THERMODYNAMICS AND TRANSPORT THEORY

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AN ACCURATE EQUATION OF STATE FOR

RIGID-SPHERE FLUIDS AND

ITS USE IN THERMODYNAMICS AND TRANSPORT THEORY

APPROVED BY

Kenneth E. Starling

Dr. Kenneth E. Starling (Chairman)

Sherril D. Christian

Dr. Sherril D. Christian

Frank B. Canfield

Dr. Frank B. Canfield

James H. Christensen

Dr. James H. Christensen

Arthur Wm Aldag Jr

Dr. Arthur W. Aldag

DISSERTATION COMMITTEE

PREFACE

This dissertation is part of the continuing program of equation of state research and development being conducted under the guidance of Professor Kenneth E. Starling. As a link between the present research and previous theses and dissertations in the overall program, the following raison d'etre is offered.

The masters theses of K. Wiley Cox, Frank D. Roberts, and James L. Bono, and the doctoral dissertation of Y. C. (David) Kwok proved the necessity of using multiproperty regression as the method of evaluating equation of state coefficients. The Benedict-Webb-Rubin (BWR) equation [J. Chem. Phys., 8, 334 (1940)] served as a model equation with which to develop the multiproperty technique which characterizes the overall program of research.

To accurately correlate low-temperature thermodynamic properties, it was necessary to add three new terms to the original BWR equation. The task of simulataneously evaluating eleven coefficients, especially in a nonlinear regression, is not trivial. This fact, coupled with the high degree of correlation between the BWR coefficients, suggested that a study of equation of state fundamentals might lead to a more condensed formula, whose coefficients would have physical significance on the molecular level.

The present research is the beginning of the theoretical studies of fluid behavior. Attention has focussed upon the development of a model of the kinetic or repulsion pressure. In particular, the rigid-sphere system (for which kinetic pressure is the total pressure) has been studied in detail. The result has been an extremely accurate equation of state for single and multicomponent systems of rigid spheres, which serve as a model of kinetic or repulsion effects in real fluids.

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ABSTRACT

A new equation of state for rigid spheres has been developed from an analysis of the reduced virial series for this system. Comparisons with existing equations show that the new formula possesses superior ability to describe rigid-sphere behavior.

The new equation has been generalized for mixtures having different diameters. Compressibility factors and other equilibrium properties of binary mixtures of rigid spheres are calculated and compared with related Monte Carlo and Molecular Dynamics data. The comparison shows excellent agreement between the predictions from the new mixture equation of state and the machine-calculated data.

The new equation has been used to generate tables of accurate thermodynamic properties for single and multicomponent rigid-sphere systems. These tables and the related formulas from which they are generated are important for those perturbational and variational studies of fluid behavior using the rigid-sphere fluid as a reference system.

The use of the new equation in rigid-sphere transport theory is discussed. Example calculations of transport properties from the Enskog and the Longuet-Higgins and Pople theories are presented and compared with the recent Molecular Dynamics rigid-sphere transport calculations.

Criteria for judging the validity of a rigid-sphere equation of state are discussed. The desirability of using only reliable data, such Molecular Dynamics calculations, as a basis for judgment is stressed.

The numerical nature of the well-known Padé approximant is explored. The sensitivity of the Pade formula to the manner in which its coefficients are determined is demonstrated. Examples of several Padé approximants are evaluated from the known virial coefficients for rigid spheres.

The utility of the rigid-sphere system as a model of the repulsion behavior of dense liquids is investigated. An accurate analytical formulation is made of the Longuet-Higgins and Widom model for the behavior of liquid argon in the neighborhood of its triple point. Comparisons between calculated and experimental data show the model to be accurate.

The general usage of the new rigid-sphere equation in real fluid models is postulated by the reformulation of van der Waals equation using the accurate rigid-sphere equation to describe repulsion effects. Properties of methane, ethane, propane, butane, isobutane, hydrogen sulfide, nitrogen, ethylene, acetylene, methyl chloride cyclohexane, pentane, and octane have been calculated. A general improvement in the calculations is obtained relative to the original van der Waals equation. The same study was made with the equation of state of Redlich and Kwong, with similar results.

Enthalpy departures of binary mixtures of real gases were computed with the mixture versions of the Redlich-Kwong and the van der Waals equations. A general improvement in the accuracy of calculations occurred when the new rigid-sphere equation was used to describe repulsion effects. A study of the mixture rules for the covolume is presented, based upon the form of the new mixture equation of state for rigid spheres.

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AN ACCURATE EQUATION OF STATE FOR RIGID-SPHERE FLUIDS AND ITS USE IN THERMODYNAMICS AND TRANSPORT THEORY

CHAPTER I

INTRODUCTION

The demand for accurate predictions of thermodynamic properties, enthalpies and fugacities, for engineering design and applied science has led to deep interest in the formulation of models of the equation of state.

There are two types of analytical equation of state models, according to their method of development. Models of the first type are wholly empirical, based upon experimental evidences. Generally such equations serve as correlation functions for PVT and/or thermodynamic property data. Examples of this type of equation of state model are the Benedict-Webb-Rubin equation (eight adjustable coefficients) and the Beattie-Bridgeman equation (five adjustable coefficients). The advantage of this type of model lies in the accuracy with which they can be fitted to experimental data. The range and accuracy of the correlation depend upon the algebraic form of the equation and the number of adjustable coefficients. A disadvantage

of this type of model is the lack of physical significance in the sign and/or magnitude of the coefficients.

The second type of equation of state model is semi-theoretical. The equations of van der Waals [49], Dieterici [17], Berthelot [8] and Redlich and Kwong [40] are examples of this type. Such equations generally express pressure as the sum of two terms, a repulsion pressure P_R and a cohesion pressure P_A. Classically, the theoretical model of the repulsion pressure has been the rigid-sphere equation developed by Clausius [39] from kinetic theory, i.e. $P_R = RT/(V - b)$. The advantage of equation of state models of this second type is the physical meaning of their coefficients. Additionally, such equations require very little experimental data to evaluate the coefficients. Therefore, they can be applied to a wider class of substances than can the models of the first type, which require extensive data for proper evaluation of their coefficients. A disadvantage of the semi-theoretical models is the lack of high accuracy in their predictions. This lack of accuracy is partly due to the approximations used for the terms, P_R and P_A. These approximations are usually made to avoid the evaluation of integrals over phase space (in statistical mechanical approaches).

There are some non-analytical models of the equation of state which are used in modern studies of fluid behavior. For example, the cohesion effect can be treated as a perturbation about a reference system of rigid spheres. The general approach, based upon radial distribution function theory, calculates the total pressure from,

$$P = P_R - \frac{2}{3}\pi n^2 \int_{\sigma}^{\infty} g_o(r) \left(\frac{du}{dr}\right) r^3 \, dr, \qquad \text{(I-1)}$$

where σ = rigid-sphere diameter

r = intermolecular separation

u = intermolecular potential

$g_o(r)$ = radial distribution function for rigid spheres

n = number density

P_R = rigid-sphere pressure.

Although there are different ways of calculating pressure in perturbation schemes, Equation (I-1) serves to illustrate the general idea. One of the first users of the perturbation approach to the equation of state, Zwanzig [55], applied the method to the study of high-temperature gas behavior. More recent efforts have seen the introduction of variational techniques into the method by Mansoori [34]. Yet, whatever the form of the perturbation or variation method, it is essential to have an accurate equation of state for the rigid-sphere reference system.

The primary objective of this dissertation is the development of an accurate equation of state for the system of nonattracting rigid spheres and their mixtures. Such an equation will serve not only to calculate the properties of the rigid-sphere reference system in pertubation schemes, but also as a model for the repulsion pressure, P_R, in approximate (van der Waals-like) equations for real fluids.

The dissertation is written in two parts. The first part deals with the formulation, development and analysis of the rigid-sphere equation of state. The second part presents examples of some empirical applications of the rigid-sphere equation, developed in part one, in approximate theories of real fluids.

CHAPTER II

DESCRIPTION OF THE SYSTEM

The rigid-sphere system is convenient to study as a basis for understanding the behavior of real fluids. It is a simple system with which many theoretical concepts can be tested. Collision phenomena, viscosity, diffusion, kinetic pressure, etc., studied in the rigid-sphere system bear, at least, qualitative resemblance to real system behavior. The behavior of the rigid-sphere system is similar to that of a collection of billiard balls, in three dimensions. Collisions are perfectly elastic and of instantaneous duration. In the absence of attractive forces, the energy of the system is entirely due to translational kinetic effects. For example, pressure is calculable from momentum transfers at the system boundaries.

The rigid-sphere system has the least sophisticated intermolecular potential function of all dimensioned-particle systems.

$$u(r) = 0 \qquad \text{for} \quad r \geq \sigma$$

$$u(r) = \infty \qquad \text{for} \quad r < \sigma,$$

where $u(r)$ = intermolecular potential function

r = separation between centers of spheres

σ = sphere diameter.

Virial Coefficients

With the foregoing introduction, consider the virial expansion for the rigid-sphere system. The compressibility factor, PV/NkT, for rigid spheres is a function of density alone.

$$PV/NkT = 1 + B/V + C/V^2 + D/V^3 + \ldots, \qquad \text{(II-2)}$$

where V = volume of the system

N = number of molecules in the system

k = Boltzmann constant

B = second virial coefficient

C = third virial coefficient

etc.

In real systems, where an analytical form of the intermolecular potential function is not known, the virial coefficients are obtained from the experimental data by numerical methods [22]. For systems with known or assumed potential functions, the coefficients are calculable from theory [24, 25]. For a one-component classical monatomic gas, Hill [24] gives

$$B = -2\pi N \int_0^\infty r^2\{\exp[u(r)/kT] - 1\}dr. \qquad \text{(II-3)}$$

For the rigid-sphere potential, the reduced virial expansion is,

$$PV/NkT = 1 + 4y + 10y^2 + 18.36y^3 + 28.2y^4 + 39.6y^5 + \ldots, \qquad \text{(II-4)}$$

where $y = B/4V$

$$B = \frac{2}{3}\pi N\sigma^3.$$

The coefficients B, C, and D are known exactly. The next three coefficients have been numerically evaluated by Ree and Hoover [42]. Due to the increasing complexity of the higher order coefficients, it is not likely that the eighth and higher coefficients will be evaluated in the near future [27].

Computer Simulation Experiments

Knowledge of the intermolecular potential function allows another kind of study of the rigid-sphere system, namely computer simulation. There have been several simulation studies of the rigid-sphere system and its mixtures [46, 45, 1, 52]. There are two simulation methods, Monte Carlo methods and Molecular Dynamics methods.

The Monte Carlo method is so-called because of its use of "random numbers". It is the easier of the two methods. In it, one specifies a system of N particles (e.g. N = 32, 64, etc.) in a cubic space grid. To initialize the calculation, the N particles are assigned random locations on the grid with coordinates generated from "random" numbers, such that no two particles overlap. In addition, the particles are assigned momenta coordinates (velocities, in essence) generated from "random" numbers. Then, the energy of the system is computed from the assumption that only pair interactions are significant, i.e.

$$U = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} u(r_{ij}). \qquad \text{(II-5)}$$

At this step, a new set of coordinates is generated and assigned to one of the N particles chosen at random. A check is made to see that the particles do not overlap, (if so, another set of coordinates is generated

for the particle). A new set of momenta coordinates is generated for the chosen element. A check is made to ascertain that the energy of the system does not increase. If so, the move is deemed not feasible and another particle is chosen and given new position and momenta coordinates. The process is repeated 50,000 to 150,000 times, at which point the system energy is assumed to be minimal and an equilibrium is reached in the distribution of the particles on the grid. Needless to say, this method is very simple and straightforward. Yet, the 50,000 to 150,000 iterations require an enormous amount of computer time, hence expense.

The Molecular Dynamics method is an attempt to simulate the properties of a system of infinite extent by solving the equations of motion for each of the elements in an N-body system. The process begins much like the Monte Carlo method by assigning to each particle a set of spatial and velocity coordinates (x, y, z, v_x, v_y, v_z). A time step is selected. Starting at time zero, the trajectory of each particle is computed by solving the equations of motion for the system. Let (x, y, z, v_x, v_y, v_z) be the coordinates of one of the N particles at the beginning of a time step. After the step, the coordinates are ($x + v_x\Delta t$, $y + v_y\Delta t$, $z + v_z\Delta t$, v_x, v_y, v_z), unless a collision has occurred which would alter the trajectory and the velocity components. A sufficiently small time step is required to accurately trace the trajectories and to detect all collisions. The calculations continue until a large number of collisions has occurred, such that an equilibrium distribution of the particles in the system is closely approximated. This method is exact, but requires a large computer because of all the variables and the many, many calculations required.

Both simulation methods provide data against which the accuracy of theoretical or empirical predictions can be tested. The Molecular Dynamics data appear to be more reliable than the Monte Carlo data, especially for single-component systems.

Discussion

In brief review, then, one has at his disposal two forms of rigid-sphere data: (1) the first seven virial coefficients, and (2) compressibility factor data from simulation experiments. These data are important for the development of an accurate rigid-sphere equation of state, as is demonstrated in the following chapters.

CHAPTER III

THE EQUATION OF STATE FOR A SINGLE COMPONENT SYSTEM OF NONATTRACTING RIGID SPHERES

In this chapter an accurate equation of state for rigid spheres is developed from an approximation to the reduced virial series for the system. The resultant equation, reported in the literature [12], is shown to have superior ability to predict the properties and behavior of the rigid-sphere system.

Review of Earlier Rigid-sphere Equations

There have been many equations of state proposed for the rigid-sphere system. These are of theoretical, numerical or purely empirical origin. The most notable of the theoretical equations is the "compressibility" solution of the Percus-Yevick integral equation, reported by Thiele [48] and by Wertheim [50],

$$PV/NkT = (1 + y + y^2)/(1 - y)^3 \qquad \text{(III-1)}$$

$$\text{where } y = b/4V; \quad b = \frac{2}{3}\pi N\sigma^3.$$

This very same equation has also been derived by Reiss, Frisch and Lebowitz [43] from "scaled particle theory". It is important that two independent fluid theories arrive at the same result. There is, however, another solution of the Percus-Yevick equation, called the "pressure" or "virial"

solution [51],

$$PV/NkT = (1 + 2y + 3y^2)/(1 - y)^2. \qquad \text{(III-2)}$$

Of the empirical equations, that proposed by Guggenheim [21] is representative,

$$PV/NkT = 1/(1 - y)^4. \qquad \text{(III-3)}$$

Of the numerically derived equations, the Padé (3,3) approximant given by Ree and Hoover [41] matches exactly the first six virial coefficients and extrapolates well the higher order terms in the virial series,

$$PV/NkT = \frac{(1 + 1.75399y + 2.31704y^2 + 1.108928y^3)}{(1 - 2.246004y + 1.301056y^2)}. \qquad \text{(III-4)}$$

It is instructive to recall the accurate reduced virial expansion, based upon the work of Ree and Hoover [41],

$$PV/NkT = 1 + 4y + 10y^2 + 18.36y^3 + 28.2y^4 + 39.5y^5 + \ldots \qquad \text{(III-5)}$$

One is able to compare the various approximate equations against the accurate virial expansion, as shown in Table III-1.

TABLE III-1

Virial Expansions from Various Rigid-sphere Equations

Equation	Virial Expansion
Percus-Yevick (pyc), III-1 & Scaled Particle Theory	$1 + 4y + 10y^2 + 19y^3 + 31y^4 + 46y^5 + \ldots$
Percus-Yevick (pyv), III-2	$1 + 4y + 10y^2 + 16y^3 + 22y^4 + 28y^5 + \ldots$
Guggenheim, III-3	$1 + 4y + 10y^2 + 20y^3 + 35y^4 + 56y^5 + \ldots$
van der Waals	$1 + 4y + 16y^2 + 64y^3 + 256y^4 + 1024y^5 + \ldots$
Padé (3,3), III-4	$1 + 4y + 10y^2 + 18.36y^3 + 28.2y^4 + 39.5y^5 + \ldots$

Quite evidently, the Padé approximant of Ree and Hoover represents the known virial coefficients very well. The simpler, theoretically based Equation (III-1) does remarkably well.

It will now be shown that there exists a closed form of equation which agrees more closely with the molecular dynamics calculations for rigid spheres than any of these approximations.

Virial Equation as a Geometric Series

If one postulates that all of the reduced virial coefficients in Equation (III-5) can be approximated by integers, a recursive relation for them can be found. Consider the series

$$Z = 1 + 4y + 10y^2 + 18y^3 + 28y^4 + 40y^5 + \ldots \qquad \text{(III-6)}$$

The coefficients of Equation (III-6) are calculable from the formula

$$B_n = (n^2 + n - 2), \qquad \text{(III-7)}$$

where B_n = nth virial coefficient, $n \geq 2$. Thus, it is possible to express Equation (III-6) as

$$Z = \frac{PV}{NkT} = 1 + \sum_{n=2}^{\infty} (n^2 + n - 2)y^{n-1}. \qquad \text{(III-8)}$$

Equivalently,

$$Z = \frac{PV}{NkT} = 1 + \sum_{n=0}^{\infty} (n^2 + 3n)y^n. \qquad \text{(III-9)}$$

The infinite sums in Equation (III-9) are derivative forms of the geometric series. As such, they may be expressed in closed form.

By manipulating the geometric series, the result is

$$Z = PV/NkT = (1 + y + y^2 - y^3)/(1 - y)^3. \qquad \text{(III-10)}$$

Equation (III-10) is strikingly similar to the result of the works of Thiele [48] and of Frisch [43]. The absence in their equations of the numerator term $-y^3$ in Equation (III-1) is possibly due to basic assumptions in the Percus-Yevick theory [38] and in the scaled-particle theory [43].

High Density Rigid-sphere Calculations

It can be demonstrated that Equation (III-10) describes rigid-sphere behavior better than any of the existing analytical forms, theoretical or empirical. This demonstration is presented in Table III-2 through comparison of calculated compressibility factors with compressibility factors from the molecular dynamics of Alder and Wainwright [4].

TABLE III-2

Comparison of Rigid Sphere Compressibility Factors

V/V_o	Z^c	Z^{pyc}	Z^p	Z^6	Z^7	Z^{AW}
1.50	12.43	13.18	12.31	10.46	11.27	12.5
1.60	10.16	10.80	10.11	8.95	9.50	10.17
1.70	8.56	9.01	8.55	7.79	8.18	8.59
2.00	5.83	6.03	5.83	5.59	5.73	5.89
3.00	3.03	3.06	3.03	3.01	3.03	3.05
10.00	1.36	1.36	1.36	1.36	1.36	1.36

Nomenclature:

V_o = rigid sphere volume at closest packing = $N\sigma^3/\sqrt{2}$

Z^c = result from Equation (III-10)

Z^{pyc} = result from Percus-Yevick compressibility equation, III-1

Z^p = result from Padé approximant, Equation (III-4)

Z^6 = result from six term virial series

Z^7 = result from seven term virial series

Z^{AW} = result from Alder and Wainwright calculations

The Z^6, Z^7, Z^P, and Z^{AW} values tabulated in Table III-2 are abstracted from a recent article by Ree and Hoover [42]. The calculations for the Percus-Yevick compressibility equation, III-1, and Equation (III-10) are new.

Discussion

The equation derived from consideration of the nearly geometric form of the virial series for rigid-spheres has proven to be the best analytical form in existence. The ability of Equation (III-10) to outperform the highly accurate Padé (3,3) approximant, Equation (III-4), indicates that the higher order virial coefficients predicted by Equation (III-10) may be closer to the true values. In support of this, consider the reduced seventh virial coefficient predicted by Equation (III-10),

$$B_7 = (49 + 7 - 2) = 54. \qquad \text{(III-11)}$$

Because of the reduced form employed in this paper, one must divide the virial coefficients of Equation (III-10) by $\left(\frac{4}{b}\right)^{n-1}$ in order to compare with the results of Ree and Hoover.

$B_7 = 0.0138 \pm 0.0004\ b^6$	Ree and Hoover [42]
$B_7 = 0.0132\ b^6$	Equation (III-10)
$B_7 = 0.0127\ b^6$	Padé approximant (III-4)

Thus, Equation (III-11) predicts (B_7/b^6) within 4.4% of 0.0138 and within 1.5% of (0.0138 ± 0.0004).

While the error in predicted higher order virial coefficients may increase, it remains that Equation (III-10) is a good rigid-sphere equation even for densities at which other predictions go astray.

CHAPTER IV

THE EQUATION OF STATE FOR A MIXTURE OF NONATTRACTING RIGID SPHERES

This chapter is devoted to the formulation of an accurate equation of state for mixtures of rigid spheres with different diameters. The resulting mixture equation, based upon Equation III-10, is developed by analogy with the work of Lebowitz [30, 31].

Preliminary Derivation of the Equation of State

From statistical mechanics, the equation of state for rigid spheres [24] may be written as

$$P/nkT = 1 + (2\pi n/3)\,\sigma^3 g(\sigma), \qquad \text{(IV-1)}$$

where $n = N/V$ = number density.

For this particular system, it is convenient to express Equation (IV-1) as follows,

$$P/nkT = Z = 1 + 4y\,g(\sigma). \qquad \text{(IV-2)}$$

In order that the equation eventually be related to a proper mixture form, it is helpful to study the work of Lebowitz on rigid-sphere mixtures [30, 31]. From the Percus-Yevick equation for rigid spheres [38], Lebowitz obtained the following form for the quantity $g(\sigma)$, the radial distribution function upon contact,

$$g(\sigma)_{pyv} = (1 + \tfrac{1}{2}y)/(1 - y)^2. \qquad \text{(IV-3)}$$

This corresponds to Equation (III-2), for the compressibility factor, $Z = PV/NkT = P/nkT$, of the pure component rigid-sphere fluid.

In his work, Lebowitz has shown that the following species radial distribution function is obtained for the Percus-Yevick virial equation for mixtures,

$$g_{ii}(\sigma_i) = [1/(1 - Y) + (3\sigma_i X)/(2(1 - Y)^2)], \qquad \text{(IV-4)}$$

where $Y = \Sigma\, n_i\sigma_i^3 = (\pi N/6V)\, \Sigma x_i\, \sigma_i^3 = (\pi N/6V)\, \langle\sigma^3\rangle$

$$X = \Sigma\, n_i\sigma_i^2 = (\pi N/6V)\, \Sigma x_i\, \sigma_i^2 = (\pi N/6V)\, \langle\sigma^2\rangle$$

$$n_i = (\pi N_i/6V) = (\pi N x_i/6V)$$

$$x_i = (N_i/N)$$

σ_i = diameter of a sphere of the i-th species.

A quick check will verify that Equation (IV-4) reduces to the correct pure component form, Equation (IV-3), for spheres of only a single species.

The purpose in looking at the Percus-Yevick results is to gain insight into the problem of what has to be done in order to extend other pure-component, rigid-sphere equations to the case of mixtures. Assume that Equation (III-10), repeated here,

$$Z = (1 + y + y^2 - y^3)/(1 - y)^3 \qquad \text{(IV-5)}$$

is such an equation. The resulting form for the pure component radial distribution function at contact is,

$$g(\sigma) = (1 - \tfrac{1}{2}y)/(1 - y)^3. \qquad \text{(IV-6)}$$

Equation (IV-6) can be written in the form

$$g(\sigma)_{cst} = g(\sigma)_{pyv} + y^2/[2(1 - y)^3], \qquad \text{(IV-7)}$$

where $g(\sigma)_{cst}$ = value from Equation (IV-6)

$g(\sigma)_{pyv}$ = value from Percus-Yevick virial equation, (IV-3).

In extending Equation (IV-6) or Equation (IV-5) to mixtures, it is assumed that the species radial distribution function at contact for a rigid-sphere mixture becomes, by analogy with Equation (IV-3) and Equation (IV-4),

$$g_{ii}(\sigma_i) = 1/(1 - Y) + (3\sigma_i X)/[2(1 - Y)^2] + (\sigma_i X)^2/[2(1 - Y)^3] \qquad \text{(IV-8)}$$

The radial distribution function at contact for unlike species is [24],

$$g_{ij}(\sigma_{ij}) = [\sigma_i g_{jj}(\sigma_j) + \sigma_j g_{ii}(\sigma_i)]/(\sigma_i + \sigma_j), \qquad \text{(IV-9)}$$

where $\sigma_{ij} = (\sigma_i + \sigma_j)/2$.

It is now appropriate to see how the above expressions fit into the equation of state for fluid mixtures. The virial theorem for mixtures gives the relation,

$$P/nkT = 1 + (2\pi N/3V) \{ \sum_{i \le j} x_i x_j \sigma_{ij}^3 g_{ij}(\sigma_{ij}) \}. \qquad \text{(IV-10)}$$

Carrying out the involved algebra and employing the required forms of Equation (IV-8) and Equation (IV-9), one gets the following equation of

state for an m-component mixture of nonattracting rigid spheres, based upon Equation (IV-5),

$$Z = (1 + Y + Y^2)/(1 - Y)^3 - C\{\sum_{i<j} (n_i n_j (\sigma_i - \sigma_j)^2 Q_{ij}) + YX^3/3\}/(1 - Y)^3 \qquad \text{(IV-11)}$$

where $C = 18V/\pi N$

$$Q_{ij} = \sigma_i + \sigma_j + \sigma_i \sigma_j X.$$

The importance of the relations developed here for the mixture rigid-sphere equation of state and radial distribution functions at contact, Equations (IV-8) and (IV-11), lies in their applicability to the variational and perturbational methods of calculation of thermodynamic properties of real mixtures, based upon the rigid sphere mixture reference system, and in the computation of transport properties. It is obvious that Equations (IV-8) and (IV-11) will be very useful in any correlation or theory which requires the evaluation of rigid-sphere behavior as part of the calculation scheme.

Comparison of the Mixture Equation with Molecular Dynamics and Monte Carlo Data

The derived equation for mixtures, Equation (IV-11), has been used to calculate compressibility factors for an equimolar binary system of rigid spheres. The ratio of the diameters, $\Psi = \sigma_i/\sigma_j$, equals three. This is the system described by Alder [1]. Table IV-1 shows the agreement between the machine data and the predictions by Equation (IV-11).

TABLE IV-1

Compressibility Factors for an Equimolar Binary Mixture of Rigid Spheres Compared to Molecular Dynamics Data [1], $\Psi = \sigma_2/\sigma_1 = 3$

Y	Z_{pyc}	Z_{IV-11}	Z_{MD}	Z_{pyv}	Z_{pya}
0.2333	2.386	2.368	2.37	2.332	2.359
0.2692	2.804	2.772	2.77	2.708	2.756
0.3106	3.414	3.356	3.36	3.239	3.326
0.3583	4.352	4.241	4.24	4.019	4.186
0.3808	4.912	4.764	4.76	4.467	4.689
0.4393	6.873	6.567	6.57	5.953	6.413
0.5068	10.590	9.898	9.77	8.514	9.552

Note: subscripts denote the following, pyc = Percus-Yevick "compressibility" equation, IV-11 = Equation (IV-11), MD = molecular dynamics data of Alder, pyv = Percus-Yevick "virial" equation, pya = the average value of the Percus-Yevick equations (suggested by Mansoori [34]).

It should be noted that the relation for the compressibility factor of a rigid-sphere fluid also can be obtained from the following linear combination of the Percus-Yevick virial and compressibility equations,

$$Z = (\tfrac{1}{3})Z_{pyv} + (\tfrac{2}{3})Z_{pyc}. \qquad \text{(IV-11)}$$

Use of this averaging procedure for obtaining the mixture equation of state has been discussed by Mansoori, Carnahan, Starling, and Leland [35]. This averaging method is not used here, for two reasons. First, in the present derivation there was interest not only in obtaining the expression for the mixture equation of state, from which thermodynamic properties can be calculated, but also the radial distribution functions

at contact, from which transport properties can be calculated. The radial distribution functions are not obtained directly in using the averaging procedure [35]. Second, the present derivation is totally a product of the research reported here, while use of the averaging procedure was reported in a cooperative effort with Mansoori and Leland of Rice University [35].

Table IV-1 is testimony to the accuracy of Equation (IV-11) for the mixture. Considering that the data are for spheres of such widely differing diameters, the agreement is all the more impressive.

The data point of highest reduced density, $Y = 0.5068$, in Table IV-1 requires some comment. In his discussion, Alder [1] points out that this value may not be truly representative of the fluid phase. At such density, it is possible that the calculation may have been influenced by the solid or glassy phase. Therefore, one should not weigh this data point too heavily in judging the accuracy of Equation (IV-11).

In further testing the equation, calculations of "excess" thermodynamic properties, relative to an ideal gas, were made. From calculation of pure component properties at the same densities, it is possible to calculate changes upon mixing at constant density. Table IV-2 shows the results of the calculations compared to the molecular dynamics data of Alder.

The excess properties are calculated relative to an ideal gas at the same temperature and pressure. Thus, the excess entropy, enthalpy and Gibbs free energy, S^E, H^E and G^E, respectively, are

TABLE IV-2

Excess Thermodynamic Properties and Effects of Mixing [1]

for Rigid Spheres ($x_1 = x_2 = \frac{1}{2}$, $\Psi = \sigma_1/\sigma_2 = 3$)

y	$-S^E/Nk$		$\Delta S^E/Nk$		G^E/NkT		$\Delta G^E/NkT$		$\Delta(PV/NkT)$	
	MD	This Work	MD	This Work	MD	This Work	MD	This Work	MD	This Work
0.2333	0.14	0.139	0.12	0.130	1.51	1.508	0.60	0.592	0.48±0.02	0.461
0.2692	0.21	0.205	0.18	0.184	1.99	1.977	0.81	0.800	0.63±0.02	0.616
0.3106	0.31	0.306	0.26	0.263	2.67	2.662	1.13	1.110	0.87±0.03	0.847
0.3583	0.48	0.467	0.37	0.382	3.72	3.709	1.63	1.593	1.25±0.04	1.211
0.3808	0.58	0.564	0.44	0.451	4.34	4.327	1.92	1.881	1.48±0.05	1.431
0.4393	0.92	0.898	0.69	0.678	6.49	6.465	2.91	2.891	2.22±0.06	2.214
0.5068	1.52	1.495	1.07	1.061	10.29	10.393	4.77	4.781	3.70±0.08	3.720

$$-S^E/Nk = \int_0^y \frac{(Z - 1)dy}{y} - \ln(Z), \qquad \text{(IV-12)}$$

$$H^E/Nk = Z - 1 = PV/NkT - 1, \qquad \text{(IV-13)}$$

$$G^E/NkT = H^E/NkT - S^E/Nk. \qquad \text{(IV-14)}$$

The changes upon mixing, at constant reduced number density, Y, are calculated from,

$$-\Delta S^E/Nk = S^E/Nk - (S^E/Nk)^*, \qquad \text{(IV-15)}$$

$$-\Delta H^E/NkT = \Delta(Z - 1) = (PV/NkT) - (PV/NkT)^*, \qquad \text{(IV-16)}$$

$$\Delta G^E/NkT = \Delta H^E/NkT - \Delta S^E/Nk, \qquad \text{(IV-17)}$$

where supercript * denotes pure component property at the same reduced number density.

The mixing effects are, thus, the difference between the property for the mixture and the property for the pure fluids at the same reduced number density.

A second set of mixture data has been generated by Smith and Lea [46]. A Monte Carlo technique was used for an equimolar system of spheres differing in diameter by the ratio $\Psi = 5/3$. Table IV-3 gives the comparison between these data and the values based upon Equation (IV-11). Clearly, the predictions are within reasonable estimates of the uncertainty of the data for PV/NkT. Smith and Lea also report data for the excess properties and the effects of mixing at constant density.

Agreement between the predictions and the reported data in Table IV-3, is not very good for the changes upon mixing. The predicted mixture

TABLE IV-3

Thermodynamic Properties for a Binary System of

Rigid Spheres [46] ($\Psi = \sigma_1/\sigma_2 = 5/3$, $x_1 = x_2 = 1/2$)

	d*	0.3	0.5	0.7	0.8
PV/NkT (Pure Fluid)	CS	1.967	3.262	5.7101	7.750
	MC	1.98	3.32	5.86	7.85
$-S^E/Nk$ (Pure Fluid)	CS	0.104	0.362	0.907	1.355
	MC	0110	0.36	0.93	1.41
PV/NkT (Mixtures)	CS	1.879	3.041	5.214	7.013
	MC	1.87 ± 5%	3.04 ± 5%	5.24 ± 5%	6.99 ± 5%
$-\Delta$(PV/NkT)	CS	0.087	0.221	0.492	0.736
	MC	0.10	0.28	0.82	0.87
$-S^E/Nk$ (Mixtures)	CS	0.083	0.294	0.747	1.123
	MC	0.08	0.29	0.74	1.13
$\Delta S^E/Nk$	CS	0.021	0.068	0.160	0.232
	MC	0.02	0.07	0.19	0.29
$\Delta G^E/NkT$ **	CS	0.108	0.290	0.656	0.968
	MC	0.12	(0.35)	(0.81)	(1.16)

MC denotes Monte Carlo data of Smith and Lea
CS denotes predictions from this work
[Note: $d^* = (N/V)(\Sigma x_i \sigma_i^3) = 6Y/\pi$].

** There is an acknowledged error in the published values of $\Delta(G^E/NkT)$ from Smith and Lea [46]. Corrected values of this quantity appear enclosed in parentheses.

properties are, however, in reasonably close accord. A study of the pure fluid data of Smith and Lea shows disagreement with the molecular dynamics data of Alder [4]. It is important to note that if the pure fluid data are somewhat inaccurate (3 - 5%), then the changes upon mixing can be strongly affected. Equation (IV-5) is in very good agreement with molecular dynamics pure fluid results. Thus, since Equation (IV-11) agrees with the mixture data for this system (Smith and Lea), it may well be that the predicted values of the pure fluid data and the effects of mixing are closer to actual behavior than the reported Monte Carlo values for those properties. Though the difference is small, it is enough to affect the computed values of $\Delta(PV/NkT)$, $\Delta(S^E/Nk)$, and $\Delta(G^E/NkT)$.

If the smoothed molecular dynamics data are used for the pure fluid, then the effects of mixing determined from the mixture data of Smith and Lea are in close agreement with the values predicted from the equation of state.

A third set of data for a rigid-sphere mixture has been given by Rotenberg [45]. The equation of state of an equimolar binary mixture of rigid spheres was again calculated by a Monte Carlo method, using a diameter ratio $\Psi = 11/10$. In this particular case, the data were reported as $g_{11}(\sigma_1)$, $g_{22}(\sigma_2)$ and $g_{12}(\sigma_{12})$. These data were converted to compressibility factor form on a GE-420 time-sharing computer at the University of Oklahoma. Table IV-4 shows the comparison between the converted data and the prediction by Equation (IV-11) for this system. The dashed line in Table IV-4 roughly separates the data for the solid phase from the fluid phase data. This transition occurs at about $Y = 0.475$ in the Rotenberg data. Since the equation of state described in this paper is

TABLE IV-4

Comparison to the PV/NkT Data of Rotenberg [45] for The Binary System ($x_1 = x_2 = \frac{1}{2}$, $\Psi = 11/10$)

y	Z_R	Z_{cst}	Z_{pyv}	Z_{pyc}
0.6465	54.710	40.398	28.246	46.473
0.6185	26.352	31.610	23.145	35.842
0.5895	18.103	24.912	19.029	27.853
0.5764	15.570	22.476	17.471	24.979
0.5342	11.610	16.415	13.419	17.914
0.5100	10.472	13.852	11.612	14.972
0.4912	9.408	12.197	10.409	13.090
0.4810	10.725	11.400	9.819	12.191
0.4703	10.688	10.633	9.243	11.328
0.4589	9.833	9.884	8.672	10.490
0.4470	8.989	9.170	8.121	9.694
0.4344	8.500	8.481	7.581	8.931
0.4301	8.358	8.261	7.407	8.688
0.4212	7.752	7.826	7.061	8.209
0.4073	7.065	7.202	6.557	7.524
0.3928	6.567	6.613	6.076	6.882
0.3902	6.446	6.514	5.994	6.774
0.3503	5.233	5.195	4.884	5.351
0.3107	4.186	4.191	4.009	4.282
0.2716	3.411	3.419	3.316	3.470
0.2544	3.129	3.134	3.055	3.173
0.2334	2.832	2.823	2.767	2.851
0.1969	2.374	2.365	2.336	2.380
0.1620	2.018	2.008	1.994	2.015
0.1296	1.715	1.732	1.726	1.736
0.1168	1.634	1.636	1.632	1.638

Note: subscripts denote the following:

R = Rotenberg data, converted to PV/NkT, according to Eq. (IV-10)
cst = prediction from Equation (IV-11) of this work
pyv = prediction from Percus-Yevick "virial" equation in mixture form
pyc = prediction from Percus-Yevick "compressibility" equation in mixture form.

only for the fluid phase, it is not expected that the predictions would be very good above the transition point. The agreement at fluid densities, $Y \leq 0.475$, is fairly good. Both positive and negative deviations are found between the predictions and the data.

Discussion

The foregoing derivation of the mixture form of the previously derived rigid-sphere equation has resulted in an analytical expression which is in very good agreement with published data for rigid-sphere mixtures. In cases where some disagreement occurs, closer analysis shows that the data could be somewhat in error. The agreement with the molecular dynamics data is most striking. As in the case of the pure fluid, the equation seems to predict rigid-sphere behavior within reasonable limits of the experimental uncertainty. In addition to the compressibility behavior, the equation does quite well in predicting the excess thermodynamic properties and the effects of mixing.

The advent of such an equation makes possible the formulation and testing of more sophisticated approaches to fluid theory including mixture behavior.

CHAPTER V

EQUILIBRIUM THERMODYNAMIC PROPERTIES OF THE RIGID-SPHERE SYSTEM: PURE FLUIDS

In studying the rigid-sphere fluid as a starting point for understanding the behavior of real fluids, a tabulation of the excess thermodynamic properties, relative to those of an ideal gas at the same temperature and pressure, might be useful.

A number of approximate expressions for the rigid-sphere pressure or compressibility factor have been proposed [43, 48, 50, 7, 21, 41, 4, 28, 19, 12, 51] and can be compared with molecular dynamics calculations [3, 4]. Relatively fewer evaluations of the thermodynamic functions have been presented. The purpose here is to present thermodynamic functions calculated with a highly accurate rigid-sphere equation, along with an evaluation of their accuracy. Pertinent comparisons are made with other equations and with molecular dynamics calculations.

Rigid-sphere Thermodynamic Functions

The calculation of rigid-sphere thermodynamic functions has been made with Equation (III-10), repeated here

$$PV/NkT = Z = (1 + y + y^2 - y^3)/(1 - y)^3, \qquad (V\text{-}1)$$

which accurately predicts compressibility behavior and which agrees quite well with the known virial coefficients for rigid spheres. The equation

has been shown to describe rigid-sphere behavior better than other existing analytical expressions [12]. For this reason, it has been chosen for the calculations. Because of the close agreement with the molecular dynamics calculations of Alder and Wainwright [4], errors in the calculated thermodynamic functions should be minor. This would be true especially for densities less than y = 0.50. Above this value, the compressibility changes so rapidly with density that further comparison with high density machine calculations should be used for future confirmation of the accuracy of Equation (V-1) for the fluid phase.

The analytical expression for the excess entropy, derived from Equation (V-1), is

$$(S - S^{o})/R = \ln(PV/NkT) - (3 - 2y)/(1 - y)^{2} + 3. \qquad (V\text{-}2)$$

The excess internal energy for a rigid-sphere fluid is,

$$(U - U^{o})/RT = 0. \qquad (V\text{-}3)$$

It is now possible to combine Equations (V-2) and (V-3) to get the expression for the Helmholtz free energy. By definition,

$$(A - A^{o})/RT = (U - U^{o})/RT - (S - S^{o})/R. \qquad (V\text{-}4)$$

Thus, for rigid spheres,

$$(A - A^{o})/RT = -(S - S^{o})/R. \qquad (V\text{-}5)$$

Using the definition of enthalpy, we find

$$(H - H^{o})/RT = (U - U^{o})/RT + (PV - RT)/RT. \qquad (V\text{-}6)$$

Simplifying the expression, for rigid spheres,

$$(H - H^{o})/RT = Z - 1. \tag{V-7}$$

From the definition of Gibbs free energy, we get

$$(G - G^{o})/RT = (H - H^{o})/RT - (S - S^{o})/R. \tag{V-8}$$

The fugacity may be evaluated from Equation (V-8) according to the following relation:

$$\ln(f/P) = (G - G^{o})RT. \tag{V-9}$$

So, knowing only the relations in Equations (V-1), (V-2) and (V-3), it is possible to derive numerical values for the excess thermodynamic properties for the rigid-sphere system.

Accuracy of the Calculations

The numerical results of the excess property calculations are presented in Table V-1. It should be kept in mind that these values are not exact. They are, however, very accurate. The basic equation, Equation (V-1), is more accurate than the Padé (3,3) approximant recently used by Alder, Hoover, and Young [3] and by Hoover and Ree [28] in making similar calculations. The latter authors state that the uncertainty in $(S - S^{o})$ is about 0.01R. Calculated values based upon the more accurate Equation (V-1) should have uncertainties no greater than 0.01R.

The fundamental expression for the molar entropy relative to an ideal gas at the same pressure and temperature is

$$\frac{(S - S^{o})}{R} = \ln(Z) - \int_{o}^{y} (Z - 1)\, d\ln y. \tag{V-10}$$

TABLE V-1

Thermodynamic Functions for a Rigid-Sphere Fluid

y	Z	$(H-H^o)/RT$	$(S-S^o)/R$	$(G-G^o)/RT$	(f/P)
0.00	1.000	0.0000	0.0000	0.000	1.0000
0.02	1.084	0.0841	-0.0013	0.085	1.0892
0.04	1.177	0.1772	-0.0052	0.182	1.2002
0.06	1.280	0.2803	-0.0123	0.293	1.3399
0.08	1.395	0.3945	-0.0228	0.417	1.5179
0.10	1.521	0.5213	-0.0372	0.559	1.7481
0.12	1.662	0.6621	-0.0560	0.718	2.0505
0.14	1.819	0.8188	-0.0795	0.898	2.4554
0.16	1.993	0.9934	-0.1083	1.102	3.0094
0.18	2.188	1.1883	-0.1431	1.331	3.7864
0.20	2.406	1.4062	-0.1844	1.591	4.9071
0.22	2.650	1.6504	-0.2330	1.883	6.5761
0.24	2.925	1.9245	-0.2898	2.214	9.1545
0.26	3.233	2.2328	-0.3555	2.588	13.308
0.28	3.581	2.5806	-0.4313	3.012	20.325
0.30	3.974	2.9738	-0.5182	3.492	32.852
0.32	4.420	3.4195	-0.6178	4.037	56.672
0.34	4.926	3.9263	-0.7314	4.658	105.40
0.36	5.504	4.5044	-0.8609	5.365	213.85
0.38	6.166	5.1660	-1.0082	6.174	480.20
0.40	6.926	5.9259	-1.1758	7.102	1214.1
0.42	7.802	6.8022	-1.3665	8.169	3529.0
0.44	8.817	7.8171	-1.5835	9.401	1.2095×10^4
0.46	9.998	8.9976	-1.8307	10.828	5.0429×10^4
0.48	11.378	10.3778	-2.1127	12.491	2.6580×10^5
0.50	13.000	12.0000	-2.4351	14.435	1.8581×10^5
0.52	14.918	13.9178	-2.8044	16.722	1.8296×10^7
0.54	17.200	16.1996	-3.2288	19.428	2.7393×10^8
0.56	19.933	18.9331	-3.7184	22.652	6.8773×10^9
0.58	23.233	22.2330	-4.2853	26.518	3.2866×10^{11}
0.60	27.250	26.2500	-4.9449	31.195	3.5302×10^{13}
0.62	32.185	31.1853	-5.7169	36.902	1.0627×10^{16}
0.64	38.311	37.3114	-6.6259	43.937	1.2070×10^{19}
0.66	46.003	45.0031	-7.7042	52.707	7.7706×10^{22}
0.68	55.785	54.7852	-8.9941	63.779	5.0002×10^{27}
0.70	68.407	67.4074	-10.552	77.960	7.2023×10^{33}
0.72	84.965	83.9650	-12.456	96.421	7.4988×10^{41}
0.74	107.10	106.10	-14.812	120.91	3.2422×10^{52}

It seems reasonable that accuracy in the calculation of Z will lead to accuracy in the calculation of $(S - S^o)/R$ and the other derived properties. Recall, $(H - H^o)/RT = Z - 1$ for this system. Also, one finds

$$\ln\left(\frac{f}{P}\right) = Z - 1 - \ln Z + \int_o^y (Z - 1)\, d \ln y. \qquad \text{(V-11)}$$

It is possible to make an error analysis of $(S - S^o)/R$. For convenience, let $W = (S - S^o)/R$. The expression for the relation between an error in Z and its effect on W is

$$\Delta W \cong (\partial W/\partial Z)\Delta Z. \qquad \text{(V-12)}$$

Now, since W involves an integral whose upper limit shares functionality with Z, the derivative, $(\partial W/\partial Z)$, must be found according to Leibnitz' rule.

Again, for the mathematical convenience, let $(Z - 1)/y = \varphi(y,Z)$. Then,

$$\frac{\partial W}{\partial Z} = \frac{1}{Z} - \varphi(y,Z)\frac{\partial y}{\partial Z} - \int_o^y \frac{\partial \varphi(y,Z)}{\partial Z}\, dy, \qquad \text{(V-13)}$$

or

$$\frac{\partial W}{\partial Z} = \frac{1}{Z} - \left(\frac{Z-1}{y}\right)\left(\frac{\partial y}{\partial Z}\right) - \int_o^y \left[\frac{y - (Z-1)(dy/dZ)}{y^2}\right] dy. \qquad \text{(V-14)}$$

Now, in order to obtain a reasonable numerical evaluation of Equation (V-14), Equation (V-1) can be used. The result is

$$\frac{\partial W}{\partial Z} = \frac{1}{Z} - \left(\frac{Z-1}{y}\right)\left(\frac{\partial y}{\partial Z}\right) + \frac{3}{\sqrt{12}} \ln\left[\frac{(2 - \sqrt{12} - 2y)(2 + \sqrt{12})}{(2 + \sqrt{12} - 2y)(2 - \sqrt{12})}\right]$$

$$- \ln[(2 + 2y - y^2)/2], \qquad \text{(V-15)}$$

where $(\partial y/\partial Z) = (1 - y)^4/(4 + 4y - 2y^2)$.

The results of Equation (V-15) over the range of the calculations presented are given in Table V-2.

TABLE V-2

Results of Error Analysis of Entropy Calculations

y	[∂W/∂Z]
0.00	0.00
0.10	0.07
0.20	0.08
0.30	0.05
0.40	0.02
0.50	0.11
0.60	0.22
0.70	0.34

Therefore, an error in Z of ± 0.01 could cause a maximum error in $(S - S^o)/R$ of about ± 0.0035 in the range of the reported values.

Another approach to this question is to look at the expansion of $(S - S^o)/R$ in terms of the virial coefficients. Recall,

$$(S - S^o)/R = \ln(Z) - \int_o^y \frac{Z - 1}{y}\, dy, \qquad \text{(V-16)}$$

where $Z = 1 + B_2 y + B_3 y^2 + \ldots = 1 + \sum_{n=2}^{\infty} B_n y^{n-1}$,

$$(S - S^o)/R = \ln(Z) - \int_o^y \sum_{n=2}^{\infty} B_n y^{n-2} dy, \qquad \text{(V-17)}$$

or,

$$(S - S^o)/R = \ln(Z) - \sum_{n=2}^{\infty} \left(\frac{B_n y^{n-1}}{n-1}\right). \qquad \text{(V-18)}$$

Now, if one has an accurate calculation of Z, the first term on the right-hand side of Equation (V-18) should be accurate also. The series which appears on the right converges faster than the virial series. This means that the excess entropy depends more on the lower-order virial coefficients than on the higher ones. Thus, the mathematical functionality in Equation (V-18) indicates that inaccuracy in calculation of Z is damped out in the calculation of $(S - S^{o})/R$. This is in accord with the findings of the preceding error analysis.

Comparison with Other Equations

Frequently, when scanning the literature pertaining to the theory of fluids, one is apt to come across some discussion of the "excess" properties. Particularly, the excess entropy $(S - S^{o})/R$ for rigid spheres in encountered [24, 44] as predicted by the Kirkwood equation and by the Yvon-Born-Green equation.

Assuming that Equation (V-1) predicts excess properties accurately, Table V-3 reveals some interesting facts. Although their compressibility predictions go astray at the low density of about $y = 0.16$, the excess entropy predictions by the Kirkwood equation and by the Yvon-Born-Green equation are reasonably accurate to a density of about $y = 0.45$. Such standard works as Hill [24] and Rice and Gray [44] contain the Kirkwood and the Yvon-Born-Green values. It would seem beneficial to have some estimate of the range of useful application of these equations. Also listed in Table V-3 are results obtained by use of the seven-term modified virial equation reported by Alder. This equation uses the known virial coefficients up through the fifth and then fits the molecular

TABLE V-3

Comparative Values of $\Delta S = -(S - S^{o})/R$ and Compressibility Factor

DENSITY		KIRKWOOD		Y-B-G		THIS WORK		ALDER		SPT		PADÉ (3,3)	
y	V/V_o	Z	ΔS	Z	ΔS	Z	ΔS	Z	ΔS	Z	ΔS	Z	ΔS
0.0884	8.38	1.44	.03	1.44	.03	1.446	.028	1.446	.028	1.447	.028	1.446	.028
0.1562	4.74	1.91	.12	1.93	.11	1.959	.102	1.962	.102	1.965	.101	1.960	.102
0.2128	3.48	2.39	.24	2.46	.23	2.559	.215	2.569	.213	2.579	.212	2.563	.214
0.2616	2.83	2.89	.39	3.04	.37	3.260	.361	3.282	.360	3.304	.360	3.266	.362
0.3060	2.42	3.40	.55	3.65	.56	4.101	.547	4.138	.548	4.187	.548	4.110	.548
0.3444	2.15	3.91	.73	4.21	.76	5.047	.759	5.093	.765	5.192	.765	5.057	.761
0.3817	1.94	4.43	.92	4.75	1.00	6.226	1.00	6.265	1.04	6.461	1.04	6.234	1.03
0.4150	1.78	4.93	1.14	5.33	1.23	7.617	1.33	7.610	1.35	7.978	1.36	7.619	1.33
0.4515	1.64	5.44	1.37	5.96	1.49	9.474	1.72	9.337	1.75	10.03	1.78	9.464	1.73
0.4840	1.53	5.95	1.60	6.54	1.77	11.68	2.17	11.28	2.21	12.50	2.27	11.64	2.18
0.5142	1.44	6.46	1.84			14.33	2.69	13.47	2.72	15.52	2.84	14.26	2.70
0.5405	1.37	6.99	2.07			17.26	3.24	15.71	3.24	18.89	3.44	17.14	3.24
0.5700	1.30	7.50	2.32			21.44	3.98	18.64	3.91	23.76	4.27	21.24	3.98
0.5972	1.24	7.93	2.60			26.63	4.85	21.90	4.66	29.89	5.26	26.32	4.83

dynamics results to get two additional terms. The calculated entropies with that equation agree with the values reported by Alder [4].

Two other equations have been compared in Table V-3. The scaled particle theory [43] yields a rigid-sphere equation which also results from one of the solutions of the Percus-Yevick equation [48, 50]. The most recent version of the Padé (3,3) approximant of Hoover and Ree [28] has also been used for entropy calculations. The difference between the Padé equation predictions and those of Equation (V-1) is very slight.

Discussion

The tabulated values of the rigid-sphere "excess" thermodynamic properties, as well as the equations given in this work, obviously can be useful to those engaged in equation-of-state development work. The idea of using the rigid-sphere core model as an integral part of molecular and semi-empirical theories is quite popular among present day researchers. This is not only true in the equation-of-state area, but in the transport property area as well. The information here will benefit both research groups.

CHAPTER VI

THE EQUILIBRIUM THERMODYNAMIC PROPERTIES OF THE RIGID-SPHERE SYSTEM: MIXTURES

The suitability of Equation (IV-11) for the computation of mixture properties has been shown in Chapter IV. For reasons much related to those of the foregoing section, an extensive tabulation of mixture properties for equimolar binary mixtures of several different diameter ratios is presented. The calculated properties include PV/NkT, H^E/Nkt, $-S^E/Nk$, $\Delta S^E/Nk$, G^E/NkT and $\Delta G^E/NkT$. These terms have all been previously defined in Chapter IV in terms of the rigid-sphere equation, so no repetition of their meaning is given here.

TABLE VI-1

Excess Thermodynamic Properties for an Equimolar Binary System of Rigid Spheres, Ψ = 1.01[illegible]

Y	PV/NkT	$-S^E/Nk$	$\Delta S^E/Nk$	H^E/NkT	$\Delta H^E/NkT$	G^E/NkT	$\Delta G^E/NkT$
0.0500	1.2274	0.0083	0.0000	0.2274	0.0000	0.2357	0.0083
0.1000	1.5212	0.0372	0.0000	0.5212	0.0000	0.5584	0.0372
0.1500	1.9036	0.0932	0.0000	0.9036	0.0000	0.9968	0.0932
0.2000	2.4061	0.1844	0.0000	1.4061	0.0000	1.5906	0.1844
0.2500	3.0739	0.3214	0.0000	2.0739	0.0000	2.3953	0.3215
0.3000	3.9736	0.5182	0.0000	2.9736	0.0001	3.4918	0.5183
0.3500	5.2055	0.7939	0.0000	4.2055	0.0002	4.9994	0.7941
0.4000	6.9256	1.1757	0.0000	5.9256	0.0003	7.1013	1.1760
0.4500	9.3842	1.7029	0.0001	8.3842	0.0004	10.0871	1.7033
0.5000	12.9993	2.4348	0.0001	11.9993	0.0006	14.4341	2.4355
0.5500	18.5024	3.4644	0.0002	17.5024	0.0010	20.9669	3.4654

TABLE VI-2

Excess Thermodynamic Properties for an Equimolar Binary System

of Rigid Spheres, $\Psi =$ 1.050

Y	PV/NkT	$-S^E/Nk$	$\Delta S^E/Nk$	H^E/NkT	$\Delta H^E/NkT$	G^E/NkT	$\Delta G^E/NkT$
0.0500	1.2272	0.0083	0.0000	0.2272	0.0002	0.2355	0.0085
0.1000	1.5207	0.0371	0.0000	0.5207	0.0005	0.5579	0.0376
0.1500	1.9027	0.0929	0.0002	0.9027	0.0009	0.9957	0.0939
0.2000	2.4047	0.1840	0.0004	1.4047	0.0015	1.5887	0.1855
0.2500	3.0717	0.3207	0.0007	2.0717	0.0023	2.3924	0.3230
0.3000	3.9703	0.5171	0.0011	2.9703	0.0034	3.4874	0.5205
0.3500	5.2006	0.7923	0.0016	4.2006	0.0050	4.9930	0.7974
0.4000	6.9185	1.1734	0.0023	5.9185	0.0073	7.0919	1.1808
0.4500	9.3738	1.6997	0.0033	8.3738	0.0108	10.0735	1.7105
0.5000	12.9839	2.4303	0.0046	11.9839	0.0160	14.4143	2.4464
0.5500	18.4792	3.4582	0.0064	17.4792	0.0241	20.9375	3.4824

TABLE VI-3

Excess Thermodynamic Properties for an Equimolar Binary System of Rigid Spheres, $\Psi = 1.67$

Y	PV/NkT	$-S^E/Nk$	$\Delta S^E/Nk$	H^E/NkT	$\Delta H^E/NkT$	G^E/NkT	$\Delta G^E/NkT$
0.0500	1.2085	0.0065	0.0018	0.2085	0.0188	0.2150	0.0254
0.1000	1.4760	0.0293	0.0078	0.4760	0.0452	0.5054	0.0746
0.1500	1.8220	0.0742	0.0190	0.8220	0.0816	0.8962	0.1558
0.2000	2.2740	0.1480	0.0363	1.2740	0.1321	1.4221	0.2802
0.2500	2.8716	0.2600	0.0613	1.8716	0.2024	2.1316	0.4625
0.3000	3.6727	0.4224	0.0958	2.6727	0.3010	3.0951	0.7234
0.3500	4.7648	0.6516	0.1423	3.7648	0.4409	4.4164	1.0925
0.4000	6.2833	0.9711	0.2047	5.2833	0.6425	6.2544	1.6136
0.4500	8.4454	1.4147	0.2882	7.4454	0.9392	8.8602	2.3540
0.5000	11.6129	2.0336	0.4013	10.6129	1.3870	12.6466	3.4207
0.5500	16.4179	2.9077	0.5570	15.4179	2.0855	18.3256	4.9932

TABLE VI-4

Excess Thermodynamic Properties for an Equimolar Binary System of Rigid Spheres, $\Psi = 2.00$

Y	PV/NkT	$-S^E/Nk$	$\Delta S^E/Nk$	H^E/NkT	$\Delta H^E/NkT$	G^E/NkT	$\Delta G^E/NkT$
0.0500	1.1977	0.0055	0.0027	0.1977	0.0296	0.2033	0.0352
0.1000	1.4504	0.0252	0.0120	0.4504	0.0708	0.4756	0.0960
0.1500	1.7760	0.0640	0.0291	0.7760	0.1276	0.8401	0.1917
0.2000	2.2000	0.1286	0.0558	1.2000	0.2062	1.3286	0.3348
0.2500	2.7588	0.2271	0.0942	1.7588	0.3152	1.9859	0.5424
0.3000	3.5058	0.3708	0.1473	2.5058	0.4679	2.8767	0.8388
0.3500	4.5215	0.5748	0.2191	3.5215	0.6841	4.0964	1.2590
0.4000	5.9304	0.8605	0.3152	4.9304	0.9954	5.7910	1.8559
0.4500	7.9320	1.2589	0.4441	6.9320	1.4526	8.1909	2.7116
0.5000	10.8580	1.8166	0.6184	9.8580	2.1419	11.6746	3.9585
0.5500	15.2878	2.6065	0.8581	14.2878	3.2155	16.8944	5.8221

TABLE VI-5

Excess Thermodynamic Properties for an Equimolar Binary System of Rigid Spheres, $\Psi = 3.000$

Y	PV/NkT	$-S^E/Nk$	$\Delta S^E/Nk$	H^E/NkT	$\Delta H^E/NkT$	G^E/NkT	$\Delta G^E/NkT$
0.0500	1.1768	0.0038	0.0045	0.1768	0.0506	0.1807	0.0544
0.1000	1.4010	0.0177	0.0194	0.4010	0.1202	0.4188	0.1380
0.1500	1.6879	0.0459	0.0472	0.6879	0.2157	0.7338	0.2616
0.2000	2.0591	0.0935	0.0908	1.0591	0.3470	1.1527	0.4406
0.2500	2.5455	0.1676	0.1538	1.5455	0.5285	1.7131	0.6961
0.3000	3.1923	0.2772	0.2409	2.1923	0.7814	2.4696	1.0586
0.3500	4.0674	0.4351	0.3588	3.0674	1.1382	3.5026	1.5734
0.4000	5.2758	0.6590	0.5167	4.2758	1.6500	4.9349	2.3091
0.4500	6.9852	0.9747	0.7283	5.9852	2.3993	6.9600	3.3741
0.5000	9.4744	1.4208	1.0141	8.4744	3.5255	9.8953	4.9463
0.5500	13.2292	2.0580	1.4067	12.2292	5.2741	14.2872	7.3322

TABLE VI-6

Excess Thermodynamic Properties for an Equimolar Binary System of Rigid Spheres, $\Psi = 5.00$

Y	PV/NkT	$-S^E/Nk$	$\Delta S^E/Nk$	H^E/NkT	$\Delta H^E/NkT$	G^E/NkT	$\Delta G^E/NkT$
0.0500	1.1602	0.0026	0.0057	0.1602	0.0671	0.1629	0.0698
0.1000	1.3624	0.0124	0.0247	0.3624	0.1588	0.3748	0.1713
0.1500	1.6198	0.0328	0.0603	0.6198	0.2838	0.6527	0.3167
0.2000	1.9514	0.0683	0.1161	0.9514	0.4548	1.0197	0.5231
0.2500	2.3842	0.1246	0.1968	1.3842	0.6898	1.5088	0.8144
0.3000	2.9577	0.2096	0.3086	1.9577	1.0160	2.1673	1.2256
0.3500	3.7312	0.3341	0.4598	2.7312	1.4744	3.0653	1.8086
0.4000	4.7962	0.5133	0.6624	3.7924	2.1296	4.3096	2.6430
0.4500	6.2988	0.7694	0.9336	5.2988	3.0857	6.0683	3.8552
0.5000	8.4819	1.1357	1.2993	7.4819	4.5180	8.6177	5.6537
0.5500	11.7682	1.6643	1.8003	10.7682	6.7351	12.4326	8.3995

TABLE VI-7

Excess Thermodynamic Properties for an Equimolar Binary System of Rigid Spheres, Ψ = 10.00

Y	PV/NkT	$-S^E/Nk$	$\Delta S^E/Nk$	H^E/NkT	$\Delta H^E/NkT$	G^E/NkT	$\Delta G^E/NkT$
0.0500	1.1492	0.0018	0.0064	0.1492	0.0781	0.1511	0.0800
0.1000	1.3370	0.0091	0.0281	0.3370	0.1841	0.3462	0.1933
0.1500	1.5757	0.0247	0.0684	0.5757	0.3279	0.6005	0.3526
0.2000	1.8827	0.0525	0.1318	0.8827	0.5235	0.9352	0.5760
0.2500	2.2827	0.0978	0.2235	1.2827	0.7913	1.3805	0.8892
0.3000	2.8120	0.1676	0.3506	1.8120	1.1616	1.9797	1.3293
0.3500	3.5253	0.2716	0.5223	2.5253	1.6803	2.7970	1.9520
0.4000	4.5066	0.4237	0.7520	3.5066	2.4192	3.9304	2.8430
0.4500	5.8904	0.6440	1.0589	4.8904	3.4942	5.5345	4.1382
0.5000	7.9002	0.9629	1.4720	6.9002	5.0997	7.8632	6.0626
0.5500	10.9253	1.4280	2.0366	9.9253	7.5780	11.3534	9.0061

TABLE VI-8

Excess Thermodynamic Properties for an Equimolar Binary System of Rigid Spheres, Ψ = 100.

Y	PV/NkT	$-S^E/Nk$	$\Delta S^E/Nk$	H^E/NkT	$\Delta H^E/NkT$	G^E/NkT	$\Delta G^E/NkT$
0.0500	1.1408	0.0012	0.0070	0.1408	0.0865	0.1421	0.0878
0.1000	1.3180	0.0065	0.0306	0.3180	0.2031	0.3246	0.2097
0.1500	1.5432	0.0185	0.0746	0.5432	0.3604	0.5618	0.3790
0.2000	1.8328	0.0407	0.1437	0.8328	0.5733	0.8736	0.6140
0.2500	2.2104	0.0779	0.2435	1.2104	0.8635	1.2884	0.9414
0.3000	2.7105	0.1366	0.3815	1.7105	1.2632	1.8472	1.3999
0.3500	3.3848	0.2262	0.5678	2.3848	1.8209	2.6110	2.0471
0.4000	4.3134	0.3594	0.8164	3.3134	2.6125	3.6728	2.9719
0.4500	5.6244	0.5554	1.1476	4.6244	3.7602	5.1798	4.3156
0.5000	7.5310	0.8428	1.5921	6.5310	5.4689	7.3739	6.3118
0.5500	10.4051	1.2671	2.1976	9.4051	8.0982	10.6722	9.3653

Discussion

An error analysis of the mixture equation is not given. Yet, the close agreement with the limited amount of reliable machine data over a wide density and diameter ratio, Ψ, range shown earlier gives no indication that large errors are to be expected.

Among the other analytical equations presented for mixtures, the proposed equation stands alone in its superior ability to predict the machine data for this system. With this in mind, the tables in this section should provide useful information on the behavior of rigid-sphere mixtures.

CHAPTER VII

THE TRANSPORT PROPERTIES OF THE RIGID-SPHERE SYSTEM

The purpose of this chapter is to demonstrate the usefulness of an accurate analytical rigid-sphere equation of state for making the calculations required in rigid-sphere transport theories. The development or defense of the theories discussed is beyond the scope of this work.

Until recently, the numerical comparisons made in this chapter were not possible. There were no reliable rigid-sphere transport data. Within the past year, molecular dynamics calculations of transport properties for a one-component system of rigid spheres have been reported by Alder, Gass and Wainwright [2]. As yet, no such data have been reported for rigid-sphere mixtures.

Evaluation of Two Rigid-Sphere Transport Theories

A comparison of the predictions of the dense-fluid rigid-sphere transport theories of Enskog [18] and of Longuet-Higgins and Pople [32] versus the recent molecular dynamics calculations of rigid-sphere transport properties [2] has been made. In order that the theories be given the best chance of success, molecular dynamics values of the quantity (PV/NkT - 1) have been used for the calculations. This comparison is shown in Tables VII-1 and VII-2.

TABLE VII-1

Comparison of Theoretical Shear Viscosities versus Molecular Dynamics Data

V/V_o	(η_{MD}/η_o)	(η_E^*/η_o)	(η_L^*/η_o)
5	1.53	1.54	0.32
3	2.88	2.82	1.20
2	7.73	6.97	4.30
1.8	10.6	9.65	6.34
1.6	21.1	14.64	10.22
1.5	41.0	19.02	13.61

subscripts: MD = Molecular Dynamics data
E = Enskog Theory
L = Longuet-Higgins and Pople theory
superscripts: * = value calculated with Molecular Dynamics $g(\sigma)$ data

TABLE VII-2

Comparison of Theoretical Thermal Conductivities versus Molecular Dynamics Data

V/V_o	(λ_{MD}/λ_o)	(λ_E^*/λ_o)	(λ_L^*/λ_o)
5	1.72	1.77	0.21
3	3.70	3.20	0.79
2	7.66	7.52	2.83
1.8	10.55	10.24	4.17
1.6	16.05	15.28	6.72
1.5	20.6	19.67	8.95

Apparently, the predictions from the Enskog theory agree better with the molecular dynamics transport data, which are assumed accurate. Neither the Enskog nor the Longuet-Higgins and Pople theory describes the molecular dynamics data very well at high density, i.e. $V/V_o < 1.8$. The predictions from the Longuet-Higgins and Pople theory seem grossly inaccurate at all densities. The Enskog theory is reasonably good (within 10%), except at the highest densities, as evidenced in Table VII-1. Thus, of the two, the Enskog theory appears to give a much better prediction of the transport properties of rigid spheres.

As previously stated, it is not the purpose of this chapter to delve into reasons why these theories predict as they do, nor will a new or modified theory be presented. The objective is to demonstrate the utility of Equation (III-10) in theories of rigid-sphere transport. In order to make the calculations indicated in such theories, it would be nice to have molecular dynamics values of the quantity (PV/NkT - 1) for any number density of interest. This is not pratical. Therefore, an alternate method for computing (PV/NkT - 1) is used, namely, the equation of state.

A summary of the Enskog equations for rigid-sphere transport properties is given to demonstrate how $g(\sigma)$, or $(PV/NkT - 1)/4y$, is used in the calculations.

Shear Viscosity:

$$(\eta/\eta_o) = 4y[1/(Z - 1) + 0.8 + 0.7615(Z - 1)]$$

$$= 1/g(\sigma) + 3.2y + 12.18y^2 g(\sigma), \qquad \text{(VII-1)}$$

where η_o = low-density limit of gas viscosity

$$= 1.016\ (5/16\sigma^2)(mkT/\pi)^{\frac{1}{2}}$$

$Z = PV/NkT.$

Bulk Viscosity:

$$(k/\eta_o) = 1.0027(4y)(Z - 1) = 16.043y^2 g(\sigma). \qquad \text{(VII-2)}$$

Thermal Conductivity:

$$\begin{aligned}(\lambda/\lambda_o) &= 4y[1/(Z - 1) + 1.2 + 0.7557(Z - 1)] \\ &= 1/g(\sigma) + 4.8y + 12.09y^2 g(\sigma),\end{aligned} \qquad \text{(VII-3)}$$

where λ_o = low-density limit of gas thermal conductivity

$$= 1.025(75k/64m\sigma^2)(mkT/\pi)^{\frac{1}{2}}.$$

Self-Diffusion:

$$(D/D_o) = 4y/(Z - 1) = 1/g(\sigma), \qquad \text{(VII-4)}$$

where D_o = low-density limit of self-diffusion coefficient

$$= (3V/8N\sigma^2)(kT/\pi m)^{\frac{1}{2}}.$$

A similar summary of the Longuet-Higgins and Pople equations for rigid-sphere transport properties is of interest.

Shear Viscosity:

$$\begin{aligned}(\eta/\eta_o) &= 0.6016(4y)(Z - 1) \\ &= 9.6256y^2 g(\sigma).\end{aligned} \qquad \text{(VII-5)}$$

Bulk Viscosity: (Same as in Enskog theory)

$$(k/\eta_o) = 16.043y^2 g(\sigma). \qquad \text{(VII-6)}$$

Thermal Conductivity:

$$\begin{aligned}(\lambda/\lambda_o) &= 0.3957(4y)(Z - 1) \\ &= 6.3312y^2 g(\sigma).\end{aligned} \qquad \text{(VII-7)}$$

Self-Diffusion: (Same as in Enskog theory)

$$(D/D_o) = 1/g(\sigma). \qquad \text{(VII-8)}$$

Comparing the transport equations from the Enskog (E) and the Longuet-Higgins and Pople (LHP) theories, it is seen that the equations from the latter theory are simpler, where different, and do not approach the correct low-density limit.

Comparison of Enskog Predictions as Calculated from Three Equations of State

Based upon the foregoing comparison, the Enskog theory has been evaluated with three rigid-sphere equations of state: (1) the Percus-Yevick compressibility (pyc) equation, Equation (III-1); (2) Equation (III-10), developed in this research; and (3) the Percus-Yevick virial (pyv) equation, Equation (III-2). Tables VII-3 through VII-10 present the calculated results.

Two types of comparisons are presented. Tables VII-3 through VII-6 present a comparison of the Enskog rigid-sphere transport properties, calculated with three different equations of state, relative to the Enskog predictions evaluated with $g(\sigma)$ from the molecular dynamics calculations of Alder [2]. This is a redundant test of the equation of state, showing that the $g(\sigma)$ calculated from Equation (III-10) agrees best with the molecular dynamics value of $g(\sigma)$.

The other kind of comparison is shown in Tables VII-7 through VII-10. In this case, the Enskog values evaluated with the equations of state are compared to the reported molecular dynamics transport data

TABLE VII-3

Calculated Enskog Shear Viscosity Relative to the Molecular Dynamics Enskog Data

V/V_o	$(\eta_E/\eta_E^*)_{pyc}$	$(\eta_E/\eta_E^*)_{cst}$	$(\eta_E/\eta_E^*)_{pyv}$
5	0.99953	1.00071	1.00266
3	1.00015	0.99407	0.98117
2	1.02679	0.99621	0.93399
1.8	1.03779	0.99537	0.90939
1.6	1.05853	0199849	0.87711
1.5	1.06988	0.99793	0.85264

pyc = value calculated with $g(\sigma)$ from Percus-Yevick compressibility equation (III-1).

pyv = value calculated with $g(\sigma)$ from Percus-Yevick virial equation (III-2).

cst = value calculated with $g(\sigma)$ from Equation (III-10).

TABLE VII-4

Calculated Enskog Thermal Conductivity Relative to the Molecular Dynamics Enskog Data

V/V_o	$(\lambda_E/\lambda_E^*)_{pyc}$	$(\lambda_E/\lambda_E^*)_{cst}$	$(\lambda_E/\lambda_E^*)_{pyv}$
5	0.99958	1.00068	1.00233
3	1.00013	0.99497	0.98361
2	1.02463	0.99671	0.93933
1.8	1.03530	0.99589	0.91535
1.6	1.05563	0.99879	0.88319
1.5	1.06702	0.99825	0.85868

TABLE VII-5

Calculated Enskog Self-Diffusion Coefficient Relative to the Molecular Dynamics Enskog Data

V/V_o	$(D_E/D_E^*)_{pyc}$	$(D_E/D_E^*)_{cst}$	$(D_E/D_E^*)_{pyv}$
5.	0.99725	1.00315	1.01517
3	0.99960	1.01696	1.05358
2	0.96524	1.00584	1.09818
1.8	0.95554	1.00642	1.12641
1.6	0.93713	1.00243	1.16470
1.5	0.92790	1.00296	1.19656

TABLE VII-6

Calculated Enskog Bulk Viscosity Relative to the Molecular Dynamics Enskog Data

V/V_o	$(K_E/K_E^*)_{pyc}$	$(K_E/K_E^*)_{cst}$	$(K_E/K_E^*)_{pyv}$
5	1.00276	0.99755	0.98504
3	1.00040	0.98400	0.94914
2	1.03601	0.99490	0.91058
1.8	1.04654	0.99431	0.88777
1.6	1.06710	0.99830	0.85860
1.5	1.07769	0.99774	0.83574

TABLE VII-7

Calculated Enskog Shear Viscosity Compared to Molecular Dynamics Data

V/V_o	$(\eta_E/\eta_{MD})_{pyc}$	$(\eta_E/\eta_{MD})_{cst}$	$(\eta_E/\eta_{MD})_{pyv}$
5	1.00962	1.01082	1.01278
3	0.98054	0.97458	0.96193
2	0.92504	0.89748	0.84143
1.8	0.94344	0.90488	0.82672
1.6	0.73509	0.69339	0.60910
1.5	0.49531	0.46200	0.39474

TABLE VII-8

Calculated Enskog Thermal Conductivity Compared to Molecular Dynamics Data

V/V_o	$(\lambda_E/\lambda_{MD})_{pyc}$	$(\lambda_E/\lambda_{MD})_{cst}$	$(\lambda_E/\lambda_{MD})_{pyv}$
5	1.03050	1.03163	1.03333
3	1.00013	0.99497	0.98361
2	1.00453	0.97717	0.92091
1.8	1.00515	0.96688	0.88869
1.6	1.00537	0.95123	0.84113
1.5	1.01621	0.95072	0.81779

TABLE VII-9

Calculated Enskog Bulk Viscosity Compared to Molecular Dynamics Data

V/V_o	$(K_E/K_{MD})_{pyc}$	$(K_E/K_{MD})_{cst}$	$(K_E/K_{MD})_{pyc}$
5	1.11418	1.10839	1.09449
3	1.02081	1.00409	0.96851
2	1.15112	1.10544	1.01175
1.8	0.95140	0.90392	0.80706
1.6	0.97009	0.90754	0.78055
1.5	1.79615	1.66290	1.39290

TABLE VII-10

Calculated Enskog Self-Diffusion Coefficient Compared to Molecular Dynamics Data

V/V_o	$(D_E/D_{MD})_{pyc}$	$(D_E/D_{MD})_{cst}$	$(D_E/D_{MD})_{pyv}$
5	0.91490	0.92032	0.93135
3	0.86172	0.87669	0.90826
2	0.91061	0.94890	1.03602
1.8	1.00584	1.05939	1.18570
1.6	1.33875	1.43205	1.66386
1.5	1.89367	2.04687	2.44197

of Alder, Gass and Wainwright [2]. This is another test of the Enskog theory, but allows some interesting observations.

From the tables, one might naively conclude that the Percus-Yevick compressibility (pyc) equation (III-1) is the best equation of state for rigid-spheres. The Enskog equations evaluated with the pyc equation for $g(\sigma)$ seem to agree best with the Alder data. The fallacy lies, of course, in the fact that the Enskog theory is not exact. Being an approximation in itself, it should not be used as an accuracy criterion for an equation of state for rigid spheres.

What one can conclude, nonetheless, is that if the Enskog theory is to be used for rigid-sphere transport calculations, then the pyc would be the best equation (of the three considered) to use for the calculation of $g(\sigma)$, in order to get the best agreement between theory and experiment. It should be kept in mind, however, that the $g(\sigma)$ from the Percus-Yevick (pyc) equation would not be in close agreement with the molecular dynamics $g(\sigma)$, especially in high densities.

As stated before, it is not within the scope of the present research to try to improve upon the Enskog theory, nor to develop a new theory of transport for rigid spheres. The main objective has been to present an evaluation of the Enskog and Longuet-Higgins and Pople theories of rigid-sphere transport relative to the recent molecular dynamics transport data, and to demonstrate how an accurate rigid-sphere equation of state can be employed in such theories.

Extension of the Enskog Dense Rigid-sphere Fluid Transport Theory to Real Fluids

Though strictly valid for the system of nonattracting rigid-spheres, the Enskog theory predicts some qualitative features of real fluid transport phenomena. This section is devoted to some examples of agreement between the Enskog predictions and observed real fluid phenomena.

The Viscosity of Simple Dense Fluids

Recall the Enskog expression for shear viscosity, Equation (VII-1), expressed here in rearranged form,

$$(\eta/b\rho\eta_o) = [1/\varphi + 4/5 + 0.7614\varphi], \qquad \text{(VII-9)}$$

where $\varphi = Z - 1$.

Looking at the quantity $(\eta/4y\eta_o)$ at a fixed temperature, it is apparent that this is only a function of density. Furthermore, as φ ranges from zero to positive infinity (i.e. the positive reals), the function on the right in Equation (VII-9), exhibits a minimum as shown in Figure VII-1.

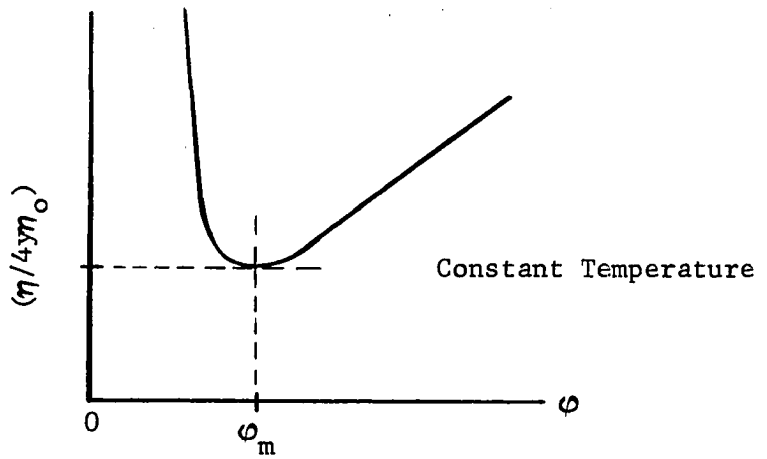


Figure VII-1 Qualitative Behavior of Equation (VII-9)

The mathematical identification of the minimum is,

$$(1/b\eta_o)\,\frac{d(\eta/\rho)}{d\varphi} = (0.7614 - 1/\varphi_m^2) = 0. \qquad \text{(VII-10)}$$

So,

$$\varphi_m^2 = 1/0.7614, \qquad \text{(VII-11)}$$

$$\varphi_m = 1.146, \qquad \text{(VII-12)}$$

$$Z_m = (P/RT\rho)_m = \varphi_m + 1 = 2.146, \qquad \text{(VII-13)}$$

$$y_m = 0.17584, \qquad \text{(VII-14)}$$

$$b = 4y_m/\rho_m. \qquad \text{(VII-15)}$$

And,

$$(1/b\eta_o)(\eta/\rho)_m = [1/1.146 + 0.8 + 0.7614(1.146)] = 2.545. \qquad \text{(VII-16)}$$

Dividing Equation (VII-9) by Equation (VII-16), at constant temperature, results in the following expression,

$$(\eta/\rho) = 0.3929(\eta/\rho)_m[1/\varphi + 0.8 + 0.7614\varphi]. \qquad \text{(VII-17)}$$

At any density, then, one can calculate the reduced density, $y = 0.25b\rho$, the rigid-sphere compressibility factor Z [from Equation (III-10)], and φ from its definition. So, knowing the experimental $(\eta/\rho)_m$ and ρ_m, the quantity (η/ρ) can be calculated at any other density.

Figure VII-2 shows results obtained using the Enskog theory in this way. Several considerations ought to be kept in mind when studying the graph. First, the molecules for which data are shown in Figure VII-2 are

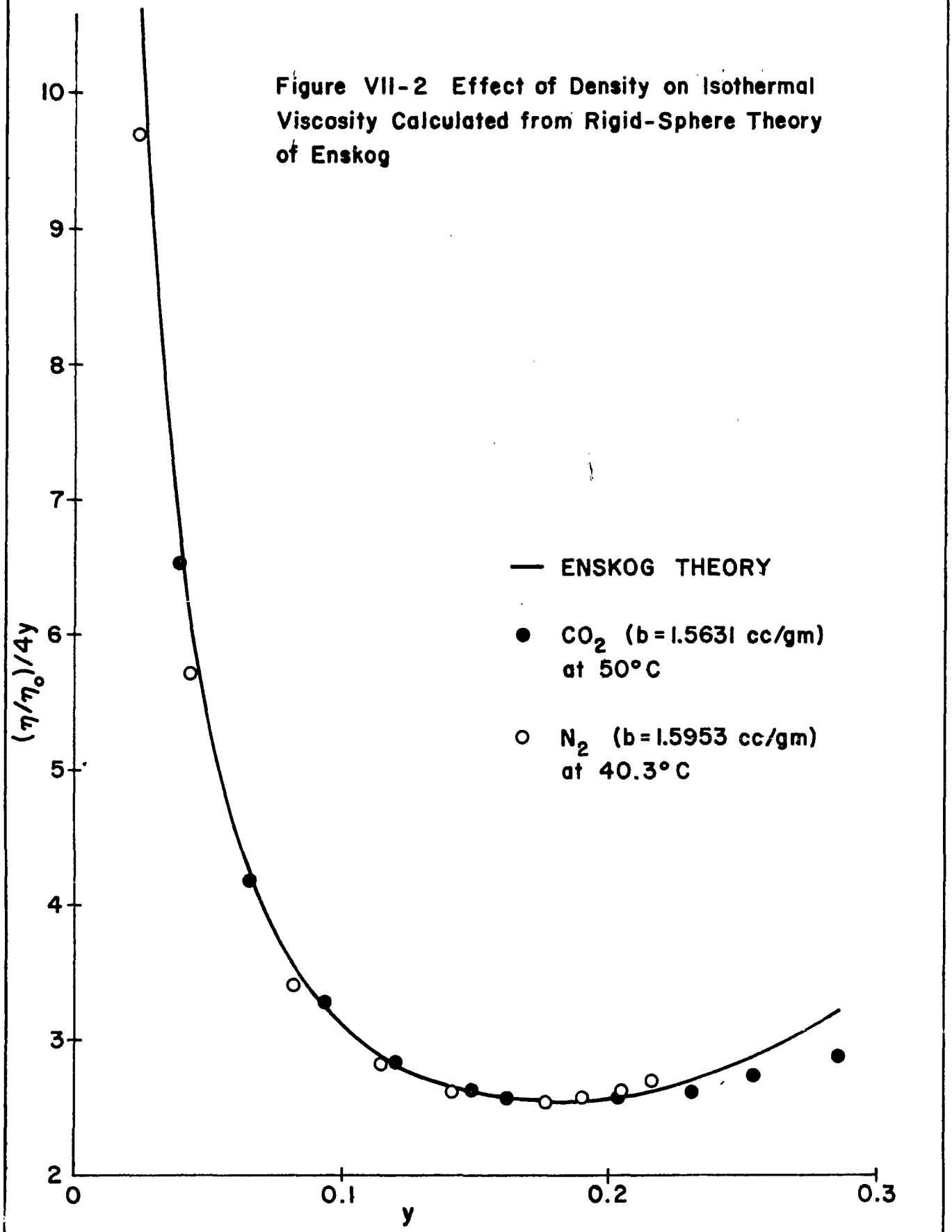


Figure VII-2 Effect of Density on Isothermal Viscosity Calculated from Rigid-Sphere Theory of Enskog

not very spherical. A better test would be to make such calculations for simple molecules like argon, krypton and methane. Yet, the agreement for nitrogen and carbon dioxide is interesting. A second point to be mindful of is that, for real fluids, Enskog suggested that the density effect would be better described by

$$\varphi = \frac{1}{R\rho}(dP/dT)_{\rho} - 1. \qquad \text{(VII-18)}$$

That is, one ought to use experimental data to evaluate φ, instead of calculating φ from a rigid-sphere equation. The purpose of the comparison shown in Figure VII-2 is to see what type of agreement one obtains following the rigid-sphere route as an approximate for real fluids. Except at high density, the agreement (all things considered) is good. If it were of interest to use the Enskog model at high density, one would get better results by matching Equation (VII-9) to a point in that region. Starling [47] has done this with encouraging success for hydrocarbon systems.

CHAPTER VIII

ANALYSIS OF THE RIGID-SPHERE EQUATION OF STATE

Having proposed an equation of state for rigid spheres and their mixtures, it is appropriate to discuss some questions which will likely arise concerning the new equation.

What Constitutes a Valid Test of a Rigid-sphere Equation?

This question has been raised by Boublik [9]. Before using Equation (III-10) to describe rigid-sphere behavior in a perturbation study, Boublik "tested" the equation by using it to calculate enthalpies of evaporation by the method of Yosim and Owens [54]. By comparing the results of using Equation (III-10) with calculations made with the Frisch equation from scaled particle theory, Equation (III-1), Boublik concluded that Equation (III-10) is the better rigid-sphere expression. Table VIII-1 summarizes the comparison. The essence of the Yosim and Owens method is,

$$\int_{V_\ell^*}^{V_g^*} P^o dV = H_g^* - H_\ell^* = \Delta H_V, \qquad \text{(VIII-1)}$$

where P^o = rigid sphere pressure

V_g^* = saturated vapor volume

V_ℓ^* = saturated liquid volume.

TABLE VIII-1

Enthalpies of Vaporization Based Upon the Yosim-Owens Method*

Substance	ΔH_V^E	ΔH_V^{spt} (g cal/g mole)	ΔH_V^{cst}
Ne	414	427	424
Ar	1558	1611	1582
Kr	2158	2188	2168
Xe	3020	3264	3224
CH_4	1988	2098	2073
F_2	1562	1581	1558

Superscripts E = experimental [54]
spt = scaled particle theory, Equation (III-1)
cst = Equation (III-10)

*Abstracted from reference [54].

It should be borne in mind that the validity of the rigid-sphere equation is not really tested by its employment in a real fluid model based upon rigid-sphere behavior. Such tests can only indicate the value of the model or theory which prescribes the use of rigid-sphere data. If a particular rigid-sphere equation improves the prediction, it does not follow that the equation is a better rigid-sphere equation. As an example, in the present research, calculations were made of enthalpies of fusion by the Yosim and Owens method [54].

$$\Delta H_f = H_\ell^* - H_s^* = \int_{V_\ell^*}^{V_s^*} P^o dV \qquad \text{(VIII-2)}$$

where P^o = rigid-sphere pressure

V_s^* = volume of the solid

V_ℓ^* = volume of the liquid.

Table VIII-2 shows the comparative results obtained with the "scaled particle theory" equation, (III-1), and with Equation (III-10).

TABLE VIII-2

Enthalpies of Fusion Calculated by the Method of Yosim and Owens

Substance	ΔH_f^E	ΔH_f^{spt}	ΔH_f^{cst}
Ne	80.1	65.5	61.9
Ar	280.8	269.9	252.3
Kr	390.7	363.4	341.1

Superscripts E = experimental [54]
spt = scaled particle theory, Equation (III-1)
cst = Equation (III-10).

If one had chosen enthalpy of fusion rather than enthalpy of vaporization as a test of validity, there might be second thought about using Equation (III-10) for other work. The notion to be stressed is, that one ought not to judge a rigid-sphere equation by such indirect tests.

The contention here is that the most valid test of any equation of state for rigid spheres is comparison with accurate molecular dynamics calculations or extremely accurate Monte Carlo calculations. To test such an equation using a real fluid theory requires "a priori" acceptance of the assumptions inherent in the theory. It has been recognized

for some time that this pitfall is removed by comparison with molecular dynamics data.

Summarizing, the argument by counter-example is offered to emphasize that rigid-sphere equations ought to be compared to reliable rigid-sphere data, not to data on pseudo-rigid spheres such as argon, krypton, etc. Such comparisons can offer, at best, only qualitative information about the rigid-sphere system. The Molecular Dynamics data and the Monte Carlo data are specifically for the rigid-sphere system, offering a direct and quantitative test of any proposed rigid-sphere equation. These arguments, which were developed in the present work because of their obvious importance in evaluating the research, have been recently reported in the literature [14].

A Study of the Padé Approximant to the Rigid-sphere Equation of State: Its Formulation, Meaning and Evaluation

Because of the strong interest [37, 44] in the Padé approximant method, as applied to the equation of state for the rigid-sphere system, it is appropriate to make a special study of the method, showing both its power and its flaws. The main concern is that some give undue credit to the method, seemingly forgetting that it is only a numerical technique. The following discourse is intended to dispel such beliefs, putting the method in the proper perspective, and answering the question, "How good is the Padé approximant for the rigid-sphere system?"

The method of Padé approximants [6] has many uses in applied physics. The method is well suited to the task of approximating slowly converging series functions. In the case where only a limited number of

coefficients in the series are known with certainty, the Padé approximant, based upon the known values, is often able to provide a very good estimate of the remaining terms. Since the approximant is a function composed of the ratio of two polynomials of finite degree, it is easily used in calculations which involve integration or differentiation.

One very interesting application in recent years has been the approximation of the virial series for the rigid-sphere system known as the Padé (3,3) approximant of Ree and Hoover [42].

These workers rearranged the virial equation in the form,

$$(Z - 1)/4y = B_2 + B_3y + B_4y^2 + B_5y^3 + B_6y^4 + B_7y^5 + \ldots \qquad \text{(VIII-3)}$$

Next, they formulated a rational approximation to the above, the so-called Padé (3,3) approximant,

$$(Z - 1)/4y = (w_1 + w_2y + w_3y^2)/(1 + \alpha_2y + \alpha_3y^2). \qquad \text{(VIII-4)}$$

Expanding the expression in Equation (VIII-4) and equating coefficients of like powers of y in this expansion and Equation (VIII-3), one finds,

$$\begin{aligned}
B_2 &= w_1 \\
B_3 &= w_2 - B_2\alpha_2 \\
B_4 &= w_3 - B_3\alpha_2 - B_2\alpha_3 \\
B_5 &= -B_3\alpha_3 - B_4\alpha_2 \\
B_6 &= -B_4\alpha_3 - B_5\alpha_2 \\
B_7 &= -B_5\alpha_3 - B_6\alpha_2 \\
&\vdots \quad\quad \vdots \quad\quad \vdots \\
B_n &= -B_{n-2}\alpha_3 - B_{n-1}\alpha_2, \text{ for } n \geq 5.
\end{aligned} \qquad \text{(VIII-5)}$$

These relations are linear in the values w_i and α_i, since the values B_2, B_3, ..., B_7 are known for this system. Thus, they can be solved for $\{w\}$ and $\{\alpha\}$. Characteristic of the rational approximation, the leading term in the denominator can be set equal to unity with no loss of generality. The first numerator term, w_1, is, therefore, equal to the first term in the series being approximated. Hence, $w_1 = B_2$. A solution of the equations, using the first five of the above relations to solve for the five unknowns, w_1, w_2, w_3, α_2 and α_3, would be

$$\begin{pmatrix} 1 & 0 & -B_2 & 0 \\ 0 & 1 & -B_3 & -B_2 \\ 0 & 0 & -B_4 & -B_3 \\ 0 & 0 & -B_5 & -B_4 \end{pmatrix} \begin{pmatrix} w_2 \\ w_3 \\ \alpha_2 \\ \alpha_3 \end{pmatrix} = \begin{pmatrix} B_3 \\ B_4 \\ B_5 \\ B_6 \end{pmatrix}. \qquad \text{(VIII-6)}$$

One equation, $w_1 = B_2$, has been solved directly; thus, the problem resolves down to the solution of four equations in four unknowns. Using matrix algebra, the solutions are,

$$\begin{aligned} \alpha_3 &= [(B_5)^2 - B_4B_6]/[(B_4)^2 - B_3B_5] \\ \alpha_2 &= (B_6 + B_4\alpha_3)/(-B_5) \\ w_3 &= B_4 + B_2\alpha_3 + B_3\alpha_2 \\ w_2 &= B_3 + B_2\alpha_2 \\ w_1 &= B_2. \end{aligned} \qquad \text{(VIII-7)}$$

It is interesting to note that an ambiguity exists in the evaluation of the Padé (3,3) coefficients. It only takes four linear relations, in addition to the $w_1 = B_2$ condition relations which apply.

Choosing to use only the relations, $B_3 \ldots B_6$ is an arbitrary selection. One might just as easily take the relations, $B_4 \ldots B_7$, for the four conditions. The point is, that it really does not matter which of the relations one uses. The goal is to formulate an approximant which does the best job of approximating the infinite virial series for Z.

With this interpretation of the Padé method, one can look at other forms of the approximant and other ways of evaluating the coefficients. A program was written to study the effect of varying the choice of the four condition equations upon the coefficients of the Padé (3,3). A test of the program was made by computing the coefficients from the same conditions used by Ree and Hoover. The result is

$$(Z - 1)/4y = \frac{1 + 0.063507(bd) + 0.0173295(bd)^2}{1 - 0.5614934(bd) + 0.0813128(bd)^2}, \qquad \text{(VIII-8)}$$

as compared to the Ree and Hoover function [42],

$$(Z - 1)/4y = \frac{1 + 0.063499(bd) + 0.017327(bd)^2}{1 - 0.561501(bd) + 0.081316(bd)^2}. \qquad \text{(VIII-9)}$$

The difference between the two functions, though almost negligible, is probably due to round-off errors in the machine computations (these and theirs). The agreement is taken as confirmation of the accuracy of the program in evaluating the Padé coefficients.

Using the program, two additional choices of condition equations, other than the one used by Ree and Hoover, have been studied. By using the relation for B_7 in place of the relation B_6, one gets the function,

$$(Z - 1)/4y = \frac{1 + 0.1544598(bd) + 0.0324163(bd)^2}{1 - 0.4705402(bd) + 0.0395544(bd)^2}. \qquad \text{(VIII-10)}$$

By using the relation for B_7 in place of the relation B_5, one gets

$$(Z - 1)/4y = \frac{1 + 0.7550627(bd) + 0.1837265(bd)^2}{1 + 0.1300627(bd) + 0.1845127(bd)^2}. \qquad \text{(VIII-11)}$$

There are, of course, many other choices that one can make. These should suffice to demonstrate the point that the Padé (3,3) approximant given by Ree and Hoover is not the only Padé (3,3) possible with the seven known virial coefficients for the rigid-sphere system. A summary of the ability of the various Padé forms to describe molecular dynamics data is presented in Table VIII-3.

It is also interesting to study another form of the Padé approximant, namely, that form which would algebraically correspond to the equation presented in this dissertation. Recall, the compressibility factor in Equation (III-10) is in the form of the ratio of two cubic polynomials. When the form is converted to $(Z - 1)/4y$, one finds that the Padé expression would be in the form of a linear over a cubic polynomial. Thus, it would be a Padé (2,4) approximant, e.g.,

$$(Z - 1)/4y = (w_1 + w_2 y)/(\alpha_1 + \alpha_2 y + \alpha_3 y^2 + \alpha_4 y^3). \qquad \text{(VIII-12)}$$

Notice that the above expression has the same number of unknowns as the Padé (3,3) expression. By expanding the above form in a density series and equating coefficients to the coefficients of terms of like powers of y in the virial series, Equation (VIII-3), one obtains the following relations,

TABLE VIII-3

Compressibility Factors from Several Pade Forms

V/V_o	R-H	VIII-10	VIII-11	VIII-15	VIII-16	VIII-17	VIII-18	CST	MD
∞	1.3594	1.3594	1.3592	1.3594	1.3581	1.3594	1.3596	1.3593	1.36
3	3.0307	3.0367	3.0032	3.0284	2.9168	3.0364	1.1091	3.0256	3.05
2	5.8345	5.9372	5.7387	5.7804	5.1655	5.8749	5.3515	5.8318	5.89
1.7	8.5472	8.9356	8.5111	8.3227	7.3687	8.6210	7.5294	8.5794	8.56
1.6	10.1079	10.7781	10.2107	9.7131	9.0320	10.1861	8.6706	10.1780	10.17
1.5	12.3082	13.5569	12.7852	11.5718	13.2388	12.3606	10.1491	12.4560	12.5

Note: R-H = value computed from Padé (3,3) of Ree and Hoover [42].
VIII-10 = value computed from Equation (VIII-10).
VIII-11 = value computed from Equation (VIII-11).
VIII-15 = value computed from Equation (VIII-15).
VIII-16 = value computed from Equation (VIII-16).
VIII-17 = value computed from Equation (VIII-17).
VIII-18 = value computed from Equation (VIII-18).
CST = value computed from Equation (III-10).
MD = Molecular Dynamics data of Alder [4].

$$
\begin{aligned}
B_2 &= w_1 \\
B_3 &= w_2 - B_2\alpha_2 \\
B_4 &= -B_2\alpha_3 - B_3\alpha_2 \\
B_5 &= -B_2\alpha_4 - B_3\alpha_3 - B_4\alpha_2 \\
B_6 &= -B_3\alpha_4 - B_4\alpha_3 - B_5\alpha_2 \\
B_7 &= -B_4\alpha_4 - B_5\alpha_3 - B_6\alpha_2 \\
&\vdots \\
B_n &= -B_{n-3}\alpha_4 - B_{n-2}\alpha_3 - B_{n-1}\alpha_2, \text{ for } n \geq 5.
\end{aligned}
\tag{VIII-13}
$$

Using the same matrix technique that was employed to analyze the Padé (3,3) equations, one finds the following relations for the Padé (2,4) coefficients, when the first six virial coefficients are used.

$$
\begin{aligned}
\alpha_4 &= [2(B_3)^2(B_5B_4) + (B_4)^2(B_5B_2) - (B_3)^3B_6 - (B_4)^3B_3 \\
&\quad - (B_5)^2(B_2B_3)]/[(B_3)^4 - 2(B_3)^2(B_2B_4) + (B_2)^2(B_3B_5)], \\
\alpha_3 &= [B_5B_4 - B_3B_6 - (B_3)^2\alpha_4]/(B_3B_4 - B_5B_2), \\
\alpha_2 &= (B_4 + B_2\alpha_3)/(-B_3), \\
\alpha_1 &= 1 \\
w_1 &= B_2 \\
w_2 &= B_3 + B_2\alpha_2.
\end{aligned}
\tag{VIII-14}
$$

It is certainly of interest to see if the Padé coefficients turn out to be approximately those found by expansion of the proposed rigid-sphere equation. One would like to see if w_2 turns out to be -2. In the course of the analysis, the computer program was modified to make case studies in which the choice of the conditions was variable. The use of the first six virial coefficients gives

$$(Z - 1)/4y = \frac{1 + 0.486555(bd)}{1 - 0.138445(bd) - 0.200422(bd)^2 + 0.054690(bd)^3}. \qquad \text{(VIII-15)}$$

By using the relation for B_7 instead of the relation for B_4, one gets

$$(Z - 1)/4y = \frac{1 - 0.425339(bd)}{1 - 1.050339(bd) + 0.406866(bd)^2 - 0.063196(bd)^3}. \qquad \text{(VIII-16)}$$

By using the relation for B_7 instead of the relation for B_6, one finds,

$$(Z - 1)/4y = \frac{1 + 3.961151(bd)}{1 + 3.336151(bd) - 2.372044(bd)^2 + 0.414919(bd)^3}. \qquad \text{(VIII-17)}$$

By using the relation B_7 instead of the relation for B_5, one finds,

$$(Z - 1)/4y = \frac{1 + 3.961151(bd)}{1 - 1.638533(bd) + 0.737133(bd)^2 - 0.1110242(bd)^3}. \qquad \text{(VIII-18)}$$

As before, there are many combinations of the seven known coefficients of the rigid-sphere virial series which can be used for evaluating the coefficients in the Padé (2,4) approximant. The four cases evaluated above

should suffice for the purpose at hand. With them, one can calculate rigid-sphere compressibility factors and compare against the molecular dynamics data of Alder and Wainwright [3]. Such a comparative calculation is shown in Table VIII-3.

From the calculated comparison, it is seen that there is, perhaps, a better Padé approximant than the Padé (3,3). The Padé (2,4) form, evaluated with B_7 in place of B_6, seems to agree better with the molecular dynamics data at high densities. Recall that the Padé (2,4) uses only six of the seven known virial coefficients for rigid spheres.

The general point to be made is that the Padé (3,3) of Ree and Hoover [42] is only a numerical approximation to an infinite series. There is no magic in the expression, simply because it reproduces "exactly" (within round-off error of a calculating machine) the first six virial coefficients. The extrapolation of the approximant to get higher order terms gives no guarantee that those terms are of good accuracy. Indeed, the users of this technique are quick to realize that the formulation of rational approximations (Padé approximants) is something of an art form [36]. To get the best approximant with a given set of condition relations, an exhaustive analysis of all possible forms would have to be made. It is not impossible. The programming is not very difficult.

Note Added in Proof

At the writing of this dissertation, an excellent paper on the use of Padé approximants was published by Carley [11]. The results reinforce

the conclusion drawn here, that the Padé approximant is a powerful numerical method, but very sensitive as to how the coefficients are computed.

Discussion

The preceding two sections of this chapter have dealt with two recurring questions which arise when discussing rigid-sphere equations of state. The Boublik question, "How does one evaluate a rigid-sphere equation of state?", is discussed in section one of this chapter. The example given is typical of the applications in which a rigid-sphere equation is used in an approximation of real-fluid behavior. Often, the approximation is forgotten and one begins to think of real fluid behavior as a truly rigid-sphere phenomenon. The point made in the conclusion of section one is that things must be kept in perspective, lest a false conclusion be drawn.

The second question, "How good is the Padé approximant?", is treated in section two. This question has been frequently asked when discussing the merits of the rigid-sphere equation of state developed in the present research, Equation (III-10). Some tend to argue that,

(1) the first seven rigid-sphere virial coefficients are accurately known;

(2) the Padé (3,3) of Ree and Hoover exactly reproduces the first six of these coefficients; therefore,

(3) the Padé (3,3) is the most accurate rigid-sphere equation.

The conclusion is, of course, false. Exact reproduction of the first six virial coefficients does not necessarily make for the most accurate equation of state. As was shown in Table III-2, the Padé (3,3) neither

reproduces the Molecular Dynamics data at high density, nor does it give the most accurate prediction of the known seventh virial coefficient. To demonstrate both the good and bad qualities of the Padé approximant method, the exposition in the preceding section has been given. From this, one realizes that the Padé approximant is only a method of approximating the remaining terms of a slowly converging series. Furthermore, the manner in which one computes the coefficients of the Padé approximant is quite important, but somewhat arbitrary. Again, the point to be made is that the Padé method should be understood, not naively accepted. In the case of the rigid-sphere equation of state, the Padé approximant can provide a very good approximation. However, it does not follow that the approximation is the most accurate when compared to Molecular Dynamics data. This is especially so with respect to the high-density Molecular Dynamics data, which demands accuracy in the higher order virial coefficients, for which the Padé method provides only an approximation.

CHAPTER IX

THE ROLE OF THE RIGID-SPHERE FLUID AS A REFERENCE SYSTEM IN THEORIES OF REAL FLUIDS

Beginning with this chapter, attention is focused upon methods of calculating the thermodynamic properties of real fluids, using the equation of state for rigid spheres. Equation (III-10) for pure fluids and Equation (IV-11) for mixtures were developed in the preceding chapters. It is shown how the rigid-sphere equation can be used in the van der Waals approach (for gases and vapors), the Longuet-Higgins and Widom model (for dense simple liquids) and in the recent perturbation methods.

Intermolecular Forces

Consider the interaction between an isolated pair of real molecules. There are two kinds of forces in evidence: (1) forces which tend to widen their separation, repulsive forces; and, (2) forces which tend to draw the two molecules closer together, cohesion or attractive forces. Figure IX-1 exhibits a typical intermolecular potential diagram. It can be seen, in Figure IX-1, that as molecules approach from infinite separation r_o is reached. As the separation becomes less than r_o, the potential rises sharply, indicative of the range and strength of the repulsive forces.

There are a number of mathematical models of the intermolecular potential function. Perhaps the most noted is the Lennard-Jones (12-6) model,

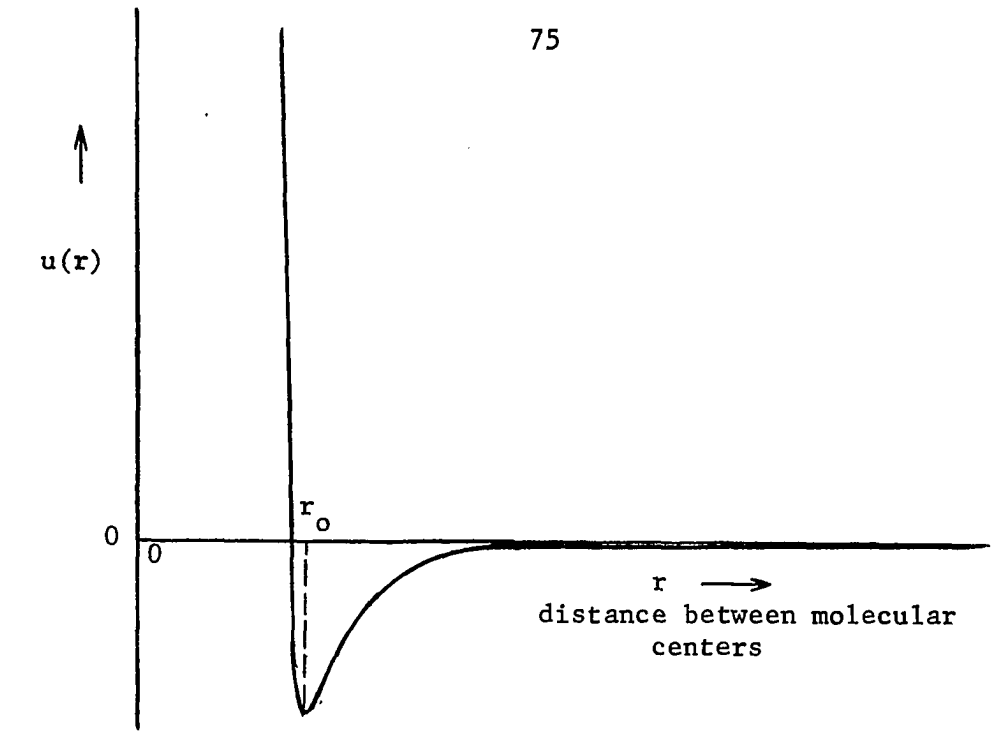


Figure IX-1 Typical Intermolecular Potential for Real Molecules

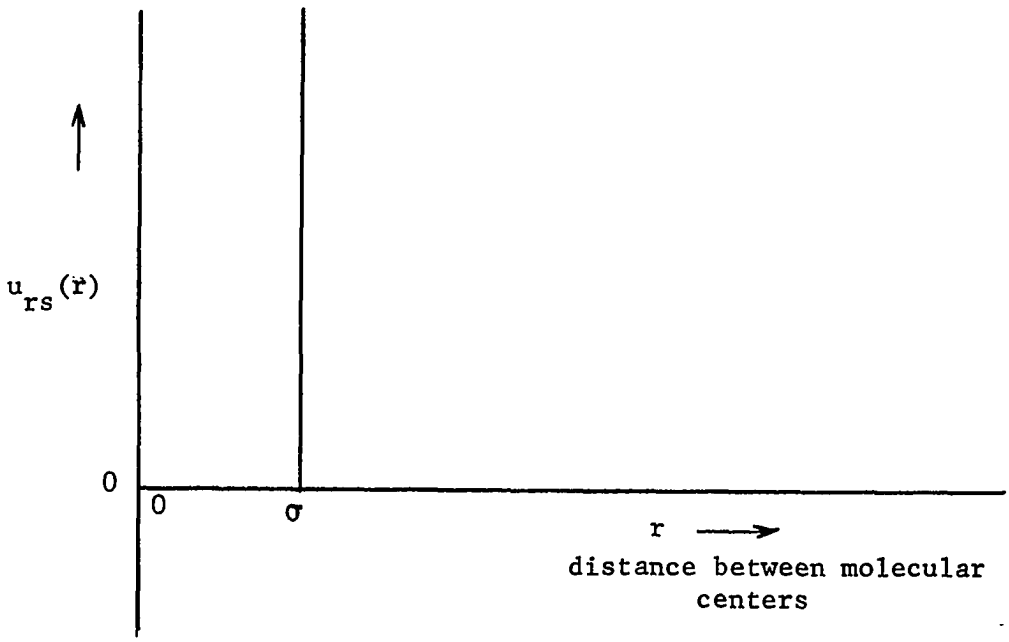


Figure IX-2 Intermolecular Potential for Rigid Spheres

$$u_{L-J}(r) = \epsilon[(r_o/r)^{12} - 2(r_o/r)^6], \qquad \text{(IX-1)}$$

where r_o = intermolecular separation at which the minimum occurs in the potential function,

ϵ = magnitude of the minimum of the potential function.

The exponent, 12, in the Lennard-Jones model is, of course, arbitrary and chosen for mathematical convenience. However, the point to be emphasized is that the repulsion effect is short-ranged, but very powerful. By comparison, the attraction effect is long-ranged, relatively weak, yet the source of the internal energy of a fluid.

Consider the following expression of the intermolecular potential function,

$$u(r) = u_R(r) + u_A(r), \qquad \text{(IX-2)}$$

where R = repulsion

A = attraction.

Recall the potential function of the rigid-sphere fluid, described in Chapter II, shown in Figure IX-2.

$$\begin{aligned} u_{rs}(r) &= \infty \qquad r < \sigma \\ u_{rs}(r) &= 0 \qquad r > \sigma, \end{aligned} \qquad \text{(IX-3)}$$

where σ = sphere diameter.

The steepness of the repulsive part of the real potential, in Figure IX-1, appears to be reasonably approximated by the rigid-sphere potential. Making this assumption, then,

$$u(r) = u_{rs}(r) + u^*(r), \tag{IX-4}$$

where $u^*(r)$ accounts for the soft repulsion and the cohesion effects.

Mathematically,

$$\begin{aligned} u(r) &= \infty, \quad r < \sigma \\ u(r) &= u^*(r), \quad r \geq \sigma. \end{aligned} \tag{IX-5}$$

One might consider the potential function of the real fluid to be a perturbation about the rigid-sphere potential. This is the basis of most of the so-called "pertubation theories" of fluids.

Summarizing, the important notion is that the intermolecular repulsion effect can be reasonably approximated by the rigid-sphere potential. This assumption leads to the general notion that the properties of dense fluids can be considered as the sum of a rigid-sphere term and a term which accounts for the soft repulsions and the cohesion effects. That is, for a typical equilibrium property, PROP,

$$\text{PROP} = \text{PROP}_{rs} + \text{PROP}^* \tag{IX-6}$$

The van der Waals Concept

In 1873, van der Waals introduced the first equation of state which predicted the continuity between the gas and liquid phases [49],

$$P = RT/(V - b) - a/V^2. \tag{IX-7}$$

The first term on the right-hand side of Equation (IX-7) is a correction to the ideal gas law, taking into account the physical volume occupied by

the molecules. This same term was derived earlier by Clausius [39] from kinetic theory, on the assumption that the system is composed of rigid, nonattracting spheres. In either case, the term is used to describe the repulsion effects for the system. The second term on the right-hand side of the van der Waals equation corrects for the presence of cohesive forces, which the ideal gas law ignores.

The purpose here is not to praise nor to condemn the van der Waals equation, but to capitalize upon the fundamental concepts embodied in the formulation of his equation. A general way of writing the van der Waals equation would be,

$$P = P_R + P_A, \qquad \text{(IX-8)}$$

where R refers to repulsion,

A refers to attraction.

Specifically, the P_R term seems to be a rigid-sphere contribution to the total pressure (based upon the Clausius result).

Anyone using the van der Waals equation, in its original form, realizes that it is not very accurate at high densities, where repulsion effects are important. It is curious, however, that the vast majority of the published modifications of or improvements upon the van der Waals equation have focused attention solely upon the cohesion term, P_A. The most noteworthy improvement of this type has been the equation of Redlich and Kwong [40], who proposed,

$$P_A = -a[\sqrt{T}\, V(V + b)]. \qquad \text{(IX-9)}$$

The efforts which have involved the correction of the repulsion term, P_R, have been few. The idea of being able to improve the equation by using a better rigid-sphere term for P_R seems to have been recognized by only a few individuals. There is no doubt, however, that both terms, P_R and P_A, need improvement.

Summarizing the commentary in this section, it is important to recognize the general principles underlying the van der Waals equation of state. These principles are far more important than the specific algebraic form of the equation of state he proposed. The recognition that the repulsion term, P_R, can be greatly improved by using a better rigid-sphere term is important to the discussion of modern equations of state.

In the following section, a recent application of the rigid-sphere correction to van der Waals' equation is discussed.

That the van der Waals equation of state can be greatly improved by replacing the repulsion term, P_R, by a better rigid-sphere term was recognized by Kirkwood [29], in the course of his theoretical researches into fluid behavior. Kirkwood came to the realization that the repulsive core primarily determines the structure of the liquid phase. Apparently the cohesion effect contributes mainly to the energy of the system, being weaker and longer-ranged than the repulsion effect.

There is yet one other notable recognition that the rigid-sphere term ought to be used to depict the repulsion effects in the equation of state. In 1922, as an empirical aside to his kinetic theory of transport phenomena in dense rigid-sphere fluids, Enskog [18] suggested that

the real gas equation of state be written as,

$$Z = [1 + 4y\, g(\sigma)] - a/RTV, \qquad \text{(IX-10)}$$

where $[1 + 4y\, g(\sigma)] = Z_{rs}$ = rigid-sphere compressibility factor.

Being apparently more involved in theories of transport, Enskog did not pursue this equation of state idea much further. Until the time of Kirkwood, the improvement of the equation of state by using a better rigid-sphere term was seemingly unrecognized by equilibrium thermodynamicists.

The Model of Longuet-Higgins and Widom for The Melting of Argon

In 1964, Longuet-Higgins and Widom [33] proposed an equation of state for liquid and solid argon based upon a model of rigid spheres with attraction. Their equation is

$$P(n, T) = P^{o}(n, T) - a\, n^{2}, \qquad \text{(IX-11)}$$

where $P^{o}(n, T)$ is the pressure which would be exerted by a system of rigid spheres at the same number density n and temperature T as the real system. The term, $- a\, n^{2}$, is a van der Waals-like uniform background cohesive pressure. The molecular dynamics calculations of Alder and Wainwright [4] were used for $P^{o}(n, T)$. However, in order to make certain integrations, Longuet-Higgins and Widom made use of the rigid-sphere equation of state resulting from "scaled particle theory" of Frisch [43] and his collaborators.

$$P^o(n, T) = nkT(1 + y + y^2)/(1 - y)^3, \qquad \text{(IX-12)}$$

where $y = b/4V = \sqrt{2}\pi N \sigma^3/3$,

σ = rigid-sphere diameter,

N = Avogadro's number,

$V_o = N\sigma^3/\sqrt{2}$ = molar volume at closest packing.

In a subsequent paper, Guggenheim [20] carried out calculations for triple-point liquid properties, using only the Frisch equation (IX-12) for rigid-sphere calculations. Guggenheim employed the Longuet-Higgins and Widom model for liquid argon successfully in this way. Calculated results agreed reasonably well with observed data. Agreement, however, was not perfect. In a later article, Guggenheim [21] repeated the calculations with several analytical rigid-sphere models. A tabular comparison of these results indicated that the calculated liquid properties are sensitive to the particular rigid-sphere equation employed.

In the present research, the sensitivity of such calculations to the mathematical form of the rigid-sphere equation was investigated further. The predicted results were shown to improve when a more accurate expression for rigid-sphere behavior is used.

In 1969, during the early phase of this research, a much-improved rigid-sphere equation [12] was developed from mathematical analysis of the reduced virial coefficients for rigid spheres. The equation, introduced in Chapter III, is

$$P^o(n, T) = nkT(1 + y + y^2 - y^3)/(1 - y)^3. \qquad \text{(IX-13)}$$

Table IX-1 shows the relative abilities of Equation (IX-12) and Equation (IX-3) in describing the fluid behavior of rigid spheres as calculated by the method of molecular dynamics [4]. Based upon these results and the detailed comparison by Guggenheim [21] involving all other currently popular rigid-sphere equations, Equation (IX-13) appears to be the best contemporary analytical expression for rigid-sphere fluids. It has been shown [42] to outperform the Padé (3,3) approximant of Ree and Hoover. There certainly seems to be no important difference between the results predicted by Equation (IX-13) and the molecular dynamics calculations up through the observed "fluid-solid" transition density of the rigid-sphere system. This transition density corresponds approximately to $(V/V_o) = 1.50$.

Recalculation of liquid argon properties using rigid-sphere behavior predicted by Equation (IX-13) and a van der Waals-like cohesion term, reveals improved agreement between calculated and observed quantities. The calculations are made in the same manner as those made by Guggenheim [20]. The Guggenheim results are compared with the results of the present work in Table IX-1.

The point keyed upon in this study of the Longuet-Higgins and Widom equation, in the Guggenheim manner, is the method by which the coefficients in the equation are evaluated. The "cohesion" term, a/RTV, is equated to the reduced internal energy of the vaporization at the triple point, $\Delta U_e/RT_t$. Guggenheim [20] gives this value to be $\Delta U_e/RT_t = 8.56$. At the triple point, (PV/RT) in the liquid phase is assumed negligible. Thus,

$$a/RT_t V_t^{\ell} = 8.56 \cong P_t^o V_t^{\ell}/RT_t. \qquad \text{(IX-14)}$$

TABLE IX-1

Triple-point Calculations for Argon

Property	Guggenheim [20]	This Work	Experiment
$(PV/NkT)_c$	0.36	0.36	0.29
T_t/T_c	0.535	0.540	0.557
y_c	0.129	0.131	0.161
T_B/T_t	5.02	4.92	4.91
$P_c V_t/RT_c$	0.109	0.108	0.108
$\ln(P_t V_t/RT_t)_l$	-5.93	-5.89	-5.89
T_b/T_t	1.048	1.042	1.042

c refers to the critical point; t refers to the triple point; l refers to the liquid phase; b refers to the normal boiling point; B refers to the Boyle temperature.

Taking a particular algebraic form for P^o, namely Equation (IX-13), a solution for y^ℓ, hence b, is possible. This method of determining a and b characterizes the present study.

The fugacity expression is,

$$\ln(f/P) = (PV/RT) - 1 - \ln(PV/RT) + \int_o^y [(PV/RT) - 1]d\ \ln y. \tag{IX-15}$$

At P^t, $f/P \cong 1$ and $\ln(f/P) \cong 0$;

so,

$$\ln(PV/RT)_t = (PV/RT)_t - 1 + \int_o^{y_t} [(PV/RT) - 1]d\ \ln y. \tag{IX-16}$$

Now, for this equation of state (IX-11),

$$(PV/RT) = (PV/RT)^o - a/RTV. \tag{IX-17}$$

Using this in the integrand,

$$\ln(PV/RT)_t = [(PV/RT)_t - 1] + \int_o^{y_t} [(PV/RT)^o - 1]d\ \ln y - \int_o^{y_t} \frac{4a}{RT_t b}\, dy. \tag{IX-18}$$

$$= [(PV/RT)_t - 1] + \int_o^{y_t} [(PV/RT)^o - 1]d\ \ln y - a/RT_t V_t. \tag{IX-19}$$

In particular, for the liquid phase,

$$\int_o^{y_t} [(PV/RT)^o - 1]d\ \ln y = 3.67, \tag{IX-20}$$

$$\ln(PV^\ell/RT) = [(PV/RT)_t^{\approx o} - 1] + 3.67 - 8.56 = -5.89. \tag{IX-21}$$

Some estimate of the vapor pressure at temperature other than T_t is possible by assuming that the liquid volume remains constant. Thus, since $(a/RTV^{\ell}) = (a/RTV^{\ell})_t(T_t/T)$,

$$\ln(PV^{\ell}/RT) = (PV^{\ell}/RT) - 1 + 3.67 - 8.56(T_t/T)$$

$$= (PV^{\ell}/RT) + 2.67 - 8.56(T_t/T). \qquad \text{(IX-22)}$$

For $PV^{\ell} \ll RT$, as before,

$$\ln(PV^{\ell}/RT) = 2.67 - 8.56(T_t/T). \qquad \text{(IX-23)}$$

One can see from the calculated values in Table IX-1 that the triple-point behavior is better described by the more accurate rigid-sphere equation, Equation (IX-13), than by Equation (IX-12). In the case of four of the exhibited quantities, there exists no essential difference between predicted and experimentally observed values. The logarithm of the liquid phase triple-point compressibility factor, $\ln(P_tV_t^{\ell}/RT_t)$ is predicted exactly. The ratio of the normal boiling temperature to the triple point temperature T_b/T_t also is predicted exactly. Neither of these quantities was predicted exactly by Guggenheim [20] using Equation (IX-12). Exact prediction also occurs for the quantity $(P_cV_t^{\ell}/RT_c)$ using the more accurate Equation (IX-13). This is the product of the critical-point compressibility factor $(P_cV_t^{\ell}/RT_c)$ and the volume ratio (V_t^{ℓ}/V_c). Because V_c is so difficult to measure, it is found that the prediction of $(P_cV_t^{\ell}/RT_c)$ is more reliable. It is also found that an accurate prediction of the ratio of the Boyle temperature T_B/T_t is possible with this model.

The remaining quantities in Table IX-1 are not as well-predicted as the above. This is attributable, in part, to the inability of this simple model to predict the critical point with accuracy. Guggenheim [20] discusses reasons for this in his paper. The calculated critical density is about $V_o/V_c = 0.18$ for Equation (IX-12) and (IX-13). Since both equations are essentially the same at low densities, the calculated value of the critical compressibility is the same for both equations, when rounded to two decimal places.

The point to be emphasized is that the Longuet-Higgins and Widom assumption that repulsion effects in dense simple liquids can be accurately described by the rigid-sphere equation appears valid. The comparison between the Guggenheim results and the present calculations merely shows that the more accurate rigid-sphere equation, Equation (IX-13) improves the agreement between the Longuet-Higgins and Widom model and real fluid data. This study has been reported in the literature [15].

Discussion

The preceding sections of this introductory chapter on real fluids have attempted to define the role played by the rigid-sphere equation in approximate theories of real fluid behavior.

Most attempts at developing the equation of state from kinetic molecular theory are based upon the assumption that the effects of hard intermolecular repulsions (e.g. collisions) can be analytically calculated from the rigid-sphere equation. From the intermolecular

potential diagrams, Figures IX-1 and IX-2, the reasonability of the assumption is readily apparent.

The van der Waals concept of the equation of state (i.e. $P = P_R + P_A$) shows the manner in which an analytical equation of state can be written to incorporate the rigid-sphere equation, plus "other terms" which are used to approximate the effects of soft repulsions and cohesive forces.

The rigid-sphere equation seemingly accounts for two effects which occur in real fluids. First, the equation describes collision phenomena in systems of spherically symmetric molecules. This is mainly true in dilute gas systems. Second, the equation describes the repulsion effects in very dense systems, e.g. liquids and dense gases. This type of ability is demonstrated in the preceding section concerning the Longuet-Higgins and Widom model for the behavior of liquid argon near its triple point.

In summary, then, the rigid-sphere equation appears to have a promising future as a tool in theoretical equation of state research. It should play the role of describing collisional effects of spherically-symmetric molecules and the effects of hard repulsions, as are often observed in dense fluids. Both effects are important in the equation of state for real fluids.

CHAPTER X

APPLICATION OF THE RIGID-SPHERE EQUATION IN GENERALIZED EQUATIONS OF STATE FOR REAL FLUIDS

The purpose of this chapter is to present the results of several studies which indicate the usefulness of incorporating the rigid-sphere equation (III-10) into approximate models of the equation of state for real fluids.

Preliminary Remarks

Since van der Waals proposed his theoretical model of the equation of state [49] in 1873, the development of improved analytical models of the equation of state has proceeded along two routes, empirical and theoretical. Indeed, some of the empirical models have been based upon theoretical forms.

The totally empirical models of the equation of state are generally employed to correlate experimental thermodynamic property data. They are, therefore, quite accurate in making calculations of the data from which they have been evaluated. These evaluations are usually made by regression techniques requiring a considerable amount of experimental data to minimize errors in interpolative calculations. These equations of state are specific to a given material. They are not easily

generalized [25] such that accurate calculations can be made for a material not included in the original correlation.

Analytical forms of theoretical or semi-theoretical equations of state do not require vast amounts of experimental data for their evaluation. Using only a few characteristic bits of experimental data (e.g. critical pressure, critical temperature, critical compressibility factor, latent heat of vaporization at the normal boiling point, etc.), these equations allow predictive calculations of properties at other temperatures and pressures. Such calculations, naturally, lack the accuracy of the regression-spawned equations of state. Yet, for calculating the properties of materials for which reliable experimental data are scarce, the theoretical and semi-theoretical equations are definitely useful.

The theoretical equation of state models are usually based, in part, upon the kinetic molecular theory [25] or upon some form of free-volume theory [7]. At some point in the theoretical formulation, a basic assumption of rigid, spherical molecules is usually made. This leads to a rigid-sphere repulsion term, plus "something else" which generally accounts for cohesion effects. Such a model corresponds to the general form of the van der Waals equation (IX-8) discussed in Chapter IX, ($P = P_R + P_A$).

The drawback to deriving the rigid-sphere repulsion term from kinetic molecular theory or free-volume theory is that the result is valid only as a low-order approximation. Recall the rigid-sphere equation of Clausius [39],

$$P_R = RT/(V - b) = RT\rho/(1 - b\rho). \qquad (X\text{-}1)$$

Consider the virial expansion of $(P_R/RT\rho)$ from Equation (X-1). In order that this equation give an accurate rigid-sphere virial expansion (refer to Table III-1, where the expansion based on Equation (X-1) is listed as "van der Waals"), the constant b must be considered a function of density. Of course, it would be simpler to replace the kinetic theory rigid-sphere term with a more accurate equation, namely Equation (III-10).

In the following sections of this chapter, the effects of the above-mentioned substitution are examined by making comparative calculations using the original and substituted forms of some simple equations of state.

Thermodynamic Properties From the Equation of State

Prior to making calculations based upon specific forms of real gas equations, it will be helpful to generalize the method used to derive the equations for the thermodynamic properties relative to an ideal gas at the same temperature and pressure. The so-called "departure properties" are commonly solved for quantities from equation of state methods.

A review of the fundamental thermodynamic relations is in order. Recall the derived equation for the internal energy of a pure component system,

$$dU = T\,dS - P\,dV. \qquad (X\text{-}2)$$

By definition, the expression for the enthalpy is,

$$dH = T\,dS + V\,dP. \tag{X-3}$$

The Gibbs free energy is,

$$dG = dH - d(TS) = V\,dP - S\,dT. \tag{X-4}$$

The Helmholtz free energy is,

$$dA = dU - d(TS) = -P\,dV - S\,dT. \tag{X-5}$$

From these relations, and the following identities, it is possible to evaluate any of the basic thermodynamic properties from an equation of state.

The following identities, derived from the fact that the foregoing equations are considered exact differentials, prove very useful in the property calculations:

$$(dS/dV)_T = (dP/dT)_V \tag{X-6}$$

$$-(dS/dP)_T = (dV/dT)_P \tag{X-7}$$

$$-(dP/dS)_V = (dT/dV)_S \tag{X-8}$$

$$(dV/dS)_P = (dT/dP)_S. \tag{X-9}$$

Another often overlooked relation which is quite useful in equation of state calculations is,

$$d(PV) = P\,dV + V\,dP. \tag{X-10}$$

Equation (X-10) helps to make the transformation from integration w.r.t. pressure to integration w.r.t. volume or density. Since most analytic

equations of state are written with pressure as a function of volume, this aids in keeping the integration straightforward.

Consider an equation of state in the general form,

$$P = P_{rs} + \phi(V,T), \tag{X-11}$$

where P_{rs} = rigid-sphere pressure, Equation (IX-12)

$\phi/(V,T)$ = soft-repulsion and cohesion pressure term [corresponds to P_A of Equation (IX-8)].

Now,

$$(dP/dT)_V = (R/V)Z_{rs} + (d\phi/dT)_V, \tag{X-12}$$

where Z_{rs} = rigid-sphere compressibility factor, e.g. Equation (III-10).

Looking at the type of functions which are of interest, as isothermal deviations from the ideal gas state,

$$\begin{aligned}(U - U^o) &= \int_{\infty}^{V} [T\,(dP/dT) - P]\,dV \\ &= \int_{\infty}^{V} [T\,(d\phi/dT) - \phi]\,dV,\end{aligned} \tag{X-13}$$

$$(H - H^o) = (U - U^o) + (PV - RT), \tag{X-14}$$

$$\begin{aligned}(S - S^o) &= R \int_{\infty}^{V} (PV/RT - 1)\, d\ln V + R \ln(Z) \\ &= (S - S^o)_{rs} + \int_{\infty}^{V} (\phi/T)\, dV + R \ln(Z/Z_{rs}),\end{aligned} \tag{X-15}$$

$$(G - G^{o}) = (H - H^{o}) - T(S - S^{o}), \tag{X-16}$$

$$(A - A^{o}) = (U - U^{o}) - T(S - S^{o}), \tag{X-17}$$

$$\ln(f/P) = [(Z - 1) - \ln(Z)] - \int_{o}^{\rho} \frac{(Z_{rs} - 1)}{\rho} \, d\rho$$

$$- \int_{o}^{\rho} \frac{\phi}{RT\rho Z} \, d\rho. \tag{X-18}$$

Doing things this way, one can easily discern the changes made in the thermodynamic property relations, derived from an assumed equation for real fluids, by the substitution of different functional forms for $\phi(T,V)$. The rigid-sphere contribution is assumed to be that obtained from Equation (III-10).

Simple Two-constant Equations of State

In this section, the rigid-sphere equation (III-10) is used to replace the kinetic theory type of repulsion term, Equation (X-1), in two popular equations of state. For the purpose of demonstrating the improvement achieved by the substitution, the present study has been limited to simple two-constant models of the equation of state. There is a twofold reason for this:

(1) The general effect can be as easily seen with the simple equations as with more complex forms and, perhaps, more clearly;

(2) The algebraic form of the more complex equations is somewhat affected by the algebraic form of the repulsion term. Thus, changing the algebraic form of the repulsion term should be followed by the corresponding reformulation of the other terms (i.e. soft repulsion and cohesion terms). Such a reformulation is considered beyond the scope of the present study.

In the category of two-constant equations of state, two examples will be considered. The van der Waals equation, mentioned in the preceding chapter, is repeated here,

$$P = RT/(V - b) - a/V^2. \tag{X-19}$$

If one assumes the first term on the right of the equal sign to be a rigid-sphere term, then the other term gives

$$\emptyset = - a/V^2. \tag{X-20}$$

The other two-constant equation to be considered is the Redlich-Kwong equation [40],

$$P = RT/(V - b) - a/[V(V + b)\sqrt{T}]. \tag{X-21}$$

Following the same assumption about the first term on the right, the second term gives,

$$\emptyset = -a/[V(V + b)\sqrt{T}]. \tag{X-22}$$

In both the van der Waals and the Redlich-Kwong equation, the repulsion term, RT/(V - b), can be replaced by a rigid-sphere pressure term, e.g.

$$P_{rs} = RT(1 + y + y^2 - y^3)/V(1 - y)^3. \tag{X-23}$$

Thus, the rigid-sphere version of the van der Waals equation is

$$P = RT(1 + y + y^2 - y^3)/V(1 - y)^3 - a/V^2. \tag{X-24}$$

Likewise, the rigid-sphere version of the Redlich-Kwong equation [40],

$$P = RT(1 + y + y^2 - y^3)/V(1 - y)^3 - a/[V(V + b)\sqrt{T}]. \quad \text{(X-25)}$$

Using the format of the preceding section, one can develop equations for the thermodynamic properties based upon the foregoing equations of state.

van der Waals (VDW) Equation

The enthalpy departure is,

$$(H - H^o)/RT = (Z_{rs} - 1) - 2a/RTV. \quad \text{(X-26)}$$

The fugacity coefficient is,

$$\ln(f/P) = (Z_{rs} - 1) + \ln(Z_{rs}) - \ln(Z) - 2a/RTV, \quad \text{(X-27)}$$

where $Z_{rs} = V/(V - b) = 1/(1 - b\rho) = 1/(1 - 4y)$

$$\emptyset = - a/V^2$$

$$d\emptyset/dT = 0$$

$$\int_{\infty}^{V} \emptyset dV = a/V.$$

The two constants, a and b, are determined by the conditions $(dP/dV) = 0$ and $(d^2P/dT^2) = 0$ at the critical point. For this particular equation of state, the resulting definitions are,

$$Z_c = 3/8,$$

$$V_c = RT_cZ_c/P_c,$$

$$b = V_c/3,$$

$$a = 9RT_cV_c/8.$$

Rigid-sphere van der Waals (RSVDW) Equation

The enthalpy departure is,

$$(H - H^{o})/RT = (Z_{rs} - 1) - 2a/RTV. \qquad \text{(X-28)}$$

The fugacity coefficient is,

$$\ln(f/P) = \ln(f/P)_{rs} + \ln(Z_{rs}/Z) - 2a/RTV, \qquad \text{(X-29)}$$

where $\ln(f/P)_{rs}$ is from Equation (V-9)

$$Z_{rs} = (1 + y + y^2 - y^3)/(1 - y)^3$$

$$\emptyset = - a/V^2$$

$$d\emptyset/dT = 0$$

$$\int_{\infty}^{V} \emptyset dV = a/V,$$

and,

$$Z_c = 0.359$$

$$b = 0.5216\ RT_c Z_c/P_c$$

$$a = 1.38\ R^2 T_c^2\ Z_c/P_c.$$

Redlich-Kwong (RK) Equation

The enthalpy departure is,

$$(H - H^{o})/RT = (Z_{rs} - 1) - a/[RT^{1.5}\ (V + b)] + [a/2RT^{1.5}\ b)]\ \ln[V/(V + b)]. \qquad \text{(X-30)}$$

The fugacity coefficient is,

$$\ln(f/P) = (H - H^{o})/RT + \ln(Z_{rs}/Z), \qquad \text{(X-31)}$$

where $Z_{rs} = V/(V + b)$

$$\emptyset = - a/[V(V + b)\sqrt{T}]$$

$$d\emptyset/dT = a/[2V(V + b)\,T\sqrt{T}]$$

$$\int_{\infty}^{V} \emptyset dV = - [a/(b\sqrt{T})] \ln[V/(V + b)]$$

and,

$$Z_c = 1/3$$

$$V_c = RT_cZ_c/P_c$$

$$b = (\sqrt[3]{2} - 1)\, V_c \cong 0.26\, V_c$$

$$a = 1.283RT_c^{1.5}\, V_c.$$

Rigid-sphere Redlich-Kwong (RSRK) Equation

The enthalpy departure is,

$$(H - H^{o})/RT = (Z_{rs} - 1) - a/[R(V + b)\, T^{1.5}] + (a/2bRT^{1.5}) \ln[V/(V + b)]. \qquad \text{(X-32)}$$

The fugacity coefficient is,

$$\ln(f/P) = \ln(f/P)_{rs} + \ln(Z_{rs}/Z) - a/[R(V + b)\, T^{1.5}] + (a/bRT^{1.5}) \ln[V/(V + b)], \qquad \text{(X-33)}$$

$$\text{where } Z_{rs} = (1 + y + y^2 + y^3)/(1 - y)^3$$

$$\emptyset = - a/[V(V + b)\sqrt{T}]$$

$$d\emptyset/dT = a/[2V(V + b)\, T\sqrt{T}]$$

$$\int_{\infty}^{V} \emptyset dV = - [a/(b\sqrt{T})]\, \ln[V/(V + b)]$$

and,

$$Z_c = 0.315715$$

$$V_c = RT_cZ_c/P_c$$

$$b = 0.3326V_c$$

$$a = 1.463RT_c^{1.5}\, V_c.$$

Calculated Enthalpies

Calculations of gas phase enthalpies have been made with the original and the modified equations. The results of these calculations are summarized in Table X-1 for a variety of substances, many of which are polar and/or not spherically-symmetric. Without exception, the ability of the equations to predict enthalpy departures is improved with the use of the more accurate rigid-sphere term, Equation (X-23), as the model for repulsion effects. Recall that these two-constant equations of state are not theoretically intended for polar molecules nor for molecules which do not have sperical symmetry. Nonetheless, the predictions show the anticipated trend favoring the use of the more accurate rigid-sphere term, Equation (X-23). The overall average of the deviations for the calculated enthalpies are:

(1) VDW..... 10.56 BTU/LBM
(2) RSVDW.... 7.59 BTU/LBM
(3) RK..... 3.82 BTU/LBM
(4) RSRK..... 1.80 BTU/LBM.

TABLE X-1

Effect of Substituting the Rigid-sphere Equation into van der Waals' Equation
And into the Redlich-Kwong Equation

Substance	Total No. of Data Pts.	Equation	Avg. Abs. Dev. (BTU/LB) Enthalpy*		Percent Avg. Abs. Dev. Density*	
Nitrogen[1]	102	VDW	4.63	(72)	2.01	(30)
	109	RSVDW	3.16	(79)	0.313	(30)
	107	RK	1.26	(77)	0.737	(30)
	101	RSRK	0.58	(71)	0.294	(30)
Carbon Dioxide	43	VDW	17.61	(19)	7.47	(24)
	49	RSVDW	13.42	(25)	5.51	(24)
	46	RK	6.09	(22)	2.64	(24)
	49	RSRK	0.915	(25)	1.49	(24)
Hydrogen Sulfide	23	VDW	----		1.79	(23)
	23	RSVDW	----		0.949	(23)
	23	RK	----		0.84	(23)
	23	RSRK	----		1.15	(23)
Ethylene	70	VDW	7.50	(39)	4.18	(31)
	70	RSVDW	5.04	(39)	2.55	(31)
	70	RK	1.99	(39)	1.33	(31)
	70	RSRK	1.18	(39)	1.17	(31)

* The values included in parentheses denote total number of data points included in the average.

TABLE X-1

(Continued)

Effect of Substituting the Rigid-sphere Equation into van der Waals' Equation

And into the Redlich-Kwong Equation

Substance	Total No. of Data Pts.	Equation	Avg. Abs. Dev. (BTU/LB) Enthalpy*		Percent Avg. Abs. Dev. Density*	
Isopentane	33	VDW	----		5.52	(33)
	32	RSVDW	----		3.91	(32)
	29	RK	----		1.42	(29)
	28	RSRK	----		1.14	(28)
Methane	40	VDW	5.93	(18)	3.89	(22)
	40	RSVDW	3.80	(18)	2.72	(22)
	40	RK	1.41	(18)	1.50	(22)
	40	RSRK	0.96	(18)	1.63	(22)
Ethane	35	VDW	13.5	(14)	8.30	(21)
	42	RSVDW	9.81	(15)	8.60	(27)
	42	RK	5.53	(15)	1.82	(27)
	42	RSRK	2.31	(15)	5.75	(27)
Propane	25	VDW	35.0	(9)	9.95	(16)
	23	RSVDW	14.9	(7)	6.01	(16)
	23	RK	7.79	(7)	3.07	(16)
	23	RSRK	2.11	(7)	1.82	(16)

* The values included in parentheses denote total number of data points included in the average.

TABLE X-1

(Continued)

Effect of Substituting the Rigid-sphere Equation into van der Waals' Equation

And into the Redlich-Kwong Equation

Substance	Total No. of Data Pts.	Equation	Avg. Abs. Dev. (BTU/LB) Enthalpy*		Percent Avg. Abs. Dev. Density*	
Butane	17	VDW	27.2	(8)	2.27	(9)
	22	RSVDW	25.3	(13)	1.80	(9)
	18	RK	10.6	(9)	0.91	(9)
	22	RSRK	2.96	(13)	0.64	(9)
Pentane	138	VDW	10.59	(124)	3.59	(14)
	138	RSVDW	7.61	(124)	3.05	(14)
	138	RK	4.55	(124)	1.34	(14)
	138	RSRK	2.60	(124)	0.95	(14)
Heptane	16	VDW	16.5	(16)	----	
	16	RSVDW	11.1	(16)	----	
	16	RK	7.5	(16)	----	
	15	RSRK	3.4	(15)	----	

* The values included in parentheses denote total number of data points included in the average.

Calculated Densities

The results of density calculations with these equations of state, (X-19), (X-21), (X-24) and (X-25), are also summarized in Table X-1. Anomalies occur for methane, ethane and for hydrogen sulfide. Densities calculated for these materials with the rigid-sphere version of van der Waals' equation (RSVDW) are more accurate than those calculated with the original van der Waals' equation (VDW). Yet, for these three substances, densities calculated from the original Redlich-Kwong equation (RK) are more accurate than those calculated with the rigid-sphere version (RSRK).

For the other eight materials included in the study, there seems to be a definite improvement in the density calculations resulting from the use of the more accurate rigid-sphere equation (X-23) in place of the kinetic theory expression, Equation (X-1). Indeed, the overall average deviations show the improvement quite markedly. Excluding ethane from the average, the results are:

(1) VDW..... 4.495%

(2) RSVDW.... 2.898%

(3) RK..... 1.496%

(4) RSRK..... 1.133%.

Calculated Pressures

The ability of the equations to calculate pressure from experimental temperatures and specific volumes is shown in Table X-2. Below the critical isotherm (143.7^{o}C for methyl chloride), all four equations of state are roughly equal, with a slight advantage held by the RSRK equation. Along the critical isotherm, the van der Waals (VDW) equation

TABLE X-2

Prediction of Methyl Chloride Pressures from Experimental Temperatures and Vapor Specific Volumes*

^{o}C	PE* (ATM)	VDW (ATM)	RSVDW (ATM)	RK (ATM)	RSRK (ATM)
125	6.975	7.063	7.051	7.02	7.006
	20.049	20.629	20.523	20.255	20.132
	30.664	32.017	31.749	31.109	30.814
	39.817	42.215	41.728	40.630	40.124
	49.015	52.848	52.039	50.407	49.649
143.7	9.567	9.632	9.616	9.571	9.549
	30.398	31.288	31.123	30.670	30.449
Critical Isotherm	51.077	53.818	53.421	52.291	51.731
	69.954	251.92	145.77	103.16	83.291
	101.510	936.55	328.59	200.86	125.46
	206.85	4265.0	666.61	398.17	196.88

* Data of Hsu and McKetta [26].

gives very poor results at and above the critical pressure. For pressures above the critical pressure (hence, densities above the critical density), the RSRK equation gives much better prediction than the other equations. At 206.85 atmospheres (roughly four times the critical pressure), the errors in the predicted pressures are:

(1) VDW..... + 1962%

(2) RSVDW..... + 222%

(3) RK..... + 92%

(4) RSRK..... - 4.8%.

From these results, and the data shown in Table X-2, one has the impression that the RSRK equation follows the critical isotherm rather well at above-critical pressures. It also appears that the RSRK equation is the best of these four for the calculation of thermodynamic properties (gas phase) at temperatures less than the critical.

Calculated Fugacities

Table X-3 summarizes the results of calculations of fugacity coefficients for the saturated vapors of methane, ethane, propane, isobutane and acetylene. Again, the results show the improved accuracy of predictions by substitution of Equation (X-23) for the kinetic theory rigid-sphere expression, Equation (X-1), in the equation of state models. The fugacities were computed according to the following scheme:

(1) Solve for a gas density such that the calculated pressure agrees with the experimental vapor pressure for a fixed temperature;

(2) Solve for fugacity coefficient with the fixed temperature and the calculated density.

TABLE X-3

Calculated Fugacity Coefficients for Saturated Vapors*

Substance	Equation	Percent Avg. Abs. Dev.	No. of Data Points
Methane	VDW	3.04	10
	RSVDW	2.49	10
	RK	0.92	10
	RSRK	0.43	10
Ethane	VDW	4.53	13
	RSVDW	3.59	13
	RK	1.14	13
	RSRK	0.81	13
Propane	VDW	4.46	14
	RSVDW	3.24	14
	RK	0.94	14
	RSRK	0.44	14
Isobutane	VDW	3.58	11
	RSVDW	2.97	11
	RK	1.37	11
	RSRK	0.86	11
Acetylene	VDW	4.93	10
	RSVDW	4.21	10
	RK	2.36	10
	RSRK	1.63	10

* Experimental values taken from Canjar and Manning [10].

Although, it is not the specific object of this study to propose a new or modified equation of state model for real fluids, it is interesting to note the generally more accurate prediction of saturated vapor fugacity by the RSRK equation. Such an improvement over the Redlich-Kwong equation could be useful in such correlations of vapor-liquid equilibrium as the Chao-Seader method [16], which uses the RK equation to predict vapor fugacity coefficients.

Yet, the point to be stressed is that the use of the more accurate rigid-sphere equation (X-23) improves the ability of the real fluid equation of state model to predict thermodynamic properties for a wide variety of materials.

Discussion

This chapter has presented the results of one type of empirical application in which the rigid-sphere equation (X-23) can be used in an approximate model of the real fluid equation of state.

The calculations of enthalpies, densities, isothermal pressures and fugacities (summarized in Tables X-1, X-2 and X-3) generally verify the hypothesis that the accurate rigid-sphere equation (X-23) improves the model of the equation of state for real fluids. The calculations also show that the shortcomings of the original van der Waals' equation (X-19) are not all attributable to the kinetic theory term used for the repulsion pressure, P_R. The Redlich-Kwong modification of the cohesion term, P_A, appears to halve the average uncertainty in calculated enthalpies, using the kinetic theory term, Equation (X-1), for repulsion pressure, P_R. Yet, the combined effect of using the more

accurate repulsion term, Equation (X-23), and the Redlich-Kwong cohesion term, Equation (X-22), is to cut the average uncertainty in the calculated enthalpies by a factor of approximately five, relative to the original van der Waals equation.

The study has used the van der Waals equation (X-19) and the Redlich-Kwong equation (X-21) as examples of equation of state models which can be improved with the substitution of Equation (X-23) for the kinetic theory rigid-sphere term, Equation (X-1). Although these are both two-constant equations of state models, the resulting improvement should be considered general for any equation of state which presently uses the kinetic theory term, Equation (X-1), or its equivalent to describe repulsion effects in real fluids. At a time when so many researchers are publishing new and/or modified equations of state (of the Redlich-Kwong variety), it should prove worthwhile to use Equation (X-23) for the repulsion model and then to focus attention on developing an improved cohesion term, P_A.

CHAPTER XI

APPLICATION OF THE RIGID-SPHERE EQUATION IN GENERALIZED EQUATIONS OF STATE FOR REAL FLUID MIXTURES

In this chapter, the generalized models of the equation of state, discussed in Chapter X, are extended to calculate properties of mixtures. Again, attention is not to be focussed upon the particular models of the equation of state used in the study. Emphasis is upon the overall improvement in the accuracy of the calculated thermodynamic properties when an accurate mixture rigid-sphere equation (IV-11) is used to describe the effects of intermolecular repulsions.

Coefficients for Mixture Equations

The majority of calculations of thermodynamic properties of mixtures from equations of state use the same algebraic form for multicomponent systems as for single-component systems. For mixtures, the equation of state coefficients are somehow averaged from the pure component coefficients. In practice, the averaging methods are usually chosen on the basis of accuracy in one of the predicted properties.

In the particular examples used in this chapter, the van der Waals equation and the Redlich-Kwong equation, the mixing rules are usually as follows,

$$b_m = \Sigma x_i b_i \tag{XI-1}$$

$$a_m = [\Sigma x_i a_i^{\frac{1}{2}}]^2. \tag{XI-2}$$

This particular combining procedure for a and b is known as the Lorentz-Berthelot rule, i.e. a linear combination of the covolume b and a geometric average for the force parameter a.

The validity of the mixing rules has been the subject of much investigation by scientists and engineers involved in the study of mixture behavior. In order to see why this has been difficult in the simple case of the van der Waals equation, it is instructive to write the mixture van der Waals equation using the rigid-sphere mixture equation (IV-11) instead of the simple kinetic theory term.

$$P = RT\rho Z_{rs} - a_m\rho^2, \tag{XI-3}$$

$$\begin{aligned}
\text{where } Z_{rs} &= (1 + Y + Y^2)/(1 - Y)^3 \\
&\quad - C\{ \sum_{n<j} [n_i n_j (\sigma_i - \sigma_j)^2 Q_{ij}] \\
&\quad + YX^3/3\}/(1 - Y)^3 \\
Y &= (\pi N/6V)\langle\sigma^3\rangle = (b_m\rho/4) \\
X &= (\pi N/6V)\langle\sigma^2\rangle = Y(\langle\sigma^2\rangle/\langle\sigma^3\rangle) \\
C &= \langle\sigma^3\rangle/3Y \\
Q_{ij} &= \sigma_i + \sigma_j + \sigma_i\sigma_j X.
\end{aligned}$$

Thus, instead of the repulsion contribution to the pressure being calculated by the simple kinetic theory term (with an averaged value of the

covolume b), the repulsion effect is calculated from a term which uses several different types of averages of the pure component covolumes. Recall, for a single component, the molar covolume is,

$$b = (2\pi N/3)\sigma^3. \tag{XI-4}$$

Also, for the generalized equations of state, b is usually related to the critical point properties, e.g.

$$b = \beta\, RT_c/P_c, \tag{XI-5}$$

where β = constant for a given equation of state.

So,

$$\sigma_i^3 = (\beta RT_{c_i}/P_{c_i})(3/2\pi N), \tag{XI-6}$$

and,

$$\sigma_i^2 = (\sigma_i^3)^{2/3} = b_i^{2/3}\,(3/2\pi N)^{2/3} \tag{XI-7}$$

$$\sigma_i = (\sigma_i^3)^{1/3} = b_i^{1/3}\,(3/2\pi N)^{1/3}. \tag{XI-8}$$

Using the length parameters σ^i obtained from the covolumes, the effect of the mixture rigid-sphere equation (IV-11) as a model of repulsion phenomena in real fluid mixtures is seen in the following study.

Enthalpy Departures of Mixtures

For the simple two-constant models of the equation of state used in this study, the algebraic form of the expression for enthalpy departures remains the same as for the pure fluids. The difference is that

the rigid-sphere compressibility factor, Z_{rs}, is calculated from the mixture equation (IV-11) rather than from Equation (III-10). The energy constant a is also replaced by the averaged value of the coefficient, i.e. a_m from Equation (XI-2).

Using the mixture equation, densities were calculated for given temperature, pressure and composition information. The densities, temperatures and compositions were then used to calculate mixture enthalpy departures. The summarized results of the calculations for twelve binaries are presented in Table XI-1.

Discussion

The results shown in Table XI-1 verify, for mixtures, that the rigid-sphere equation (IV-11) is a more effective model of repulsion and collision phenomena in real fluids. The general effect is easily seen in the overall deviations between predicted and observed data. The overall results are:

(1) VDW..... 14.25 BTU/LBM

(2) RSVDW..... 10.05 BTU/LBM

(3) RK..... 6.50 BTU/LBM

(4) RSRK..... 4.47 BTU/LBM.

The use of the rigid-sphere equation roughly decreases the average deviation by a factor of one-third. Since the number of coefficients remains the same as in the original equations, the more accurate predictions are attributable to a better algebraic model of intermolecular repulsion effects.

TABLE XI-1

Results of Enthalpy Departure Calculations
For Gas Mixtures

Mixture	No. of Data Pts.	Equation	Avg. Abs. Dev. (BTU/LBM)
(94.8 Methane, 5.2 Propane)	27	VDW	2.74
	27	RSVDW	1.94
	27	RK	0.81
	27	RSRK	0.62
(88.3 Methane, 11.7 Propane)	26	VDW	2.63
	26	RSVDW	2.09
	26	RK	1.03
	26	RSRK	0.72
(72.0 Methane, 28.0 Propane)	21	VDW	5.77
	21	RSVDW	4.77
	21	RK	2.16
	21	RSRK	1.23
(49.4 Methane, 50.6 Propane)	16	VDW	10.78
	16	RSVDW	8.85
	16	RK	4.19
	16	RSRK	2.65
(38.5 Pentane, 61.5 Cyclohexane)	102	VDW	9.51
	102	RSVDW	6.62
	102	RK	3.56
	102	RSRK	1.76

TABLE XI-1
(Continued)

Results of Enthalpy Departure Calculations
For Gas Mixtures

Mixture	No. of Data Pts.	Equation	Avg. Abs. Dev. (BTU/LBM)
(61.2 Pentane, 38.8 Cyclohexane)	101	VDW	9.21
	101	RSVDW	6.67
	101	RK	4.02
	101	RSRK	2.41
(56.6 Methane, 43.4 Nitrogen)	45	VDW	3.33
	45	RSVDW	1.77
	45	RK	0.23
	45	RSRK	1.14
(19.7 Pentane, 80.3 Cyclohexane)	91	VDW	12.18
	91	RSVDW	9.07
	91	RK	5.59
	91	RSRK	3.46
(80.9 Pentane, 19.1 Octane)	45	VDW	17.90
	45	RSVDW	14.29
	45	RK	10.02
	45	RSRK	7.59
(59.7 Pentane, 40.3 Octane)	49	VDW	24.3
	49	RSVDW	19.27
	49	RK	13.62
	49	RSRK	10.1

TABLE XI-1
(Continued)

Results of Enthalpy Departure Calculations
For Gas Mixtures

Mixtures	No. od Data Pts.	Equation	Avg. Abs. Dev. (BTU/LBM)
(39.5 Pentane, 60.8 Octane)	40	VDW	28.2
	40	RSVDW	22.26
	40	RK	16.15
	40	RSRK	11.80
(21.8 Pentane, 78.2 Octane)	44	VDW	30.1
	44	RSVDW	23.2
	44	RK	16.7
	44	RSRK	11.6

CHAPTER XII

CONCLUSIONS AND RECOMMENDATIONS

The primary objective of this research has been the development of an accurate model of the equation of state for nonattracting rigid spheres. The significance of the derived equation is linked with the importance and popularity of the rigid-sphere system as a model for the repulsion effects in real fluids.

Comparison with the Molecular Dynamics data of Alder [3] shows that Equation (III-10), developed in this research, is the most accurate of existing analytical rigid-sphere equations. Likewise, comparison with Molecular Dynamics data and with Monte Carlo data shows that Equation (IV-11), the mixture version of Equation (III-10), is an extremely accurate model for rigid-sphere mixtures.

The analysis of entropy calculations in Chapter V shows that rigid-sphere properties calculated with Equation (III-10) are very accurate. Therefore, they should be quite useful in perturbation theories for calculating properties of the reference system.

The effectiveness of Equation (III-1) as a model for the repulsion behavior of real fluids is shown by several examples in the second part of this dissertation. The equation was used for calculating repulsion behavior, according to the Longuet-Higgins and Widom model, in liquid argon near its triple point. The improved accuracy of calculated

quantities indicates Equation (III-10) to be a useful repulsion model.

In a second example, Equation (III-10) is used to replace the kinetic theory form of the rigid-sphere equation in the van der Waals equation and in the Redlich-Kwong equation. The accuracy of predicted enthalpies, densities, pressures and saturation fugacities is improved, verifying that the rigid-sphere equation developed in this research can be used in approximate theories of real fluids as a more accurate model of repulsion behavior.

The improvement of the prediction of mixture enthalpy departures (Chapter XI) amplifies the conclusion that the accurate rigid-sphere equation of state, Equation (IV-11), is an effective model for the calculation of repulsion behavior in real fluids.

Insofar as the overall equation of state research and development project discussed in the Preface is concerned, this study has produced an accurate model of the repulsion contribution to the total pressure containing only one coefficient. Thus, either a reduction in the number of empirical equation of state coefficients or an increase in accuracy with the same number of coefficients is possible by using the rigid-sphere equation as a repulsion pressure model. Additionally, the form of such an equation would have a basis in molecular theory.

RECOMMENDATIONS

Based upon the research leading to this dissertation, it is recommended that Equation (III-10) and its mixture version (IV-11) be used whenever applications call for the calculation of rigid-sphere properties. In addition, the equations can be used in place

of the simpler kinetic theory form of the rigid-sphere equation in approximate theories of real fluids.

Further study of the empirical use of the rigid-sphere formalism in equation of state development work should investigate the effect of allowing the rigid-sphere diameter to vary with the temperature of the system.

With regard to transport theory, the resulting equations for the rigid-sphere contact radial distribution function, Equations IV-6 and IV-8, should find application in the testing of proposed formulae for the transport coefficients of pure fluids and of rigid-sphere mixtures. Having analytical expressions for the contact radial distribution function facilitates the evaluation of transport coefficient relations.

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NOMENCLATURE

Upper Case

A	Helmholtz free energy
A^o	Helmholtz free energy of an ideal gas
B	Second virial coefficient
B_n	n-th virial coefficient
C	Third virial coefficient
	Constant term in Equation (IV-11)
D	Fourth virial coefficient
	Self-diffusion coefficient
D_o	Self-diffusion coefficient of low-pressure gas
G	Gibbs free energy
G^o	Gibbs free energy of an ideal gas at T, P of system
G^E	excess Gibbs free energy, $(G - G^o)$
H	enthalpy
H^o	enthalpy of an ideal gas at T, P of system
H^E	excess enthalpy, $(H - H^o)$
H_g^*	saturated gas enthalpy
H_ℓ^*	saturated liquid enthalpy
H_s^*	saturated solid enthalpy
ΔH_v	enthalpy of vaporization
ΔH_f	enthalpy of fusion
K	coefficient of bulk viscosity

N	number of molecules in the system (Avogadro's number for a molar system)
P	total pressure
P^o	rigid-sphere pressure
P_c	critical pressure
P_t	triple point pressure
P_{rs}	rigid-sphere pressure
P_R	repulsion pressure
R	molar gas constant
S	entropy
S^o	ideal gas entropy at T, P of system
S^E	excess entropy, $(S - S^o)$
T	absolute temperature
T_c	critical temperature (absolute)
T_t	triple-point temperature (absolute)
U	energy of the system
V	Total volume of the system
V_s^*	Specific volume of saturated solid
V_g^*	Specific volume of saturated gas
V_{ℓ}^*	Specific volume of saturated liquid
V_c	Specific volume at liquid-vapor critical point
V_t^{ℓ}	Specific volume of liquid at triple point
V_o	Volume of rigid-sphere system at closest packing
Y	reduced density for rigid-sphere mixtures
Z	Compressibility factor, PV/NkT
Z_c	Critical compressibility factor

Lower Case

a, b	coefficients of two-constant equations of state
b	system covolume, $(2\pi N\sigma^3/3)$
d	density, 1/V
d^*	reduced rigid-sphere mixture density $6y/\pi$
f	fugacity
g_o	rigid-sphere radial distribution function
$g(\sigma)$	radial distribution function for rigid-spheres in contact
$g_{ii}(\sigma_i)$	radial distribution function for the number of i-molecules in contact
$g_{ij}(\sigma_{ij})$	radial distribution function for the number of i-molecules in contact with j-molecules
k	Boltzmann constant
	coefficient of bulk viscosity (Chapter VII)
n	number density, N/V
	index of virial coefficients (Chapter III)
r	center-to-center molecular separation
r_{ij}	distance between centers of molecules i and j
r_o	Lennard-Jones length parameter
u(r)	intermolecular potential function
u_{L-J}	Lennard-Jones potential function model
u_R	repulsion potential
u_A	attraction potential
u_{rs}	rigid-sphere potential function
V_x	component velocity in x-direction
V_y	component velocity in y-direction
V_z	component velocity in z-direction

w_1, w_2, w_3	coefficients of Padé approximants
x	spatial coordinate (Chapter I)
x_i	mole fraction of i-molecules in system
y	spatial coordinate (Chapter I)
z	spatial coordinate (Chapter I)

Greek

α_1, α_2, α_3, α_4	coefficients of Padé approximants
β	general coefficient (Chapter XI)
Δ	difference operator
ϵ	Lennard-Jones energy parameter
η	coefficient of shear viscosity
η_o	coefficient of shear viscosity of a low-pressure gas
λ	coefficient of thermal conductivity
λ_o	coefficient of thermal conductivity of a low-pressure gas
π	3.1415926...
ρ	density, 1/V
Σ	summation operator
σ	rigid-sphere diameter
σ_i	sphere diameter of i-molecules
σ_{ij}	$\frac{1}{2}(\sigma_i + \sigma_j)$
φ	$[(PV/NkT) - 1]$ (Chapter VII)
$\emptyset$	pressure due to cohesion and soft repulsion $P - P_{rs}$
Ψ	rigid-sphere diameter ratio (in mixtures), σ_i/σ_j