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MOLECULAR MODELING OF SOLID-FLUID PHASE BEHAVIOR

Final Report

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ABSTRACT

This report gives a summary of the achievements under DOE contract No. DOE/ER/14150 during the period September 1, 1990 to December 31, 2007. This project was concerned with the molecular modeling of solid-fluid equilibrium. The focus was on understanding how solid-fluid and solid-solid phase behavior are related to molecular structure, and the research program made a seminal contribution in this area. The project led to 34 journal articles, including a comprehensive review article published in Advances in Chemical Physics. The DOE funding supported the work of 5 Ph.D. students, 2 M.S. students and 5 postdoctoral researchers.

1. INTRODUCTION

In this report we summarize our progress over the course of this grant in modeling the phase behavior of systems that include solid phases, using methods from statistical mechanics. This project had its origin in the realization that solid phases, while very important in petroleum and chemical processing had not featured prominently in molecular thermodynamics research. We have pursued the goal of developing a systematic understanding of how solid-fluid and solid-solid phase behavior are related to molecular structure. Substantial progress has been made, leading to some important insights into problems ranging from the origin of the odd-even trends in melting points of the n-alkanes to the stability of solid phase compounds for binary mixtures to the phase behavior of chiral molecules to the stability of natural gas hydrates.

2. SUMMARY OF RESEARCH ACHIEVEMENTS UNDER THE PROJECT

Here we give a summary of your research achievements under several subject headings accompanied by citations to the publications generated by the work.

2.1 Influence of molecular shape on solid-fluid equilibrium [1-8]

The most important contribution we made here was to establish the complete phase diagram for the hard dumbbell model[1-4]. This model of a diatomic molecule gives the simplest model of the effects of nonspherical shape. We established that this model has both orientationally ordered and orientationally disordered solid phases. Using the free energy of this model system as a reference system in a generalized van der Waals theory of the phase diagram gives a very nice qualitative description of the departures from the principle of corresponding states in the solid-fluid phase behavior of nonspherical molecules[8]. The effect of quadrupolar interactions was also investigated[5, 6, 9].

2.2 A theory of solid-fluid equilibrium for mixtures [7, 10-15]

We developed a theory of the free energy of for solid phase binary mixtures based on the cell theory[10-13, 15]. The theory was applied to hard sphere mixtures and to Lennard-Jones 12-6 mixtures and gave predictions that were generally superior to those from other methods. A very important result was establishing the stability of substitutionally ordered solid mixtures for binary hard sphere mixtures[12].

2.3 N-alkane systems [7, 16-22]

The n-alkanes are the simplest class of molecules that exhibit both the effects of nonspherical molecular shape and molecular flexibility on phase behavior. They represent model compounds for understanding solid phases of chain molecules in general and understanding the properties of n-alkanes is an important step in understanding petroleum waxes, which to a significant extent are solid mixtures of n-alkanes. We studied a flexible united atom hard sphere chain model of n-alkanes. The simplicity of this model made it possible for a study of the role of chain length, flexibility and packing on the solid-fluid phase behavior and provided an explanation for the odd-even effect in the n-alkane melting points[18, 19]. The work was extended to n-alkane mixtures[20, 22].

2.4 Aromatic systems [23-25]

Aromatic molecules represent an important class of systems for studies of solid-fluid phase equilibrium of organic molecules. In the first place there are classical industrial solid-fluid processes involving such systems and a large proportion of the systems for which experimental solid-fluid equilibrium data are available are aromatic mixtures. We have made two sets of calculations on aromatic molecules. In the first we considered the role of electrostatic interactions on the phase diagram of benzene, in addition to the effect of the molecular shape[23, 24]. In the second we studied the mixture of benzene and hexafluoro-benzene and, in particular, the stability of the congruent melting compound solid phase[25].

2.5 Water and Hydrates [26-30]

We have studied the influence of hydrogen bonding on solid-fluid equilibrium for water and for gas hydrates. For water we began by asking what is the simplest model that might generate the important features of ice-water equilibria including the increase in density of water on freezing at ambient pressure[26]. We found that a simply model of hard spheres with tetrahedrally coordinated association sites was sufficient to reproduce these important effects in the water phase diagram.

We also developed a new theoretical approach for the thermodynamics of solid phases of hydrogen bonded molecules[30]. This approach focuses principally on the orientational ordering within the hydrogen bond network that is a key feature of the low pressure freezing of water. The theory was developed in the context of the density functional formalism. The results from this theory agree quantitatively with Monte Carlo simulation results and qualitatively with experimental results.

We have made an important contribution to understanding gas hydrate stability[27-29]. Previous work on modeling gas hydrates has been built around the ideas of van der Waals and Platteuw (VDWP). In this approach statistical mechanics is treated in terms of single molecule partition functions for individual guest molecules in the cages of the hydrate structure. In our own work we have set out to place the gas hydrate problem in the same context as other problems in solid-fluid phase equilibrium and we treat the hydrate as a mixed solid phase. This frees us from the constraints imposed by the VDWP formulation at the cost of some additional computational complexity. We have focused on three aspects of the problem: i) development of a methodology for calculating phase diagrams for hydrate forming systems, including hydrate and other solid phases[27-29]; ii) investigating the underlying physics behind the phase behavior[28]; iii) developing insights into the accuracy of the VDWP theory[29].

2.6 Chiral Molecules [31]

We have made a study of the solid-fluid phase behavior of a model of chiral molecules. Our goal was to understand the origin of the stability of racemic compund solid phases. This is an important problem for chiral separations with applications in the pharmaceutical industry. In our model we consider the chirality created by four different size functional groups coordinated around a carbon atom, a very common type of chirality. As a base case we considered a five-site hard sphere model with four different sized spheres tetrahedrally coordinated around a central sphere. In the fluid phase, in common with earlier studies of similar models, we found little chiral discrimination and the systems behave as almost ideal solutions. The solid phases show much more significant effects of chirality. The solid-fluid phase diagrams for the mixtures are determined by the relative stabilities of the pure enantiomer and racemic mixture solid phases. This relative stability correlates well with the relative densities of the solid phases, as should be expected for a molecular model with only excluded volume interactions.

2.7 Crystal Nucleation [32-34]

With the substantial knowledge of solid-fluid phase diagrams for molecular models developed from our work it becomes worthwhile to investigate the mechanisms of crystallization. In the first case we have investigated crystallization mechanisms for hard spheres and hard sphere mixtures. In our work we have taken two approaches. We have studied the dynamics of hard sphere crystallization using an isobaric molecular dynamics technique that we developed for quenching hard sphere fluids to supersaturated states[32, 33]. We have also used biased Monte Carlo methods to directly sample the properties of crystal nuclei[34]. As part of this work we demonstrated the role of compositional changes between phases in the crystallization mechanism for mixtures and solutions.

3. CONTRIBUTIONS TO THE DEVELOPMENT OF HUMAN RESOURCES

Ph.D. students:

Xavier Cottin, Anthony Malanoski, Joseph Schroer, Maohua Cao, Monica Navarro

M.S. Students:

Eleanor Paras, Wei-Ning Shen

Postdoctoral Associates:

Carlos Vega, Thomas Gruhn, Hyung-June Woo, Scott Wierzchowski, Sudeep Punnathanam

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