ANNUAL REPORT

THE GENERALIZED VAN DER WAALS THEORY OF PURE FLUIDS AND MIXTURES

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INTRODUCTION

During this past year we have completed some work which was in progress, continued other work, and initiated some pioneering, derivative work which has led to exciting new results. Each of these areas will be described in this report. For reference, titles and abstracts of all our work which has been published, or submitted for publication, supported by this grant appear in a later section. Complete reprints and preprints are appended to this report.

FUNCTIONAL GROUP ANALYSIS

I will start the discussion with our newest research thrust. As part of our work with activity coefficient models, we continue to be impressed by the success, in some cases, of group contribution methods, and especially UNIFAC. The underlying basis of these models is that of "group additivity," that is, that a group always makes the same contribution to the properties of a pure fluid or a mixture independent of the molecule on which the group appears. In many cases this is a remarkably successful assumption, allowing chemical engineers to make phase equilibrium predictions about mixtures for which they have no experimental data. However, in some cases group contribution methods fail. For example, we show in publication list item 11 an example in which UNIFAC predicts the occurrence of liquid-liquid equilibrium while only an azeotrope is found experimentally, and another in which UNIFAC predicts almost ideal solution behavior when an azeotrope occurs. Consequently, in some cases UNIFAC leads to good predictions, while in other cases the predictions are quite poor. More seriously, the chemical engineer has no *a priori* way of knowing which of these alternatives will occur.

This past year we broadened our research program to try to understand the causes of failure of UNIFAC and other group contribution methods. One of our first observations was that the definition of a functional group differed among the different group contribution methods. Consequently, we decided to examine the basis for defining functional groups.

The basis of our analysis is that the electrostatic charge, because of the Coulombic interaction, is the dominant term in the interaction between functional groups, so that for the proper definition of a group in functional group analysis, its charge should remain the same regardless of the molecule in which the group appears. Therefore, we initiated a program of molecular orbital calculations which allows us to compute the charge on individual atoms and on groups of atoms in many molecules. In fact, we studied 93 different molecules in item #11 in the publication list.

Based on these calculations we found that many, but not all, functional groups should be as chosen in the current UNIFAC model, groups which have been chosen completely empirically. However, approximately 30% of the groups should be defined differently because the charges on the analogous UNIFAC groups varied from molecule to molecule. When such group redefinitions are made we find, in some cases, the group contribution predictions are far more accurate than had been the case in the past. This is shown in item #12 in the publication list. Also, from these quantum mechanical calculations, we could identify a number of cases, such as some hydrogen-bonding mixtures and small chlorofluorocarbons where, for different reasons, the group additivity assumption is invalid, so that no group contribution method would be accurate.

Thus, on the basis of quantum mechanical calculations, we have been able to improve group contribution prediction methods by defining better, theoretically based groups, and providing *a priori* information on when group contribution methods will fail. As far as we know, this is the first time that computational quantum chemistry has led to results of direct use in solution thermodynamics of interest to chemical engineers.

PARTITION FUNCTION ANALYSIS

A goal of some of our continuing work has been to extend equations of state we have derived for simple model fluids, such as the square well and exponential-six atomic fluids, based on theory and computer simulation, to more realistic and complex fluids. Over the last year we have been concentrating our efforts on small, rigid molecular fluids such as nitrogen, ethane, carbon disulfide, and propane, and trying to understand what are the important features of these fluids which must be accounted for in their thermodynamic description. To be more specific, we are trying to understand why empirical equations, such as the Peng-Robinson equation of state, are useful for spherical and nonspherical molecules (provided the molecules are not too large) even though they contain no structural information; only critical property information. Our principal tools for gaining insight into the thermodynamic and structural behavior of molecular fluids has been the generalized van der Waals partition function, a generalization of perturbation theory based on other than the hard-core reference fluid, and Monte Carlo computer simulation.

During the period of this grant we have accumulated a significant body of simulation results for diatomic molecules of different elongations, linear triatomic molecules, and nonlinear triatomic molecules over a wide range of state conditions, as well as a large amount of data on the exponential-six, Lennard-Jones, and hard-core Lennard-Jones fluids. The underlying approach to

building the equations of state for these fluids has been statistical mechanical partition function and perturbation theories. We have found that our previously derived equation of state for monatomic square-well fluids, which is both the simplest and most accurate square-well fluid equation of state, can be extended to the Lennard-Jones and hard-core Lennard-Jones fluids using a generalized perturbation theory based on a choice on any convenient reference fluid. Thus, we are able to make the transition from a short-range hard potential to a long-range smoothly varying potential. Indeed the equation of state we have developed based on this theory, with only four parameters, has been found to be as accurate in describing the Lennard-Jones fluid as the currently used equation with 33 adjustable parameters! [see items 13 and 14 in publication list section].

With suitably adjusted parameters this same equation of state can also be used to correlate the thermodynamic properties of small, rigid molecular fluids such as nitrogen, carbon disulfide, and ethane. Next, using the perturbed hard chain formalism in our partition function to rewrite our monatomic fluid equation of state for longer chain fluids, we have found that it performs well for the homologous series of straight chain hydrocarbons, up to at least n-octane. This last work has not yet been written up for publication.

The equation of state for square-well fluids previously derived under this grant is based on a lattice model in which the interaction energy of each atom with its nearest neighbors is given by the constant ϵ . Since the range of this interaction is equal to that of the square well, we were able to develop a simple and accurate model with no adjustable parameters for coordination number of the square-well fluid [1]. Using this model in the generalized van der Waals partition function, we derived an equation of state for the square-well fluid that is both simple and accurate. However, we found that when using more realistic continuous intermolecular potential a somewhat different form of the equation is more accurate, and nearly as simple, as the original square-well equation. A novel part of the work leading up to this new equation has been the development of an especially useful separation of the free volume and interaction contributions to the partition function, and thus to the repulsive and attractive parts of the equation of state, for continuously varying potentials. This is described in items 1, 8, and 13 in the list of our publications.

The new equation of state we have derived for the Lennard-Jones fluid is based upon the use of a square well reference system in perturbation theory, rather than the more traditional hard sphere system. We developed simple and accurate analytic expressions for the equivalent square well diameter and width, and found the functional form of the higher order terms in the perturbation expansion both by computing the Helmholtz free energy of a Lennard-Jones fluid

using Barker-Henderson perturbation theory [2] and from computer simulation. The details can be found in our reprints and preprints. The success of this procedure results from the fact that the correction term to the free energy and equation of state when using square well reference system is smaller in magnitude than the one based on the hard sphere reference. That is, more of the properties of the fluid are already included in the properly chosen reference system.

In order to extend our equations of state to nonspherical molecular fluids, we need to formulate the generalized van der Waals partition function and/or perturbation theories for these systems. For fluids whose molecules can be treated as rigid bodies, we have proved (but not yet published) that the partition function is formally very similar to the partition function for atomic fluids. However, both the free volume and mean potential of these molecular fluids contain contributions which result from the molecular character of these fluids. Consequently, it is inappropriate to use either a hard sphere repulsive term or an atomic fluid mean potential term in the equation of state for a molecular fluid. Fortunately, the free volume term for rigid molecular fluids is reasonably well known from the work of Boublik [3] and others, so we have been concentrating our efforts on the mean potential.

By definition, the mean potential is an integral of the configurational energy of the system from infinite temperature to the temperature of interest. Consequently, we previously needed configurational energies from computer simulation at extremely high temperatures to compute the mean potential numerically. One accomplishment during the current year of the project was to show that if the free volume of the rigid fluid is known, a simple thermodynamic relation between the mean potential and the compressibility exists which can be used to obtain the mean potential. As a result we have been able to reduce the amount of computer simulation that one needs to do for atomic and small rigid molecular fluids by an order of magnitude. During this year we have carried out the simulations for diatomic fluids of two different bond lengths, linear symmetric triatomic, and nonlinear symmetric triatomic molecules over a wide range of conditions. The novel method we have developed for computing the mean potential has made it possible to study *all* of these fluids using a smaller number of simulations than we previously needed for only a single fluid. These simulation results are currently being used to test the extension of equation (1) to rigid molecular fluids.

We are also interested in extending our analysis of equations of state and the partition function to molecular fluids which are not rigid, such as the normal alkanes from C₄ and above. We have chosen the general class of perturbed hard chain partition functions [4] as the basis of this

work, but have developed a different, more rigorous derivation of, and different result for, the partition function for such chain molecules than has previously appeared in the literature. We found that the recent equation of state for hard chains due to Hall et al. [5] can be used in conjunction with the perturbed hard chain partition function to determine two of the three adjustable parameters which appear in our analysis, parameters that previously could only be found by fitting an equation of state to experimental data. Further, our method of choosing the parameters is independent of any particular equation of state. Thus this work has much greater applicability than just to the systems we have considered. Also, we have used calculated second virial coefficients for Lennard-Jones diatomic and triatomic fluids along with computer simulated mean potentials and compressibilities to determine the third parameter in the perturbed hard chain partition function for these fluids. We have found that in using these parameters we are able to make quite reasonable predictions for the phase diagrams of the normal alkanes up to n-pentane. Some work remains to be done on this approach, however, because our equation of state still does not lead to predictions of the phase diagram that are comparable in accuracy to those obtained by using parameters fit to the experimental data; that is, we want to have a predictable rather than merely correlative equation of state. We are actively working on improving the methods of determining the perturbed hard chain parameters, as well as providing a fundamental, molecular basis for their role in the partition function. This will be one of the major continuing activities during the coming year of this grant. The goal of this work is the formulation of a general method for choosing these parameters without fitting to experimental data.

We have been using perturbation theory as a framework for deriving new equations of state for molecular fluids. Here we provide some details about the way we are proceeding. The intermolecular pair potential for nonspherical molecules depends on the relative orientation of two molecules as well as their distance of separation. First consider the center-of-mass frame of reference, in which the position of each molecule is specified by a vector from a laboratory-fixed origin to the center-of-mass, and a set of three Euler angles denoting the orientation of the molecule. In this frame of reference, the perturbation free energy can be written as

$$\frac{\beta A_p}{N} = 2\pi\rho\beta \int_0^1 \int_0^\infty \langle \omega(r, \omega_1, \omega_2) g(r, \omega_1, \omega_2; \lambda) \rangle \omega_1 \omega_2 r^2 dr d\lambda \quad (1)$$

where the angle brackets denote angle averaging over the orientational coordinates and the perturbation potential is

$$\omega(\mathbf{r}, \omega_1, \omega_2) = u_0(\mathbf{r}, \omega_1, \omega_2) - u(\mathbf{r}, \omega_1, \omega_2). \quad (2)$$

Equation (1) shows that the perturbation free energy for a molecular fluid is similar to that of an atomic fluid, provided that the appropriate angle averaging is done. Perturbation theories in this frame of reference have been successfully applied to nonpolar [6] and multipolar [7,8] fluids of small nonspherical molecules. This division of the potential into reference and perturbation parts is not unique because the potential depends on the orientation of a pair of molecules, and implies that the size of the hard fused sphere reference system in the perturbation theory depends on the orientation as well, and is inconvenient to use in a simple equation of state. The molecular pair correlation function $g(\mathbf{r}, \omega_1, \omega_2)$ is also difficult to tabulate or use because of its dependence on six variables. A coordinate transformation from the center-of-mass frame, in which each molecule is described by a set of vectors from a laboratory-fixed origin to the center of each atom in the molecule, simplifies the perturbation theory considerably [9]. In the atom-atom frame, the perturbation free energy is

$$\frac{\beta A_p}{N} = 2\pi\rho\beta \sum_{\alpha=1}^m \sum_{\gamma}^m \int_0^1 \int_0^\infty \omega_{aa}(r_{a\gamma}) g_{aa}(r_{a\gamma}; \lambda) r_{a\gamma}^2 dr_{a\gamma} d\lambda \quad (3)$$

where the subscript aa denotes an atom-atom quantity and the sums are over all atoms in the molecule. The perturbation potential is defined as

$$\omega_{aa}(r_{a\gamma}) = u_{0aa}(r_{a\gamma}) - u_{aa}(r_{a\gamma}) \quad (4)$$

and depends only on the distance of separation between an atom on molecule 1 and an atom on molecule 2. All of the quantities in an atom-atom frame perturbation theory depend on only this variable. The size of the hard body reference system is independent of the orientation of a pair of molecules and depends only on state conditions. Our work on molecular fluids has concentrated on generalized perturbation theory in the atom-atom frame of reference.

In order to compute the perturbation free energy for molecular fluids we must know its compressibility as a function of density at a series of temperatures. We have carried out Monte Carlo simulation of six different molecular models to obtain this information. Our results for homonuclear diatomics of four different bond lengths, linear triatomics, and nonlinear triatomics represent one of the most extensive collections of simulation data for molecular fluids in existence.

These data have been used to compute the perturbation free energies for each molecular model studied from the relation

$$\frac{\beta A_p}{N} = \int_0^p \frac{Z - Z_0}{\rho'} dp' \quad (5)$$

where Z is the compressibility from simulation and Z_0 is the compressibility of the hard-fused-sphere reference system computed from the Boublik [10] equation of state. We have found that, providing the reduced density is defined as ρV_m , where V_m is the volume of the molecule, the perturbation free energy of rigid molecular fluids can be described by the same models we used for atomic fluids. We have also used our equations of state, suitably modified for molecular fluids, to study the effects of molecular shape on the phase diagram and critical properties. The results of this study are being written up for publication. We are also interested in extending our equations of state to molecular fluids which are not rigid, such as the normal alkanes from C_4 through C_8 . We have based our work on the perturbed hard chain theory [11], but have used a somewhat different derivation of the partition function than has previously appeared in the literature. We found that the recent equation of state for hard chains due to Hall et al. [5] can be used in conjunction with the perturbed hard chain partition function to determine two of the three adjustable parameters in the partition function, parameters than were previously found only by fitting a particular equation of state to experimental data. Our method of choosing the parameters is independent of any particular equation of state. Further, these two parameters are exactly linear functions of the number of segments in the chain molecule. This result explains the success of the perturbed hard chain theory and the behavior of the adjustable parameters when the theory is applied to real fluids. We are currently investigating whether other hard chain equations of state, such as the Chapman-Jackson-Gubbins [12] equation, produce the same behavior, with the goal of determining whether it is a general phenomenon or a mathematical artifact of the Honnell-Hall equation of state.

Our next application of generalized perturbation theory will be to mixtures in which one of the components is nonspherical. We have modified our simulation programs to handle molecular fluids mixtures and will begin to collect simulation data in the near future. Our goal is to investigate the effect of nonspherical shape on the mixing rules commonly used in equations of state. We plan to so this be simulating binary mixtures where the molecular volume ratio of the two species is held fixed, while the molecular shape of one component is varied. Other researchers have found [13] that the volume difference between the molecules of two different components has a much greater

effect on the excess properties of the mixture than does the difference in shape. This conclusion was based on a study of hard convex body mixtures, where no attractive forces are present. We would like to determine if this conclusion is still valid when attractive forces are present in the mixture, especially when the interaction energy of each component is different. There is also a general lack of simulation data for binary mixtures of nonspherical molecules, in particular for structural information. Our new simulation results will provide new data for researchers who lack the capability to do computer simulations themselves.

In work described in item numbers 3 and 9 of the publication list section, we show that the new mixing rules we have already derived based on theory and simulation satisfy the proper boundary conditions, apply corrections to the traditional mixing rules exactly where they are needed and, without the use of any adjustable parameters, are more successful than either the van der Waals or the empirical mixing rules, also without adjustable parameters. That is the success we have found; the frustration arises from the fact that when comparable numbers of adjustable parameters are included, both the empirical and our theoretically based mixing rules perform equivalently away from the mixture critical point. It is only near the mixture critical point that our mixing rules retain some advantage. The main observation, however, is that as a result of the introduction of adjustable parameters fit to experimental data, the advantages of our new mixing rules are less obvious.

In addition to using the generalized van der Waals partition function to derive new mixing rules, we have also been developing new activity coefficient models. Here we have had more success in that a new activity coefficient model that we have developed is able to correlate low pressure vapor-liquid equilibrium data for chemically dissimilar systems better than any other activity coefficient model with the same number of parameters (two) currently in use. Further, this new model is comparable to others for simple, easy-to-describe systems. This is in contrast to other composition and density dependent mixing rules which have been proposed and tuned to certain complex mixtures but failed for simple mixtures.

Other work we have completed or published during the year include a clarification of how one should calculate free energies of mixing when starting with statistical mechanics or computer simulation [item 2 on the publication list], a two-paper review series on the generalized van der Waals partition function for incorporation into instructional programs [items 6 and 7 on our publication list], a critical evaluation of mixing rules developed by us and others to describe high pressure phase equilibria with equations of state [items 4 and 5 on our publication list], and a

review of simplifications of the thermodynamic description to be used with mixtures containing large numbers of components [item 10] as in reservoir fluids for simulation or enhanced oil recovery, and polymer solutions.

WORK TO BE CARRIED OUT DURING THE COMING YEAR

As a result of our current success, a major activity during the coming year will be to continue our research on computational quantum chemistry and group contribution methods. Our efforts here will be in two directions:

- 1) To explore the applicability of the new functional groups we have identified in other functional group methods [so far our work has been restricted to studying only UNIFAC]. We have hopes that our theoretically based method of choosing functional groups will have broad applicability, both in the properties than can be described, and in the functional groups and compounds that can be considered including, perhaps, such materials as heavy oil resids and coal derived liquids.
- 2) Our present method of determining functional groups is based on complex and complete molecular orbital calculations using the Gaussian 86 and, more recently, the Gaussian 88 packages. These are complex and incredibly time consuming calculations, which makes the study of new molecules for the purpose of identifying new classes of functional groups very slow and expensive. However, our interest is solely in molecular charge which is determined by the outermost or frontier orbitals. Consequently, we are now exploring approximate quantum mechanical calculations to give information on the frontier orbitals directly, quickly and inexpensively. In particular we will, in the immediate future, be using the program MOPAC 5.0 (available from the Quantum Chemistry Program Exchange) to compute the electronic charges on atoms and groups of atoms, and comparing the results with the accurate molecular orbital computations we have already completed and reported in publication list item #11.
- 3) We also want to explore whether quantum mechanical molecular orbital calculations can be used to predict values of the parameters in UNIFAC and other group contribution methods. This would be an especially important development since most unavailable parameters are for groups in molecules which are very difficult to work with, either because of toxicity, chemical stability, carcinogenicity or availability.

The second major activity during the coming year will be, as described in the original proposal, to continue our partition function research on chain molecules, now that the work on spherical molecules has been completed. Our explicit goal here is to develop equations of state and mixing rules for use with such molecules, and especially for mixtures of molecules which differ greatly in size and shape (and thus critical properties) as occurs, for example, in enhanced oil recovery and in coal liquefaction processes.

During the coming year Dr. Hasan Orbey, Professor of Chemical Engineering at the Middle East Technical University, Ankara, Turkey will be providing some additional help on this project. Dr. Orbey will be a Fulbright Scholar at the University of Delaware this year.

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PUBLICATIONS OF WORK SUPPORTED BY THIS CONTRACT (1989-90)

Abstracts of Research Publications for 1989-90

1. Monte Carlo Study of the Buckingham Exponential-Six Fluid by Lawrence R. Dodd and Stanley I. Sandler, *Molecular Simulation* 2, 15-32 (1989).

In this paper we report the results of extensive Monte Carlo simulations of a pure fluid of Buckingham modified exponential-six molecules. Data are presented for the configurational energy and pressure covering a wide range of temperatures and densities. These data are interpreted using the generalized van der Waals partition function with a novel separation into free volume and mean potential terms. We find, surprisingly, that the Buckingham fluid is described by a simple van der Waals-like equation of state provided that the b parameter is temperature dependent and chosen in a theoretically correct manner.

2. Free Energies of Mixing, by S. I. Sandler, J. Fischer, and F. Reschke, *Fluid Phase Eq.* 45, 251-264 (1989).

The differences between the excess Gibbs free energy for mixing at constant pressure and the excess Helmholtz free energy for mixing subject to other constraints are considered. For three mixing processes subject to other constraints these differences are calculated directly and from approximate equations for hard sphere mixtures and mixtures of Lennard-Jones molecules. It is found that only for mixing at ideal solution volume, i.e., "Scatchard mixing," is the difference small, while for the other mixing processes the difference may be an order of magnitude larger than the excess Gibbs free energy. One consequence is that excess Helmholtz free energies obtained from lattice theories should be corrected to obtain excess Gibbs free energies of mixing at constant temperature and pressure, for which the approximate equation given in this communication will be useful. A second consequence is that for the calculation of the excess Gibbs free energy of mixing from computer simulations, the isobaric-isothermal ensemble is preferred over the canonical ensemble.

3. The Generalized van der Waals Partition Function. V. Mixtures of Square-Well Fluids of Different Sizes and Energies, by K. H. Lee, L. R. Dodd, and S. I. Sandler, *Fluid Phase Eq.* 50, 53-77 (1989).

In this communication we report the results of Monte Carlo simulations for mixtures of square-well molecules of different sizes and interaction energies. We use these results to test various local composition models which have been suggested, and find that only the model proposed earlier is in reasonable agreement with the simulations. This local composition model is then used in the generalized van der Waals partition function to derive a new density-dependent equation of state mixing rule. This mixing rule increases the order of the volume dependence of any equation to which it is applied, though a simple modification to the solution algorithm proposed here easily handles this problem. We find that this new density-dependent mixing rule leads to more accurate predictions than the van der Waals one-fluid mixing rule when no binary interaction parameters are used, and retains only the advantage of smaller values of these parameters and slightly better critical region predictions when binary interaction parameters are used.

4. Critical Evaluation of Equation of State Mixing Rules for the Prediction of High Pressure Phase Equilibria, by S. K. Shibata and S. I. Sandler, *IEC Research* 28, 1893-1898 (1989).

Some recent data on the high pressure phase compositions and densities for the asymmetric nitrogen + n-butane mixture are used to test a number of different combining and mixing rules for use with the Peng-Robinson equation of state. We find that the van der Waals one-fluid mixing rules with two adjustable parameters is superior to the mixing rules of Panagiotopoulos and Reid, Huron and Vidal, Luedecke and Prausnitz, and is as good as the Lee-Sandler density-dependent mixing rule which is computationally more complicated. Further, by use of fluid-specific (rather than generalized) pure component parameters, very good predictions are obtained for the densities of both the coexisting vapor and liquid phases.

5. The Measurement and Correlation of High Pressure Phase Equilibria Composition and Density Data, by S. K. Shibata and S. I. Sandler, in "Experimental Thermodynamics: Measurement and Correlation," edited by S. Malanowski and A. Anderko, Polish Academy of Sciences, Warsaw, 1989, 2-22.

In this paper we briefly describe a new apparatus from measuring the coexisting vapor and liquid equilibrium compositions and densities at high pressures. We also report the results of correlating these data with a simple cubic equation of state with the van der Waals one-fluid mixing rules and less common mixing rules such as those of Panagiotopoulos and Reid, Huron and Vidal, Luedecke and Prausnitz, and Lee and Sandler.

6. From Molecular Theory to Thermodynamic Models. Part I. Pure Fluids by S. I. Sandler, *Chem. Eng. Educ.*, Winter 1990, 12-19.
7. From Molecular Theory to Thermodynamic Models. Part II. Mixtures by S. I. Sandler, *Chem. Eng. Educ.*, Spring 1990, 80-87.

These two papers are presented for the general chemical engineering audience as a summary of the results of our research and the understandings obtained, based on the generalized van der Waals partition function. These review papers are written in a form to provide classroom instruction in the molecular level basis of thermodynamic model building.

8. A Study of the Buckingham Exponential-Six Fluid Mixtures by L. R. Dodd and S. I. Sandler. Submitted for publication to *Fluid Phase Eq.*

Extensive Monte Carlo computer simulation results for the configurational energy, compressibility and the radial distribution functions of mixtures of exponential-six molecules at 352 state points are presented. These data are used to test mixture models that have been proposed, and to develop a model which describes the exp-6 fluid quite well. Using this model, we obtain explicit expressions for the partition function for pure fluids and mixtures of exp-6 molecules. We also show how, by redefinition of the free volume and mean potential terms, simple models can be used to describe the behavior of exp-6 fluids and that with this definition the behavior of the exp-6 and square-well fluids are very similar.

9. Equation of State and Activity Coefficient Models Based on the Exponential-Six Fluid by L. R. Dodd and S. I. Sandler, to be submitted to *Fluid Phase Eq.*

This work uses the mixing rules for configurational energy and mean potential obtained from the simulation studies in the previous paper to develop equation of state mixing rules and excess Gibbs free energy (activity coefficient) models of use in engineering. The density and composition-dependent mixing rules we develop are more accurate in the critical region than other mixing rules now in use, and reduce to the traditional van der Waals one-fluid mixing rules at low density and for mixtures of molecules of equal size at all densities. The new activity coefficient model we developed is found, for many mixtures, to be more accurate than current models with the same number of parameters.

10. Lumping or Pseudocomponent Identification in Phase Equilibrium Calculations by S. I. Sandler. Accepted for publication by Mobil Research and Development Corporation [to be published as part of a proceedings volume on The Reaction Kinetics and Thermodynamics of Multicomponent Mixtures].

Phase equilibrium calculations for mixtures of many components, such as reservoir fluids or polymer solutions, or even the weathering of oil spills, present special difficulties since the CPU time for the computations increases with approximately the square of the number of components. The problem is especially severe for intensive calculations such as reservoir simulations. To decrease the computational effort, larger numbers of species are usually lumped into smaller numbers of pseudocomponents. Traditionally, this lumping has been done empirically, by trial-and-error. This paper will demonstrate the simplicity and success of a lumping (or pseudocomponent identification) method based on well-founded mathematical principles for the calculation of reservoir fluid bubble points and the modeling of enhanced oil recovery by miscible gas injection.

11. The Use of *ab initio* Quantum Mechanics Calculations in Group Contribution Methods. I. Theory and the Basis for Group Identifications by H. S. Wu and S. I. Sandler. Submitted for publication to *IEC Research*.

Group contribution methods are powerful tools for estimating the thermophysical and thermodynamic properties of pure components and mixtures from experimental data on related substances. Among the problems with current group contribution methods is that there is no theoretical basis for defining functional groups, and no *a priori* way of determining when a group contribution prediction may be in error. Here we show that based on quantum mechanical *ab initio* molecular orbital calculations on single molecules, we can develop a simple theoretical basis for defining functional groups. Further, by "supermolecule" calculations involving two or more molecules, we can identify situations in which group contribution methods may fail.

12. The Use of *Ab Initio* Quantum Mechanics Calculations in Group Contribution Methods. II. Test of New Groups in UNIFAC by H. S. Wu and S. I. Sandler. Submitted for publication to *IEC Research*.

In this paper we show that functional groups identified previously from *ab initio* molecular orbital calculations lead to better UNIFAC predictions of vapor-liquid equilibrium, especially for mixtures involving molecules in which proximity effects are important. We also find that, for the functional groups we have defined, it is generally not necessary to distinguish between subgroups. This reduces the total number of main and subgroups that must be considered. For some hydrogen-bonding mixtures, neither

the new nor the old functional groups lead to satisfactory excess Gibbs free energy predictions. This is in agreement with our previously reported supermolecule calculations which showed that hydrogen-bonding energies could not be accounted in group contribution methods.

13. Equations of State from Generalized Perturbation Theory. I. The Hard-Core Lennard-Jones Fluid by G. M. Sowers and S. I. Sandler. Submitted for publication to *Fluid Phase Eq.*

A framework for deriving equations of state from perturbation theory is presented and used to investigate reference fluids more realistic than the hard sphere fluid in perturbation theory for the hard-core Lennard-Jones (HCLJ) fluid. We present new simulation results for the compressibility and internal energy of this simple fluid. We use generalized perturbation theory to derive two new simple equations of state for the HCLJ fluid that provide a very accurate fit of the simulation compressibilities. One of these equations is novel in that it is based on a square well reference system, while the other is an extension of commonly used perturbed-hard-sphere equations of state. We also discuss the similarities between perturbation theory and generalized van der Waals theory.

14. Equations of State from Generalized Perturbation Theory. II. The Lennard-Jones Fluid by G. M. Sowers and S. I. Sandler. Submitted for publication to *Fluid Phase Eq.*

We use perturbation theory to derive extensions of our equations of state used previously for the hard-core Lennard-Jones fluid to the more realistic soft-core Lennard-Jones fluid. We find that the use of a "hybrid" Baker-Henderson diameter (Aim and Nezbeda, 1987) for the hard sphere reference fluid leads to perturbation free energies for the soft-core Lennard-Jones fluid that are similar to the perturbation free energies for a hard-core Lennard-Jones fluid. One of the equations of state presented here is more accurate than the 33-parameter equation of Nicolas et al. (1979) for the data sets considered here, even though it has only four adjustable parameters. The other equation of state is a straightforward, theoretically based extension of a square well equation of state (Lee, Lombardo, and Sandler, 1985) to the Lennard-Jones fluid. Both equations of state can be used to correlate the phase diagrams and supercritical PVT data of noble gases and methane, and perform especially well in the correlation of saturated liquid volumes.

PUBLICATIONS OF S. I. SANDLER (1986-1990)

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2. "Chemical Engineering Education in a Changing Environment" edited by S. I. Sandler and B. A. Finlayson. Published by the Engineering Foundation and distributed by the American Institute of Chemical Engineers, 1989.

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