"Theoretical Treatment of the Bulk and Surface Properties of Fluids Containing Long, Flexible Molecules"

Application for Continuation of DOE Funding for the Period June 1, 1993 - May 31, 1994

Introduction:

This research program is designed to enhance our understanding of fluids containing long, flexible, chain-like molecules. The objective is to develop an equation of state which is capable of predicting the experimentally observed thermodynamic properties, including phase equilibria, of fluids containing chain-like molecules ranging in length from alkanes to polymers. The theories resulting from this research could eventually serve as the foundation upon which to build correlations of petroleum, natural gas, polymer solutions, polymer melts and polymer blends.

The foundation for this work is the Generalized Flory Dimer (GFD) theory, a simple, physically-intuitive approach whose touchstone is the idea that equations of state for chain-like molecules can be assembled by intelligently combining the equations of state for the segments and groups of segments comprising the chain. The Generalized Flory Dimer theory and its predecessor, the Generalized Flory (GF) theory, rely on two key concepts: the insertion probability and the osmotic equation of state. The insertion probability is the probability of inserting a single chain into a chain fluid at a given volume fraction. The osmotic equation of state is an exact equation which gives the pressure of a chain fluid in terms of the insertion probability. The approach used in the GF and GFD theories is to estimate the chain insertion probability in terms of the monomer and dimer insertion probabilities and then to substitute the estimated chain insertion probability into the osmotic equation of state to obtain the chain equation of state. Since the monomer and dimer insertion probabilities can be obtained from the monomer and dimer equations of state, the GFD approach yields an expression for the chain equation of state in terms of the monomer and dimer equations of state.

The short term objectives of our original proposal to DOE were: (1) to extend the GFD theory to fluids and fluid mixtures containing chain-like molecules which interact via square well attractions as well as hard core repulsions, and (2) to develop a new method for the computer simulation at constant chemical potential of fluids and fluid mixtures containing chain-like molecules in narrow pores. Below we give a status report which details our progress towards these objectives.

Prior to the start date on our DOE funding, we completed work on the development of the new, constant-chemical-potential computer simulation technique. This technique was designed to study the equilibrium between chain fluids in bulk and chain fluids in narrow pores (A. Yethiraj and C. K. Hall, Molec. Phys. 73, 503 (1991)). We have discontinued this project since we have already met our objective. We also extended the GFD theory to pure fluids containing square-well chain molecules prior to the start date on our DOE funding. (A. Yethiraj and C. K. Hall, J. Chem. Phys. 95, 1999, 8494 (1991).) Thus, we are now focussing on the second half of our original first objective which is to extend the GFD theory to fluid mixtures containing square well chains. Below we describe our progress thus far. We also report on some of our new projects which DOE has supported fully or in part.

Summary of Work Accomplished

1. Extending the GFD Theory to Square-Well Chain Mixtures

In order to extend the GFD theory to square-well chain mixtures, we first had to make two improvements in our original version of the GFD theory for hard chain mixtures. The first improvement was to derive a new mixture osmotic equation of state which allows species to be inserted simultaneously in proportion to their mole fractions. The motivation for this was that the original version of the GFD equation of state depended upon the order of inserting the two species into the chain mixture. The second improvement was to extend the GF theory to hard chain mixtures containing species which differ in segment size. This was done by using the Mansoori, Carnahan, Starling and Leland hard sphere mixture equation of state to determine monomer insertion probabilities. The GF equation of state resulting from these two improvements was tested by comparing the predictions for the pressure of monomer/8-mer hard chain mixtures with computer simulation results. Since the accuracy of these predictions is comparable to the accuracy of the GF equation of state for pure hard chains, we feel that we are on the right track.

We are currently attempting to derive a GFD equation of state for hard chain mixtures containing species which differ in segment size. This requires an equation of state for mixtures of hard dimers; we shall either obtain this from the literature or develop our own. Once the GFD equation of state for hard chain mixtures containing species which differ in segment size is developed, we will use this as a basis upon which to build a GFD equation of state for mixtures of square well chain molecules.

The work described above is the PhD research of Mr. John Wichert, a fourth year graduate student.

2. Virial Coefficients for Chain-like Molecules

We have been evaluating the second virial coefficient for hard-chain and square-well chain fluids using a Monte Carlo approach. The motivation for this work is that the GFD theory is least accurate at low densities. This is not unexpected since it is based on mean-field arguments which implicitly assume that the fluid is uniform. Our goal is to use second virial coefficient information as a low-density correction to the GFD equation of state.

Thus far we have completed the evaluation of second virial coefficients for hard chain fluids. Work on the second virial coefficients for square well chain fluids has also been completed; a manuscript describing these results is being prepared for publication.

This work is being done by Mr. Wichert.

3. Integral Equation Approaches to Chain Fluids

An alternative approach to the development of equations of state for chain molecules is the polymer RISM theory. We have used this approach and Monte Carlo simulation to determine the segment-segment radial distribution function for hard chain fluids. The knowledge that we have gained in this study has assisted us in the development of equations of state for square well chain fluids.

This work was performed by Mr. Arun Yethiraj, a graduate student who received his PhD in May 1991.

4. Transport Coefficients for Fluids Containing Chain-like Molecules

A new objective of our program is to determine if the Generalized Flory approach can be used in the description of the transport properties of chain fluids. As a first step, we are performing intensive Monte Carlo simulations of the self-diffusion coefficient, the shear and longitudinal viscosities, and the thermal conductivity for hard chain fluids ranging in length from 2 to 16 segments at volume fractions between 0.1 and 0.5.

This work is being performed by Mr. Steven Smith, a third-year PhD student who is being supported by a DOE Computational Sciences Graduate fellowship.

Summary of Work Planned for June 1, 1993 - May 31, 1994

During the period June 1, 1993 - May 31, 1994, we expect to complete the following tasks:

1. GFD Theory for Square Well Chain Mixtures

Since we expect to complete work on the GFD theory for hard chain mixtures this spring, we will begin work on extending this to square well chain mixtures this summer. This will involve both analytical work and computer simulation, and should be completed before the summer of '94. Once the theory is complete, we will investigate the phase change behavior of these fluid mixtures.

2. GFD Approach to a Group Contribution Method

We are now beginning work on extending the GFD theory to heteronuclear chain fluids, i.e. chains containing segments which differ in size and strength of attraction. The aim will be to use the GFD approach as a theoretical foundation for developing a better group contribution method than has heretofore been possible. Group contribution is a method in which the contributions from segments or groups of segments along the chain are judiciously combined to develop thermodynamic properties for a molecular fluid. In our opinion, a group contribution approach based on GFD would be more successful than the UNIQUAC, UNIFAC, ASOG, etc., methods, because if has a sounder foundation in the fundamentals. We base this opinion on the fact that the current group contribution methods are grounded in lattice theories, which are poor in comparison to simulation results for off-lattice chains, whereas the GFD theory is based on a continuum approach and is very good in comparison to simulation results for off-lattice chains.

3. Transport Properties for Chains

Once we have completed our simulations work on transport properties of hard chain fluids, we will wrestle with the problem of developing a theory which agrees with the simulations. Our hope is that the transport properties for a fluid of hard chain molecules can be obtained in terms of the transport properties of a fluid containing hard sphere molecules by using the building up approach of Generalized Flory theory. This work is going to be a real challenge.

Publications Resulting from DOE Sponsored Research
June 1, 1991 - February 18, 1993

Refereed Journals - Published

1. "Interaction Between Colloids in Solutions Containing Dissolved Polymer", A. Yethiraj, C. K. Hall and R. Dickman, Journal of Colloid and Interface Sci. 151, 102 (1992).
2. "Monte Carlo Simulations and Integral Equation Theory for Microscopic Correlations in Polymer Fluids", A. Yethiraj and C. K. Hall, J. Chem. Phys. 96, 797 (1992).
3. "Monte Carlo Calculation of the Osmotic Second Virial Coefficience of Off-Lattice Athermal Polymers", A. Yethiraj, K. G. Honnell and C. K. Hall, Macromolecules 25 3979 (1992).
4. "Local Composition Model for Square-Well Chains Using the Generalized Flory-Dimer Theory", C. P. Bokis, M. D. Donohue and C. K. Hall, J. Phys. Chem. 96, 11004, 1992.

Refereed Journals - In Press

1. "On Equations of State for Hard Chain Fluids", Molecular Physics (in press).
2. "Equations of State for Square Well Chain Fluids Using the Generalized Flory Approach", Fluid Phase Equilibria (in press).

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