Final Report

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Summary

This award supports collaborative research between Kansas State University and Sandia National Laboratories. The objectives of this work are to develop new methodologies for fast and accurate simulations and apply simulations to various problems of interest to DOE. The success of this work will address several deficiencies in the Sandia's capabilities in the area of molecular simulations. In addition, it provides educational opportunities for students and will enhance the science and technology capabilities at Kansas through partnership with the national laboratories.

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Publications

1. Q. Zhang, J. Zheng, A. Shevade, L. Zhang, S.H. Gehrke, G.S. Heffelfinger, and S. Jiang, Transport Diffusion of Liquid Water and Methanol Through Membranes, *Journal of Chemical Physics*, **117**, 808 (2002).
2. J. Zheng, Ramkumar Balasundaram, Stevin H. Gehrke, Grant S. Heffelfinger, William A. Goddard III, and Shaoyi Jiang, Cell Multipole Method for Molecular Simulations in Bulk and Confined Systems, Submitted to the *Journal of Chemical Chemistry*, 2002.
3. L. Zhang, R. Balasundaram, S.H. Gehrke, and S. Jiang, Nonequilibrium Molecular Dynamics Simulations of Confined Fluids in Contact with the Bulk, *Journal of Chemical Physics*, **114**, 6869-6877 (2001).
4. A. Shevade, J. Zhou, M. Zin and S. Jiang, Phase Behavior of Mixed Self-Assembled Monolayers of Alkanethiols on Au(111): A Configurational-Bias Monte Carlo Simulation Study, *Langmuir*, **24**, 7566-7572 (2001).
5. A. Sheveda, S. Jiang, and K.E. Gubbins, Adsorption of Water-Methanol Mixtures in Carbon and Aluminosilicate Pores: A Molecular Simulation Study, *Molecular Physics*, **97**, 1139-1148 (1999).

Presentations:

1. Q. Zhang, J. Zheng, A. Shevade, L. Zhang, S.H. Gehrke, G.S. Heffelfinger, and S. Jiang, Transport Diffusion of Liquid Water and Methanol Through Membranes, AIChE Meeting, Los Angeles, CA, November 2000.
2. J. Zheng, Q. Zhang, A. Shevade, L. Zhang, S.H. Gehrke, G.S. Heffelfinger, and S. Jiang, Transport Diffusion of Liquid Water and Methanol Through Membranes, AIChE Meeting, Reno, NV, November 2001.
3. J. Zheng, Ramkumar Balasundaram, Stevin H. Gehrke, Grant S. Heffelfinger, William A. Goddard III, and Shaoyi Jiang, Cell Multipole Method for Molecular Simulations in Bulk and Confined Systems, AIChE Meeting, Reno, NV, November 2001.
4. L. Zhang, R. Balasundaram, S.H. Gehrke, and S. Jiang, Nonequilibrium Molecular Dynamics Simulations of Confined Fluids in Contact with the Bulk, AIChE Annual Meeting, Dallas, TX, November 1999.
5. A. Shevade, J. Zhou, M. Zin and S. Jiang, Phase Behavior of Mixed Self-Assembled Monolayers of Alkanethiols on Au(111): A Configurational-Bias Monte Carlo Simulation Study, AIChE Meeting, Los Angeles, CA, November 2000.
6. A. Sheveda, S. Jiang, and K.E. Gubbins, Adsorption of Water-Methanol Mixtures in Carbon and Aluminosilicate Pores: A Molecular Simulation Study, AIChE Annual Meeting, Dallas, TX, November 1999.

Theses:

1. Q. Zhang, Transport Diffusion of Liquid Water and Methanol Through Membranes, Department of Chemical Engineering, KSU, Dec. 2000.
2. J. Zheng, Cell Multipole Method for Molecular Simulations in Bulk and Confined Systems, Department of Chemical Engineering, KSU, Dec. 2000.
3. A. Shevade, Adsorption of Complex Fluid Mixtures by Molecular Simulations, Department of Chemical Engineering, KSU, May, 2001.
4. L. Zhang, Molecular Simulation and Experimental Studies of Thin Films on Solid Surfaces, Department of Chemical Engineering, KSU, August, 2001.

Results

We reported five projects relating to this grant with the first two as the main projects. The first two projects were mainly funded through this grant while another three projects were partially supported through this grant. All these projects focus on the main theme of this grant - molecular simulations of complex fluids in confined geometries. Key results and their relevance to DoE interests are reported and discussed in the following.

Project 1. Implementation and Extension of the Cell-Multipole Method (J. Zheng)

One of the bottlenecks in molecular simulations is to treat large systems involving electrostatic interactions. Computational time in conventional molecular simulation methods scales with $O(N^2)$, where N is the number of atoms. The conventional approach, such as the Ewald sum is computationally very expensive. The cell-multipole method (CMM) is an effective method to handle long-range forces in molecular dynamics (MD)

simulations of three-dimensional systems with significantly low computational time and good accuracy. With the emergence of the CMM and massively parallel supercomputers, simulations of 10-million atoms have been performed. In the CMM, computational speed scales as approximately number of particles N instead of N^2 in traditional MD simulations. Due to the complexity of the method, few research groups have implemented the method. In this work, the CMM was first implemented for MD simulations of three-dimensional systems. The optimal hierarchy cell level and the algorithm for Taylor expansion were recommended for fast and accurate MD simulations of three-dimensional (3D) systems. Simulation results show that the level of the cell hierarchy tree (or average atom occupancy) in the deepest cell is a key factor in determining computational time and accuracy. The optimal number of atoms in the deepest cell is 3~10. The complex Taylor expansion algorithm is faster than the simple one without losing its accuracy. Under the optimal conditions, average error in total potential energy is less than 1% and RMS force is about 0.015 when compared with the Ewald summation method while computational efficiency improves significantly. Results also show that computational time of the CMM method scales almost linearly with the number of atoms in the cell for large systems.

The CMM method was extended to confined systems from bulk systems in MD simulations *for the first time*, which is very important for condensed matter physics problems. Potential energies calculated from our CMM2D program are consistent with those from the EW3D technique applied to quasi-2D systems by adding a sufficiently large vacuum space on the top of the slab. The difference in total potential energy between these two methods is ~1%. Moreover, the CMM method was applied to GCMC simulations for both 3D and 2D systems for the first time. Our CMM code is readily incorporated in the GCMC, MD, and grand canonical molecule simulation (GCMD) programs for applications, such as studies of adsorption and diffusion in pores. For a system of ~3500 particles, for example, our results show that the CMM method will speed up calculations by 30-50 times.

This capacity is important to our collaborators at Sandia National Laboratories to address their deficiencies in their simulations.

Project 2. Transport Diffusion through Nano-Scale Pores by DCV-GCMD (Q. Zhang)

Membrane separation of mixtures is currently a subject of great interest. Many new processes emerge in the recent years for liquid separation. Molecular-level understanding of the interactions between complex fluid molecules and surfaces plays a critical role in membrane separation. Such interactions are governed by a number of parameters, such as fluid-fluid interactions (e.g., relative contribution from dispersion and hydrogen bonding), solid-fluid interactions (e.g., hydrophilic or hydrophobic nature of the surface), pore geometries (e.g., shape and size), and operating conditions (e.g., temperature and pressure). For designing an appropriate membrane for a separation process, it is important to determine and control the surface properties of the membrane at the molecular level.

In this work, we studies transport diffusion of liquid water and methanol through nano-scale channels consisting of two Au(111) surfaces covered by self-assembled monolayers (SAMs) under a chemical potential gradient using the dual-control volume grand canonical ensemble molecular dynamics simulation (DCV-GCMD) technique. Methanol and water are selected as model fluid molecules because water represents a strongly polar molecule

while methanol is intermediate between nonpolar and strongly polar molecules. Surface hydrophobicity is adjusted by varying the terminal group of $-\text{CH}_3$ (hydrophobic) or $-\text{OH}$ (hydrophilic) of SAMs. Simulations in this work was set up in such a way to mimic a pervaporation process and to take into account all three important factors in membrane separation (i.e., adsorption/desorption, diffusion, and pore entrance effects) simultaneously. While DCV-GCMD simulations have been used to study gases or gaseous mixtures over the last few years, there are few DCV-GCMD simulation studies of membrane separation of liquid mixtures. Science and engineering for membrane separation of liquid mixtures are quite different from gaseous mixtures due to much more complex interactions involved. In this work, we observed for the first time from simulations the convex and concave interfaces of fluids transporting across the slit pores under a chemical potential gradient. The nature of the interfaces depends on the fluid-fluid and fluid-surface interactions. Water forms concave and convex interfaces in hydrophobic and hydrophilic pores, respectively. Methanol with stronger dispersion and weaker hydrogen bonding forms the similar interface to water, but with less clear interfaces. Simulation results show that methanol has a much higher flux than that of water in the hydrophobic pore. Thus, it is expected that the separation of water-methanol mixtures could occur in hydrophobic pores.

This work will have a broader impact on (a) energy-efficient membrane separation and nanofiltration, (b) membrane separation for those mixtures (e.g., racemic and near-boiling point mixtures) difficult to separate with conventional methods, (c) environmental remediation, (d) nanofluidic flow in chemical and biological sensing, (e) ion diffusion through ion channels under ion concentration gradient of DoE interest.

Project 3. Rheological Properties of Confined Fluids by NEMD (L. Zhang)

A non-equilibrium molecular dynamics (MD) simulation study is reported of the structural and rheological properties of confined n-decane between two Au(111) surfaces in contact with its bulk under constant normal loads or constant heights. In the constant-load MD simulations, it was observed that fluid molecules were squeezed out of the pore continuously in a single simulation upon compression, whereas fluid molecules in the bulk were soaked into the pore when applied normal load was released. Pore separation depends on bulk pressure under the same normal load and approaches a steady value as normal load increases. In the constant-height simulations, density, velocity, and orientational profiles of the confined film were accumulated along the Z (perpendicular to the walls) and Y (parallel to the walls and finite due to the bulk) directions. These distributions are not uniform not only along the Z direction but also along the Y direction, particularly for weak fluid-wall interactions. The shear-thinning behavior and 'slip' boundary conditions were also studied in this work. Even though the shear thinning behavior was reported by several studies before, the number of particles was fixed and the bulk condition was unknown in those simulations. The simulation geometry employed in this work is closer to that of surface force apparatus (SFA) experiments and of engine lubricating systems where confined liquid is in contact with its bulk.

This work will have impact on the development of microelectromechanical systems (MEMS) currently going on at Sandia National Laboratories, for which the understanding of confined fluids at dynamic interfaces is very important.

Project 4. Adsorption of Complex Mixtures in Micropores by GCMC (A. Shevade)

We report a theoretical study of the adsorption behavior of water-methanol mixtures in slit activated carbon micropores. The adsorption isotherms are obtained for a pore of width 2 nm at a temperature of 298 K from grand canonical ensemble Monte Carlo simulations. The water molecules are modeled using the four point transferable intermolecular potential functions TIP4P and methanol by the optimized potentials for liquid simulations OPLS. Carboxyl -COOH groups are used as active sites on a structured carbon surface. The effect of the relative contributions from dispersion and hydrogen bonding interactions of adsorbates, and of the chemical activation of adsorbents on adsorption behavior is investigated. The adsorption of the mixture components in activated carbon pores occurs by continuous filling, without the sharp capillary condensation observed in graphite pores. Water is preferentially adsorbed over methanol in activated carbon pores for a wide range of pressures, except at lower pressures. The hydrophilic nature of activated carbon pores results in the complexation of both water and methanol molecules with the active sites on the surfaces, leading to bulklike water behavior over the entire pore width. Solvation forces are also calculated as a function of pore size. The negative values found for the solvation force for all pore sizes reflect the hydrophilic interactions of the mixtures with the activated carbon surfaces.

This work lays down foundation for the Project 2 in this report - the study of the transport diffusion and membrane separation of fluids through nano-scale fluidic channels. DCV-GCMD simulation work in the Project 2 is the direct extension of GCMC simulation work in this project.

Project 5. Phase Behavior of Mixed SAMs by Configurational-Bias MC (A. Shevade)

We report a configurational-bias Monte Carlo simulation study to investigate the effect of chain length, system size, and temperature on the preferential adsorption and phase behavior of mixed self-assembled monolayers (SAMs) of alkanethiols on Au(111). Simulations were performed in both semigrand canonical and canonical ensembles. The semigrand canonical simulations were carried out at conditions corresponding to low concentration of $\text{HS}(\text{CH}_2)_8\text{CH}_3$ - $\text{HS}(\text{CH}_2)_9\text{CH}_3$ and $\text{HS}(\text{CH}_2)_8\text{CH}_3$ - $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$ alkanethiol mixtures in solutions at 300 and 373 K. The canonical ensemble simulations were performed at 300 K for a fixed composition of $\text{HS}(\text{CH}_2)_9\text{CH}_3$ - $\text{HS}(\text{CH}_2)_{9+n}\text{CH}_3$ mixed SAMs, where $n = 1, 2, \dots, 10$. Continuous and discrete models were used in these simulations for describing the alkanethiol chains, and an analytical potential was used to model their interactions with the gold surface. Results show the preferential adsorption of long chains on the surface over in the solution and the occurrence of phase segregation when the two components in the mixed SAMs differ by more than three carbon atoms at a fixed surface composition (1:1). Calculated translational, orientational, and conformational orders of the mixed SAMs reveal a more pseudocrystalline structure consisting of closely packed and inclined chains at 300 K than at 373 K. The effect of system size on various properties was also studied.

This work lays down foundation for the Project 2 in this report - the study of the transport diffusion and membrane separation of fluids through nano-scale fluidic channels. Mixed SAMs of different terminal groups were used for surface modification for the Project 2.