

2009 MIDWEST THERMODYNAMICS AND STATISTICAL MECHANICS CONFERENCE
WAYNE STATE UNIVERSITY, DETROIT, MI 48202

Start	End	Speaker	Title
10:00:00 AM	10:45:00 AM	Jennifer Wilcox	Minimizing Environmental Impacts of Coal-based Energy Generation
10:45:00 AM	11:05:00 AM	Trinh Train	Molecular simulation study of CO ₂ selectively captured from pre- and post-combustions mixture using latent porous crystal copper-organic framework adsorbents
11:05:00 AM	11:25:00 AM	Dong-Hee Lim	Density functional theory studies on the relative reactivity of chloroethenes on Fe(110)
11:25:00 AM	11:45:00 AM	Susan Duncan	Folding of lipid monolayers containing lung surfactant proteins SP-B and SP-C studies via coarse-grained molecular dynamics simulations
11:45:00 AM	12:05:00 PM	Zeena Issa	Ca ²⁺ -dimethylphosphate complex formation: insights into membrane fusion
12:05:00 PM	12:25:00 PM	John Stubbs	Modeling heterogeneous melting equilibria of surface-immobilized DNA using Monte Carlo molecular simulation
12:25:00 PM	1:55:00 PM	LUNCH	
1:55:00 PM	2:15:00 PM	Huajun Yuan	Gas permeation studies of biological membrane using coarse-grained molecular dynamics simulations method
2:15:00 PM	2:35:00 PM	Nikolai Priezjev	Shear rate threshold for the boundary slip in dense polymer films
2:35:00 PM	2:55:00 PM	Adam Burley	Toward a fundamental understanding of bubble nucleation in polymer foaming
2:55:00 PM	3:15:00 PM	Katie Maerzke	TraPPE-UA force field for acrylates and prediction of Hildebrand solubility parameters
3:15:00 PM	3:35:00 PM	Abu Hassan	Vapor pressures of oxygenated compounds: SPEAD Parameters and applications
3:35:00 PM	3:55:00 PM	Alvaro Orjuela	Phase equilibria for mixtures containing diethyl succinate
3:55:00 PM	4:15:00 PM	BREAK	
4:15:00 PM	4:35:00 PM	Ganesh Kamath	All-atom force field for the prediction of vapor-liquid equilibria and interfacial properties of HFA134a
4:35:00 PM	4:55:00 PM	Hye Min Kim	Development of a molecular based computational approach to fluid-phase equations of state
4:55:00 PM	5:15:00 PM	Ehasn Moharreri	Implications of compressed liquid density for intermolecular potential models
5:15:00 PM	5:35:00 PM	Katherine Schadel	Improving the efficiency of virial-coefficient calculations: a hybrid approach employing integral-equation theories and Mayer-sampling Monte Carlo
5:35:00 PM	5:55:00 PM	Jake Rafferty	Understanding shape selectivity of PAHs in reversed-phase liquid chromatography via Monte Carlo simulations
Wednesday			
9:00:00 AM	9:45:00 AM	Krista Walton	Nanostructure Inorganic-organic hybrids: engineering a new class of porous materials
9:45:00 AM	10:05:00 AM	Andrew Paluch	An adaptable method to calculate the solubility limit of solids by molecular simulation
10:05:00 AM	10:25:00 AM	Marcos Perez-Blanco	Molecular dynamics simulations of CO ₂ at an ionic liquid interface: adsorption ordering and interfacial crossing
10:25:00 AM	10:45:00 AM	Michael Sellers	Atomistic modeling of tin surface and grain boundary diffusion
10:45:00 AM	11:05:00 AM	BREAK	
11:05:00 AM	11:25:00 AM	Denise Ford	Molecular dynamics studies of n-alkane and benzene self-diffusion in the metal-organic framework IRMOF-1
11:25:00 AM	11:45:00 AM	Eric Grzelak	How does nanoscale roughness influence wetting behavior?
11:45:00 AM	12:05:00 PM	Ravi Chopra	Relationship between the thermodynamics and dynamics of a molecular fluid
12:05:00 PM	12:25:00 PM	Liqun Zhang	Transport properties investigation on generic species in silica melts using molecular simulation
12:25:00 PM	1:55:00 PM	LUNCH	
1:55:00 PM	2:15:00 PM	Amir Vahid	Asymptotic trends in athermal mixture entropy in the long chain limit
2:15:00 PM	2:35:00 PM	Tai Boon Tan	Consideration of the entropy in the free-energy calculation for the stable crystalline polymorphs
2:35:00 PM	2:45:00 PM	Jeffrey Potoff	Concluding remarks and departure

INVITED TALK

MINIMIZING ENVIRONMENTAL IMPACTS OF COAL-BASED ENERGY GENERATION

Jennifer Wilcox, Ph.D., Assistant Professor

Department of Energy Resources Engineering, Stanford University

With the United States generating over half of its electricity from coal combustion, and with more than five hundred 500 megawatt, coal-fired power plants existing in the United States with an average age of 35 years, coal as a significant future energy source is inevitable. To minimize the environmental impacts of coal burning and to increase the sustainability of this abundant resource, advancing “clean coal” technologies is imperative. Worldwide, the primary power-generating coal-based technology is pulverized coal combustion. Within the past two decades there have been great strides in reducing harmful emissions associated with this technology, specifically involving the reduction of pollutants such as SO_x , NO_x , particulates, and mercury. In addition to the release of these pollutants, coal burning is the largest contributor to global CO_2 emissions from energy generation; therefore, in the production of new coal-based power-generating technologies, e.g., coal gasification, minimizing these environmental hazards must be taken into consideration.

In particular, a complete homogeneous kinetic model for mercury oxidation generated from *ab initio*-based rate constant data was developed and validated through focused experiments which included simulating flue gases through methane combustion. It has been concluded that the majority of mercury oxidation occurs heterogeneously, likely via unburned carbon. Knowledge of mercury’s oxidation pathway has also led to the design of a nanostructured sorbent material for its subsequent capture. This new palladium-based material that was generated in our lab has been computationally designed using density functional theory-based energetics obtained from VASP (Vienna *ab initio* Simulation Package), which allow for mercury capture at the higher temperatures, 260-315 °C, typical of coal gasification applications. We discovered that the addition of small amounts of gold, i.e., 12.5%, created more favorable hcp three-fold palladium adsorption sites for mercury binding. In contrast to this unique application, palladium-based materials have been modeled for their solubility, diffusivity, and subsequent permeability of hydrogen to be applied to separation applications. The addition of a membrane reactor utilizing this technology will be useful for the separation of CO_2 in a syngas stream from coal gasification processes. In total, the overall motivation behind these efforts has been to minimize the environmental impacts of energy generation from coal-based technologies.

MOLECULAR SIMULATION STUDY OF CO₂ SELECTIVELY CAPTURE FROM PRE- AND POST-COMBUSTION MIXTURE USING LATENT POROUS CRYSTAL COPPER-ORGANIC FRAMEWORK ADSORBENTS

Trinh D. Tran¹, Christian M. Lastoskie¹ and Katsumi Kaneko²

¹Department of Civil & Environmental Engineering, University of Michigan, Ann Arbor,
USA 48109-2125

²Department of Chemistry, Chiba University, Chiba, JAPAN 263-8522

. Carbon capture and storage (CCS) is a promising strategy to address anthropogenic CO₂ emissions. CO₂ capture at the source is conventionally accomplished using chemical absorption with amine solvents. Recovery of the CO₂ and solvent is energy-intensive, however, and problematic due to corrosion and other environmental hazards. Porous materials are thus sought for cost-effective CO₂ capture using physical adsorption at power plants utilizing coal and natural gas.

Latent porous crystal metal-organic frameworks (MOFs) are an intriguing class of inexpensive adsorbents for high-capacity, high-selectivity capture of CO₂ from flue gas. MOF architectures are readily modified to yield porous two- and three-dimensional networks with wide-ranging dimensions. Certain copper-based MOFs exhibit highly selective “gated” CO₂ adsorption and desorption at temperatures and pressures relevant for flue gas treatment. We report molecular simulation results for CO₂ isotherms and isosteric heats of adsorption on copper-organic framework materials. Sorption selectivities for CO₂/N₂ and CO₂/H₂ mixtures in excess of 600 are observed at conditions representative of post-combustion flue gas in conventional power plant and pre-combustion syngas mixtures from Integrated Gasification Combined Cycle plant. The simulated selectivities of mixture are found to be comparable to the Ideal Adsorption Solution Theory (IAST) estimation based on pure isotherms of CO₂ and H₂.

DENSITY FUNCTIONAL THEORY STUDIES ON THE RELATIVE REACTIVITY OF CHLOROETHENES ON Fe(110)

Dong-Hee Lim and Christian M. Lastoskie

Department of Civil and Environmental Engineering, University of Michigan,
1351 Beal Avenue, Ann Arbor, Michigan 48109-2125, USA.

Email Address: Dong-Hee Lim (limkr@umich.edu),
Christian M. Lastoskie (cmlasto@umich.edu)

ABSTRACT

The adsorption and dissociation of perchloroethene (PCE), trichloroethene (TCE), and *cis*-dichloroethene (*cis*-DCE) on Fe(110) were investigated using density functional theory (DFT) and the generalized gradient approximation (GGA) to evaluate hypotheses concerning the relative reactivity of these compounds on zerovalent iron. Of adsorption sites investigated, an atop site, where the chloroethene C=C bond straddles a surface iron atom, was the most energetically favorable site for the adsorption of all three chloroethenes. Electronic structure and property analyses provide an indication of the extent of sp^2 - sp^3 hybridization. The strong hybridization of the π -bonding orbital between the chloroethene C=C bond and the iron surface suggests that adsorbed chloroethenes are strongly activated on Fe(110) and are likely precursors for subsequent chloroethene dissociation on the Fe surface. The climbing image nudged elastic band (CI-NEB) method was employed to calculate activation energies of the chloroethene compounds according to the principal dechlorination mechanism of β -elimination. Chloroethenes with a higher number of chlorine atoms were found to have lower activation energies than those with fewer chlorine atoms. The activation energies of PCE, TCE, and *cis*-DCE at their rate-limiting steps in the gas phase are 9.9, 16.6, and 23.8 kJ/mol, respectively. Energy profiles along the reaction coordinate for the dechlorination paths are presented. The relative reactivity order among the chloroethenes was found to be PCE > TCE > *cis*-DCE.

FOLDING OF LIPID MONOLAYERS CONTAINING LUNG SURFACTANT PROTEINS SP-B₁₋₂₅ AND SP-C STUDIED VIA COARSE-GRAINED MOLECULAR DYNAMICS SIMULATIONS.

Susan Duncan and Ronald G. Larson

Department of Chemical Engineering, University of Michigan
Ann Arbor, MI 48109-2136

To explore the role of lung surfactant proteins SP-B and SP-C in storing and redelivering lipid from lipid monolayers during the compression and re-expansion occurring in lungs during breathing, we simulate the folding of lipid monolayers with and without these proteins. We utilize the recently developed MARTINI coarse-grained force field to simulate monolayers containing pure dipalmitoylphosphatidylcholine (DPPC) and DPPC mixed with palmitoyloleoylphosphatidylglycerol (POPG), palmitic acid (PA), and/or peptides. The peptides considered include the 25-residue N-terminal fragment of SP-B (SP-B₁₋₂₅), SP-C, and several SP-B₁₋₂₅ mutants in which charged and hydrophilic residues are replaced by hydrophobic ones, or vice versa. We find that folding will occur if the monolayer is sufficiently fluidized. The addition of peptide or POPG to the DPPC monolayer has a fluidizing effect, which assists monolayer folding. In contrast, the addition of PA has a condensing affect. In some cases, peptide aggregation nucleates a defect in the monolayer, further assisting the folding process. However, we find that if the number of hydrophobic residues is decreased significantly monolayer folding does not occur. Also, we observe that the system-size affects the folding mechanism: if the system size is large enough, then peptide-containing monolayers can fold without the formation of a peptide aggregate.

Ca²⁺-DIMETHYLPHOSPHATE COMPLEX FORMATION: INSIGHTS INTO MEMBRANE FUSION

*Zeena K. Issa, Charles Manke, Bhanu Jena, and Jeffrey J. Potoff,
Department of Chemical Engineering,
Wayne State University, 5050 Anthony Wayne Dr. Detroit, MI 48202*

Prior x-ray diffraction, light scattering, photon correlation spectroscopy, and atomic force microscopy experiments suggest that SNARE-induced membrane fusion in cells proceeds as a result of calcium bridging opposing bilayers, which leads to the release of water from hydrated Ca²⁺ ions as well as the loosely coordinated water at PO-lipid head groups [1]. It is hypothesized that the combined effect of local dehydration of phosphate head groups, as a result of Ca²⁺ bridging, leads to a destabilization of lipid bilayers and resulting membrane fusion. This hypothesis was tested in the current study by performing atomistic molecular dynamic simulations in the isobaric-isothermal ensemble on dimethylphosphate anions (DMP⁻) and Ca²⁺ in water at 298 K and 1.01 bar. Examination of molecular configurations obtained from the molecular dynamics simulations reveals extensive formation of DMP-Ca-DMP bridges. It was also observed that two Ca²⁺ are able to combine with two DMP⁻ to form a “ring complex” by bridging the anionic oxygens in DMP⁻ [2]. Average distances between Ca²⁺ and the anionic oxygens of bridged DMP⁻ are calculated as 2.92 Å, which is in close agreement with the 2.8 Å separation between vesicles reported by light scattering experiments of tv-SNARE induced membrane fusion [1]. Simulations also show that upon calcium bridging to DMP⁻, water is removed from the anionic oxygens of DMP⁻ as well as the hydrated calcium ions.

Additional molecular dynamics simulations are performed to determine if other divalent cations, such as Mg²⁺ and Ba²⁺, can also self-assemble with DMP⁻. Simulations of Mg²⁺ show significantly fewer incidents of cation binding to DMP⁻ and no ring complexes are observed. Simulations of Ba²⁺ show no incidents of binding dimethylphosphate oxygens. The hypothesis that Ca²⁺ can bridge the head groups of apposed bilayers is tested with NPT molecular dynamics simulations of apposed bilayers containing either pure DMPC bilayers or mixed DMPC/POPS bilayers composed of 128 lipids of different compositions. Simulations were performed with a 0.3 nm initial spacing between the bilayers, corresponding to the closet approach detected by light scattering experiments of tv-SNARE mediated vesicle fusion. Calcium bridging of apposing bilayers was observed after 10 ns. Additionally, simulations show structural changes in the lipid bilayers as well as the water molecules associated with the lipids upon calcium bridging the head groups.

[1] Jeremic, A., Cho, W-J., Jena, B.; *J. Biol. Phys. & Chem.* 4:139-142 (2004)

[2] Potoff, J., Issa, Z., Manke, C., Jena, B., *Cell Biol. Int.* 32:361-366 (2008)

MODELING HETEROGENEOUS MELTING EQUILIBRIA OF SURFACE-IMMOBILIZED DNA USING MONTE CARLO MOLECULAR SIMULATION

Nicholas B. Tito and John M. Stubbs
Department of Chemistry and Physics
The University of New England, Biddeford, ME 04005

A new coarse-grained model for DNA is applied to denaturation (melting) equilibria for short sequences of 10 bases. Predicted perfect match and single mutation melting temperatures agree to within 5 K with empirical predictions fit to experimental data. Heterogeneous melting equilibria was then investigated by fixing one strand at a hard surface where the destabilizing nature of the surface was minimized with the use of a covalently-linked spacer between the surface and immobilized strand. Additionally, the effect of a mutation is lessened when it is located at the surface-bound end.

GAS PERMEATION STUDIES OF BIOLOGICAL MEMBRANE USING COURSE-GRAINED MOLECULAR DYNAMICS SIMULATIONS METHOD

Huajun Yuan, Cynthia J. Jameson, Sohail Murad
Department of Chemical Engineering, University of Illinois at Chicago
810 South Clinton Street, Chicago, IL 60607

Molecular transport through biological membranes occurs in a range of interesting processes. To understand basic permeation functions of a biomembrane, we have carried out molecular dynamics simulations using dipalmitoylphosphatidylcholine (DPPC) as the bilayer membrane. By reducing the degrees of freedom and employing suitable potentials, a coarse-grained model can provide direct insight into collective phenomena in biological membranes at longer time and length scales. We used a coarse-grained model for DPPC bilayer which had been parameterized to mimic fundamental structural properties. The permeation process of small molecules such as Xe, O₂ and CO₂ through the lipid bilayers was investigated. The density profiles and the local diffusion coefficients of the permeating gases across the bilayer membranes are obtained from the molecular dynamics simulations. By studying gas molecules permeating through the lipid bilayer, we obtain an improved understanding of transport processes across membranes in biological systems. We also explored gas permeation assisted by antibiotics channels and conditions that will give better control of the gas permeability and the possibility of membrane applications in environment friendly separation processes. The simulation results can be further compared with experiments measurement in the future so that we can fine-tune the parameters to get better permeability evaluations.

SHEAR RATE THRESHOLD FOR THE BOUNDARY SLIP IN DENSE POLYMER FILMS

Nikolai V. Priezjev

Dept. of Mechanical Engineering, Michigan State University
2465 Engineering Building, East Lansing, MI 48824-1226

Movies and preprints at <http://www.egr.msu.edu/~priezjev>

A brief overview of the slip phenomena at liquid/solid interfaces and its relation to microfluidics will be provided. In this talk we describe our recent results on the dynamic behavior of the slip length in thin polymer films confined between atomically smooth surfaces using molecular dynamics simulations. The polymer melt is modeled as a collection of bead-spring chains of 20 Lennard-Jones monomers interacting through the FENE potential. We found that at high melt densities and low shear rates the fluid velocity profiles acquire a pronounced curvature near the walls and the slip length is approximately equal to the thickness of the immobile boundary layer. The linearity of the fluid velocity profiles is restored at higher shear rates where the slip length increases rapidly as a function of shear rate. The gradual transition from no-slip to steady-state slip flow is associated with faster relaxation of the polymer chains near the wall evaluated from decay of the time autocorrelation function of the first normal mode. We will show that the friction coefficient at the interface between a polymer melt and a solid wall follows power law decay as a function of the slip velocity. At large slip velocities the friction coefficient is determined by the product of the value of surface induced peak in the structure factor and the contact density of the first fluid layer near the solid wall. A relation to recent slip flow experiments is discussed.

TOWARD A FUNDAMENTAL UNDERSTANDING OF BUBBLE NUCLEATION IN POLYMER FOAMING

Adam Burley, Isamu Kusaka^{*}, David Tomasko, Kurt Koelling

Department of Chemical and Biomolecular Engineering, The Ohio State University
Columbus, OH 43210

burley.27@osu.edu, kusaka.2@osu.edu, tomasko.1@osu.edu, koelling.1@osu.edu

*corresponding author

Polymer foaming is an extremely important industrial process that is used to produce a variety of products including insulation, cushioning, and lightweight materials. However, a fundamental understanding of the link between these systems' macroscopic phenomena and their microstructure is largely absent. This project aims to bridge this gap.

The use of polymer density functional theory (PDFT) is of key importance to the development of this work. A particular formulation that utilizes the statistical associating fluid theory equation of state (SAFT EOS) has been demonstrated to be able to handle both bulk and interfacial properties. It is first necessary to properly capture the phase behavior of these systems. To that end, current work is aimed at determining proper parameter values for components of interest. In particular, fitting for the homologous alkane series is being undertaken, with a view toward determining the trend of each parameter's values with increasing molecular weight. In this way, parameter values for high molecular weight polymers can be accurately predicted.

The eventual goal of this project is to study bubble nucleation and interfacial phenomena, many aspects of which are not easily accessible with experimental methods. Developing a scaling approach that uses reasonably well-understood phase diagrams to inform about less clear nucleation behavior is also of interest.

TRAPPE-UA FORCE FIELD FOR ACRYLATES AND PREDICTION OF HILDEBRAND SOLUBILITY PARAMETERS

Katie A. Maerzke,¹ John L. Lewin,^{1,2} Nathan E. Schultz,³ Richard B. Ross,³ and J. Ilja Siepmann^{1*}

(1) Departments of Chemistry and of Chemical Engineering and Materials Science, University of Minnesota, 207 Pleasant Street SE, Minneapolis, MN 55455

(2) Department of Chemistry, Augsburg College, 2211 Riverside Ave, Minneapolis, MN 55455

(3) Corporate Research Materials Laboratory, 201-2E-23, 3M Company, St. Paul, MN 55144

(*) Corresponding author. Email: siepmann@umn.edu

Acrylate-based polymers are used in numerous industrial applications, such as films and adhesives, and their properties can be tailored through blending with additives, such as plasticizers. The transferable potentials for phase equilibria-united atom (TraPPE-UA) force field is extended here to acrylates and methacrylates. New parameters are fit to the liquid density, normal boiling point, and saturated vapor pressure using Gibbs ensemble Monte Carlo simulations of methyl acrylate and methyl methacrylate. Excellent agreement with experiment was obtained for other monomers, with average errors in the liquid density and normal boiling point of ~1%. The TraPPE-UA force field accurately predicts solubility parameters for monomers with up to ten carbon atoms in the alkyl side chain, as well as mixtures of monomers. In addition, simulations of binary vapor-liquid equilibria for the mixtures methyl acrylate/1-butanol and methyl acrylate/*n*-decane show that the TraPPE-UA acrylate force field performs well for mixtures with both polar and non-polar molecules. These mixture simulations exhibit structural microheterogeneity in the liquid phase.

VAPOR PRESSURES OF OXYGENATED COMPOUNDS: SPEAD PARAMETERS AND APPLICATIONS

Abu M. Hassan¹, Dung T. Vu², Damien Bernard-Brunel¹, J. Richard Elliott³, Dennis J. Miller¹
and Carl T. Lira^{1,C}

1. *Department of Chemical Engineering and Materials Science,
Michigan State University, East Lansing, MI, U.S.A.*
2. *MBI International, Lansing, MI, U.S.A.*
3. *Department of Chemical and Biomolecular Engineering,
University of Akron, Akron, OH, U.S.A.*

Vapor pressure is an important property of a fuel because vaporization affects ignition and combustion inside an engine. For emerging biofuel components, vapor pressure data are scarce. In this work, we extend the SPEAD molecular dynamics method (Baskaya, F. S.; Gray, N. H.; et al., *Fluid Phase Equil.* 2005, 236, 42-52) to predict the vapor pressures of oxygenated compounds like esters, ethers, and alcohols. Starting with groups present in alkanes, we discuss parameters for the functional groups present in the compounds mentioned above. We demonstrate transferability of parameters and present the vapor pressure predictions for cyclic acetals which have multiple functional groups. We discuss modifications that permit highly accurate density predictions. We also discuss the use of vapor pressure curves obtained from SPEAD to predict important fuel properties like flash point (lowest temperature at which fuel vapors form an ignitable mixture with air) and boiling curve. Selected comparisons are made with the TRAPPE model.

C. Corresponding Author and Speaker

Keywords: vapor pressure, simulation, biofuel.

Submitted to: 2009 Midwest Thermodynamics and Statistical Mechanics Conference

PHASE EQUILIBRIA FOR MIXTURES CONTAINING DIETHYL SUCCINATE

Alvaro Orjuela^{1,2,S}, Abraham J. Yanez¹, Peter K. Rossman¹, Dung T. Vu³, Carl T. Lira^{1,C}, and
Dennis J. Miller¹

(1) Michigan State University, 2527 Engineering Building, Department of Chemical Engineering
& Material Science, East Lansing, MI 48824

(2) Universidad Nacional de Colombia, Ciudad Universitaria, Dept. de Ingeniería Química.
Bogotá

(3) Michigan Biotechnology Institute, 3900 Collins Road, MI 8910

Abstract

Liquid-Liquid equilibrium data at 101.3 kPa were measured for the ternary systems: water-ethanol-diethyl succinate at 303.15 K and 313.15 K; water + ethyl acetate + diethyl succinate and water + acetic acid + diethyl succinate at 398.15 K. The reliability of the LLE data was confirmed using the Othmer-Tobias correlation. Vapor-Liquid equilibrium data were also measured for the binary systems ethyl acetate + diethyl succinate at 313.15 K, acetic acid + diethyl succinate at 323.15 K and ethanol-diethyl succinate at 323.15 K. Binary parameters for the modified UNIQUAC and NRTL equations were obtained by fitting experimental and reported data using the regression tool in Aspen Plus[®]. The Hayden-O'Connell equation was used to represent interactions in the vapor phase. The model agrees reasonably well with the experimental data and can predict reported azeotropic conditions.

Keywords

Diethyl succinate, Ethyl acetate, LLE, VLE, UNIQUAC, NRTL

C – Corresponding author

S - Speaker

Submitted to: 2009 Midwest Thermodynamics Conference

ALL-ATOM FORCE FIELD FOR THE PREDICTION OF VAPOR–LIQUID EQUILIBRIA AND INTERFACIAL PROPERTIES OF HFA134A

Robson P. S. Peguin, Ganesh Kamath, Jeffrey J. Potoff and Sandro R. P. da Rocha*

Department of Chemical Engineering and Materials Science, Wayne State University, 5050 Anthony Wayne Drive, Detroit, Michigan 48202

A new all-atom force field capable of accurately predicting the bulk and interfacial properties of 1,1,1,2-tetrafluoroethane (HFA134a) is reported. Parameterization of several force fields with different initial charge configurations from ab initio calculations was performed using the histogram reweighting method coupled with the grand canonical ensemble in Monte Carlo simulations. The 12-6 Lennard-Jones well depth and diameter for the different HFA134a models were determined by fitting the simulation results to pure-component vapor-equilibrium data. Initial screening of the force fields was achieved by comparing the calculated and experimental bulk properties. The surface tension of pure HFA134a served as an additional screening property to help discriminate an optimum model. The proposed model reproduces the experimental saturated liquid and vapor densities, and the vapor pressure for HFA134a within average errors of 0.7%, 4.4%, and 3.1%, respectively.

Critical density, temperature, vapor pressure, normal boiling point, and heat of vaporization at 298 K are also in good agreement with experimental data with errors of 0.2%, 0.1%, 6.2%, 0%, 2.2%, respectively. The calculated surface tension is found to be within the experimental range of 7.7-8.1 mN · m⁻¹. The dipole moment of the different models was found to significantly affect the prediction of the vapor pressure and surface tension. The ability of the HFA134a models in predicting the interfacial tension against water is also discussed. The results presented here are relevant in the development of technologies where the more environmentally friendly HFA134a is utilized as a substitute to the ozone depleting chlorofluorocarbon propellants.

DEVELOPMENT OF A MOLECULAR BASED COMPUTATIONAL APPROACH TO FLUID - PHASE EQUATIONS OF STATE

Hye Min Kim, Andrew J. Schultz and David A. Kofke

Department of Chemical and Biological Engineering, University at Buffalo

In a polar molecular system, the hydrogen bonding attraction causes a breakdown of the virial series approach which does not consider fluid association via hydrogen bonding. Also, the virial series with different truncations are difficult to converge near the critical temperature of polar molecular system. Therefore, it is essential to find the innovative thermodynamic methods based on molecular level cluster integral calculations to evaluate the thermodynamic behavior of polar molecular system. As one of the possible methods, Wertheim's association fluid theory is evaluated with a single attraction site model. The cluster diagram expansion of the association theory describes the P-V-T behavior better than the conventional virial expansion. Based on Wertheim's theory, use of the single attraction site model has a clear improvement to predict the thermodynamic behavior of polar molecular system.

IMPLICATIONS OF COMPRESSED LIQUID DENSITY FOR INTERMOLECULAR POTENTIAL MODELS

Ehsan Moharreri and J. Richard Elliott
Chemical and Biomolecular Engineering Department
The University of Akron, Akron OH 44325 USA

The compressed liquid density of Xenon was studied using step potential models to improve understanding of what is necessary for a potential model to achieve an accurate description. In general, two densities were considered: 2.9 and 2.6 g/cm³. Properties for Xenon were available in the range of 0-750MPa and 160-500K from the NIST Webbook. The overall goal was to fit potential parameters to the high density then predict the isochoric properties and the lower density. Comparisons were based on compressibility factor ($Z = PV/RT$), temperature, and liquid density. Deviations are summarized in terms of the difference between temperatures needed to achieve the experimental Z at the specified density. The Lennard-Jones equation of state (LJEOS) Kolafa and Nezbeda is applied as a basis for comparison. An initial investigation using the square-well model exhibited remarkably large deviations (53K) when applied in this manner, compared to the LJEOS value of 6K. Adding a soft shoulder induced the curvature that was reflected at high temperature, but failed to substantially reduce the large deviations. Applying a 7-step potential to mimic the LJ model similar to Chapela et al. reduced the deviations substantially (~10K). The greatest reduction in error derives from details of the attractive range of the potential model, rather than the repulsive shoulder. A systematic study shows how the minimal deviations can be achieved for 2-step, 3-step, and 4-step potential models, both with and without soft repulsive shoulders. The accuracy and utility of thermodynamic perturbation theory is assessed in addressing this problem. In conclusion, step potential models display mixed results with regard to compressed liquid density. Square-well models appear to be grossly inadequate, despite acceptable accuracy for vapor pressure. Multi-step models provide adequate accuracy, however. Even a 2-step potential model provides substantially improved accuracy relative to the square-well model. This conclusion illustrates that details of the potential model are important and that accurate physical properties provide a sensitive probe of these details, even in exercises that can be appreciated by engineering sophomores using the DMD module at etomica.org.

IMPROVING THE EFFICIENCY OF VIRIAL-COEFFICIENT CALCULATIONS: A HYBRID APPROACH EMPLOYING INTEGRAL-EQUATION THEORIES AND MAYER-SAMPLING MONTE CARLO

Katherine Schadel, Andrew Schultz, David Kofke

Department of Chemical and Biological Engineering
University at Buffalo, The State University of New York

The ability of a potential model to reproduce the pressure isotherms and critical point of the fluid it describes is an important measure of its efficacy, and analysis of the model's performance can help improve its parameterization. Calculation of these quantities from the model's truncated virial equation of state (VEOS) is trivial, but computation of high-order virial coefficients is not. The truncation of the model's VEOS limits the range of densities over which pressures calculated from it may be compared to experimental values.

Mayer-Sampling Monte Carlo (MSMC) has enabled calculation of higher-order virial coefficients than previously possible for a variety of potential models, including virial coefficients of up to sixth order for several water models. However, computation of the high-order virial coefficients required to apply the VEOS at densities approaching the critical density is still not feasible. The higher the order of the virial coefficient, the more operations there are per MSMC step, and the more steps must be taken to achieve a desired precision. Eventually, at an order of virial coefficient depending upon the potential model's complexity, MSMC calculations become prohibitively long.

We illustrate this problem through results for three potential models of methanol. Virial coefficients of satisfactory precision have been computed up to the fourth order for each model. As for many real fluids, there is consensus in the literature for experimental values only of the second and third virial coefficients of methanol. The quality of fourth and higher-order virial coefficients can only be assessed through the VEOS. For each model's third- and fourth-order VEOS, the spinodal curves are computed up to the critical point. As the order of the VEOS increases, the calculated critical point should approach that of the potential model. For these models, fourth order is insufficient to observe such convergence, but fifth virial coefficients are impractical to calculate because of the time required to achieve a satisfactory precision.

An approach which could prove more efficient is a hybrid method, in which only a part of the virial coefficient is computed by MSMC. For spherically symmetric potentials, approximate virial coefficients derived from integral-equation theories can be computed quickly using a deterministic recursive algorithm. In one hybrid approach, only the correction to this approximation is computed by MSMC. For the Lennard-Jones potential, we demonstrate that this hybrid approach would be faster than MSMC alone for computing fourth virial coefficients.

However, in the recursive algorithm, approximations of lower-order density-expansion coefficients of the direct correlation function are employed to compute approximations of higher-order, such that the approximations of virial coefficients computed from these become successively worse. Because these approximations become more severe as the order of the virial coefficient increases, computing only the correction by MSMC becomes less beneficial.

We present another hybrid approach which could prevent the rapid deterioration of the quality of the approximations. In this second hybrid method, MSMC would be used to compute the

correction to the density-expansion coefficient of the direct correlation function before it is used within the integral equation to compute an approximate coefficient of higher order.

Generalized integral-equation theories have been developed to compute correlation functions for multisite potentials models, like those commonly used to describe methanol. We describe how we will apply these same concepts to generalize the hybrid method for virial-coefficient calculation. This extension is imperative as these detailed models are those for which MSMC calculations require the most time.

UNDERSTANDING SHAPE SELECTIVITY OF PAHS IN REVERSED-PHASE LIQUID CHROMATOGRAPHY VIA MONTE CARLO SIMULATIONS

Jake L. Rafferty,^{a,*} J. Ilja Siepmann,^a and Mark R. Schure^b

^a*Department of Chemistry and Minnesota Supercomputing Institute, University of Minnesota, Minneapolis, MN 55455, USA.*

^b*Theoretical Separation Science Laboratory, Rohm and Haas Company, Box 0904, Spring House, PA 19477-0904, USA*

An important ability of reversed-phase liquid chromatography (RPLC), and one that is difficult to explain, is its power to separate analytes with very similar chemical functionalities and physical properties, but with only slightly different shapes. This ability is instrumental for many separation tasks involving species of environmental and biological importance, for example, polycyclic aromatic hydrocarbons (PAHs) and steroids. Sander and co-workers have devoted great effort to explore this phenomenon through chromatographic and spectroscopic experiments [1,2], but a molecular-level description remains lacking. To probe the origins of this shape selectivity in RPLC at the molecular level, particle-based simulations using efficient Monte Carlo sampling algorithms and accurate force fields were carried out for various dimethyl octadecylsilane (ODS) stationary phases (surface coverages from 1.6-4.2 $\mu\text{mol}/\text{m}^2$) in contact with commonly used mobile phase solvents (acetonitrile/water or methanol/water) at a temperature of 308 K. The retention of aromatic hydrocarbons ranging in size from benzene to PAHs of the formula $\text{C}_{18}\text{H}_{12}$ was examined.

From the simulation trajectory, one can obtain a vast amount of molecular-level information on the ODS conformation and the complex distribution of analyte positions and orientations relative to the stationary phase. At the highest grafting density studied, the PAH isomers show highly specific positional and orientational distributions within the stationary phase. The solutes prefer to reside at specific sites above unreacted silanol groups, i.e., where the local alkyl surface coverage is lower, and align their long axis perpendicular to the silica substrate. However, it does not appear that there are different types of retention sites that will exclude a particular PAH, rather each site is available to all of the PAHs and the conformations of the ODS chains adapt to the presence of the solutes. As the surface coverage is lowered, these positional and orientational preferences diminish. At all grafting densities, the PAHs fully embed themselves into the stationary phase and thus do not show the mixed partition-adsorption behavior we have found for alkanes and alcohols [3].

[1] S. A. Wise and L. C. Sander, 'Factors affecting the reversed-phase liquid chromatographic separation of polycyclic aromatic hydrocarbon isomers,' *J. High. Res. Chromatogr.* 89, 248-255 (1985).

[2] L. C. Sander, M. Pursch, and S. A. Wise, 'Shape Selectivity for Constrained Solutes in Reversed-Phase Liquid Chromatography,' *Anal. Chem.* 71, 4821-4830, 1999.

[3] J.L. Rafferty, L. Zhang, J.I. Siepmann, and M.R. Schure, 'Retention mechanism in reversed-phase liquid chromatography: A molecular perspective,' *Anal. Chem.* 79, 6551-6558 (2007).

*Corresponding author. Email: raff0028@umn.edu

INVITED TALK
NANOSTRUCTURED INORGANIC-ORGANIC HYBRIDS:
ENGINEERING A NEW CLASS OF POROUS MATERIALS

Krista S. Walton

*Department of Chemical Engineering, 1005 Durland Hall
Kansas State University, Manhattan, Kansas 66506*

Porous materials play a crucial role in many important applications including air purification, gas separations, catalytic processes, and chemical sensing. The design of materials for such applications requires a fundamental understanding of the adsorption and reactivity between target molecules and high surface area nanomaterials, but serious gaps exist in this area. Metal sites in zeolites and impregnated carbons are known to give rise to special adsorption and catalytic behavior. However, tailoring these materials for specific interaction with adsorbate molecules is limited by the inherent disorder of such sites, large pore size distributions, and rigid structures that are not amenable to chemical modification.

Metal-organic frameworks represent a new direction in porous materials research that could lead to the creation of designer-specific multifunctional materials. The rich field of coordination chemistry provides a versatile platform from which these materials may be assembled from an almost infinite set of building blocks. These new inorganic-organic hybrid materials are formed through interconnection of metal clusters and organic ligands. They have demonstrated interesting adsorption properties and have a clear potential for impacting a wide range of adsorption-based technologies.

Understanding the adsorption and catalytic properties of MOFs will help narrow down the design scope and facilitate the development of functional materials to perform targeted separations and purifications. In this presentation, this new class of materials will be introduced and current research in this emerging area will be discussed. Adsorption experiments and molecular modeling results will be presented for several gases on model MOFs. Specific discussion will be given regarding the effect of pore size, unsaturated metal sites, and functionalized ligands on the adsorption of light gases. The implications of these results for impacting adsorption applications such as separations, catalysis, and controlled storage and release will be discussed.

AN ADAPTABLE METHOD TO CALCULATE THE SOLUBILITY LIMIT OF SOLIDS BY MOLECULAR SIMULATION

Andrew S. Paluch¹, Saivenkataraman Jayaraman, Jindal K. Shah and Edward J. Maginn²
Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre
Dame, Indiana 46556, USA

Despite the development of sophisticated methods to study vapor-liquid equilibrium, the development of methodologies to study solid-liquid equilibrium has received much less attention due to the inherent complexity involved with the calculation of the free energy of solids. In this talk, we will demonstrate a robust method to calculate the solubility limit of solids in different solvents. The method combines pseudo-path integration for the free energy calculations of the solid phase, and recently developed Wang-Landau Transition-Matrix Monte Carlo for phase equilibria calculations. We will validate the method by computing the solubility limits of sodium chloride in water.

¹ Presenting Author

² Author to whom correspondence should be addressed: ed@nd.edu

ATOMISTIC MODELING OF TIN SURFACE AND GRAIN BOUNDARY DIFFUSION

Michael S. Sellers^{1*}, Andrew J. Schultz¹, Cemal Basaran², and David A. Kofke¹

¹*Department of Chemical and Biological Engineering, 303 Furnas Hall*

²*Department of Civil, Structural and Environmental Engineering*

University at Buffalo, The State University of New York

Buffalo, NY 14260

Abstract

As analysis tools in computational materials science develop, transport properties at the atomistic level play an increasingly important role in the study of a material's behavior at large scales. Quantitative transport data explaining diffusion, cracking, or crystal growth, often difficult to study experimentally, can be had with relative ease using a molecular simulation package and a few workstation grade computers. This information, used in conjunction with a larger-scale model, plays a key part in the accurate description of such phenomena in that model.

The field of electronics packaging can benefit from this kind of analysis, specifically in the study of electromigration in thin films and SnAgCu (SAC) alloy solder joints. Surface and grain boundaries in these structures provide fast diffusion paths for tin solute atoms, alloyed compounds, and atomic vacancies. In addition, all are given a strong diffusive force resulting from a high current density's inherent electron wind. Modeling these specific processes and quantifying the diffusivity of tin atoms and vacancies, both on surfaces and in grain boundaries, will aid in the prediction of failure rates of these types of joints—key parameters for the realization of nano-electronics.

Two methods of molecular simulation are used to compute the diffusivity of tin atoms in our systems. First, common molecular dynamics simulations are used to determine an overall atomic diffusivity in varying angles of symmetric tilt grain boundaries. Second, we use a potential energy surface walking method, called the Dimer method, to seek out diffusion mechanism saddle points in a molecular statics style simulation. From the Dimer method results, we can use harmonic transition state theory to compute tracer diffusivities of tin in our surface and grain boundary systems. These methods are compared and quantitative values for activation energies and diffusion coefficients are presented.

MOLECULAR DYNAMICS STUDIES OF N-ALKANE AND BENZENE SELF-DIFFUSION IN THE METAL-ORGANIC FRAMEWORK IRMOF-1

Denise C. Ford and Randall Q. Snurr

Department of Chemical and Biological Engineering, Northwestern University,
2145 Sheridan Road, Evanston IL 60208 USA

Metal-organic frameworks (MOFs) are a new class of synthetic, micro- and mesoporous, crystalline materials with tunable pore sizes and chemical functionalities. Potential applications for MOFs include gas storage, separations, sensing, and catalysis, and the rate of diffusion of guest molecules within the MOF framework is important for all of these applications. We have investigated the self-diffusion of C1-C16 n-alkanes and benzene in the prototypical metal-organic framework IRMOF-1 with molecular dynamics simulations and will present the calculated self-diffusion coefficients and activation energies for diffusion of these species. The location preferences of a subset of these species in IRMOF-1 will be discussed and diffusion pathways are highlighted from these results. The effect of concentration on the diffusivity of three species showing qualitatively different behavior will also be presented.

MOLECULAR DYNAMICS SIMULATIONS OF CO₂ AT AN IONIC LIQUID INTERFACE: ADSORPTION, ORDERING AND INTERFACIAL CROSSING.

Marcos Perez-Blanco, Edward J. Maginn

Using classical molecular dynamics simulation techniques, the molecular scale characteristics of the gas liquid interface of the ionic liquid 1-n-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([bmim][Tf₂N]) have been studied. The vacuum-liquid surface of the ionic liquid, and the gas liquid interface of the ionic liquid with carbon dioxide, were simulated at a range of temperatures and pressures. The process of carbon dioxide adsorption on the liquid surface and absorption into the bulk liquid was quantified in terms of flux and concentration difference across the interface. Adsorption onto the interface occurs rapidly, in approximately 100 ps, but interfacial crossing and diffusion into the bulk is much slower. At the lower pressures the fraction of CO₂ molecules adsorbed is very high, but as the pressure increases a monolayer is formed and a greater fraction of the CO₂ molecules stay in the gas phase.

Density profiles with respect to the interfacial normal were computed for each atom in the ionic liquid and CO₂. The dependence of the density profiles on the carbon dioxide pressure was evident from comparison of the simulations at different pressures. Interfacial ordering and orientational tendencies were indicated by the relative densities of different atoms as a function of position on the interface normal.

The distribution of angular orientation of selected bond directions, at regular points along the interface normal, was also calculated. This analysis was performed both for the ionic liquid molecules and the CO₂ molecules. For the CO₂ molecule orientations, a dependence on CO₂ pressure is noted.

Residence time distributions of CO₂ molecules in the interfacial region were created. It was observed that the rate at which molecules penetrate the surface, relative to the rate at which molecules desorb, is affected by the temperature. The analysis of the residence time distribution seems to indicate that adsorption and desorption occurs on a rapid timescale relative to diffusion through the interface. The time evolution of the density profile of CO₂ was studied as it diffused across the interface over the 7 ns time period. Potentials of mean force were also computed for CO₂ penetration into the liquid.

HOW DOES NANOSCALE ROUGHNESS INFLUENCE WETTING BEHAVIOR?

Eric M. Grzelak and Jeffrey R. Errington

*Department of Chemical and Biological Engineering,
University at Buffalo, The State University of New York, Buffalo, NY 14260*

The way in which a fluid wets a surface depends greatly on the properties of that surface, including its roughness. This is indicated by the ability of a lotus leaf to self clean, or the adhesive strength of metal welded ceramics. In this presentation we share our recent computational effort performed to better understand the wetting of surfaces with roughness ranging from molecular to nanoscopic length scales. We use grand canonical and expanded ensemble transition matrix Monte Carlo simulations to determine the surface free energy of a fluid in contact with an atomistically defined surface. This free energy is then used to calculate spreading coefficients, contact angles and interfacial tensions. In this study we use a Lennard-Jones fluid interacting with a substrate comprised of static particles in a crystalline form. This substrate is then etched to provide nanoscopic contours. By comparing the nanoscopic roughness to the measured contact angle we are able to compare our results to those predicted by the empirical relationship defined by Wenzel.¹

¹ R. N. Wenzel, *Industrial & Engineering Chemistry* **28** (8), 988 (1936).

RELATIONSHIP BETWEEN THE THERMODYNAMICS AND DYNAMICS OF A MOLECULAR FLUID

Ravi Chopra,¹ Thomas M. Truskett², and Jeffrey R. Errington,¹

¹Department of Chemical and Biological Engineering
University at Buffalo, Buffalo, New York

²Department of Chemical Engineering and Institute for Theoretical Chemistry,
The University of Texas at Austin, Austin, Texas

Transport coefficients such as the diffusivity, viscosity, and thermal conductivity are important quantities for both scientific research and engineering design. Empirical scaling relationships have emerged as a promising approach for predicting such quantities. In fact, recent studies have demonstrated that entropy-scaling relations provide a robust means to describe the dynamics of bulk and confined atomistic fluids. In this work we examine the extent to which these ideas can be used to characterize molecular fluids. Through the use of molecular dynamics and transition-matrix Monte Carlo simulations we study relationships between transport (translational and rotational diffusivity, characteristic relaxation times), thermodynamic (excess entropy), and structural (two-body excess entropy) properties of the extended simple point charge water model and a dumbbell model. Calculations are performed over a broad range of conditions that span from the supercooled liquid regime to the critical region. Our results suggest that entropy-scaling relations could serve as a powerful means for predicting transport properties of molecular fluids.

TRANSPORT PROPERTIES INVESTIGATION ON GENERIC SPECIES IN SILICA MELTS USING MOLECULAR SIMULATIONS

Liqun Zhang, Daniel J. Lacks, James A. Van Orman

The transport properties of silicate melts are strongly dependent on seemingly minor changes in composition. For example, mixing a silica-rich melt with just several weight percent of another oxide (e.g., MgO, Na₂O, etc.) or water can lower the melt viscosity by several orders of magnitude. Furthermore, the diffusivities of volatiles dissolved in the melt can be much higher than the diffusivities of the silicate ions, and depend strongly on volatile concentration. To elucidate these effects, we carry out molecular dynamics simulations of a silica melt with small amounts of generic dissolved species. We systematically vary how this generic species interacts with the melt, in order to identify specifically the factors by which the transport properties of a silicate melt are affected by composition. We focus on the role of the size and charge of the dissolved species. Our results show that neutral dissolved species have a negligible effect on the structure and bonding of the silica network, regardless of the size of the species; these neutral species are decoupled from the network, and can diffuse orders of magnitude faster than the network ions. In contrast, the charged species strongly disrupt the network, which leads to significant enhancement of the transport properties (e.g., lower viscosity and higher diffusivity the network ions). The effects of the charged dissolved species are strongly dependent on their size.

ASYMPTOTIC TRENDS IN ATHERMAL MIXTURE ENTROPY IN THE LONG CHAIN LIMIT

Amir Vahid,¹ Neil H. Gray,² and J. Richard Elliott^{*,†}

Chemical and Biomolecular Engineering Department

The University of Akron, Akron OH 44325 USA

Chemstations Inc., 2901 Wilcrest Dr., Houston TX 77042 USA

ABSTRACT

Polymeric mixtures of hydrocarbons, alcohols have been simulated with discontinuous potential models to characterize the Helmholtz energy of the repulsive reference fluids (A0). Several related mixtures were reported on previously. The specific hydrocarbons studied previously were methane, ethane, propane, n-butane, n-hexane, n-heptane, n-decane, and benzene. The specific alcohols were water, methanol, ethanol, n-propanol, and n-octanol. Unfortunately, a slight inconsistency was encountered when the trend observed for these small molecules was extrapolated to the long chain limit. In the present work, we extend the analysis to mixtures of n alkanes, branched hydrocarbons, and aromatics with polymeric molecules of: nalkanes, ethylstyrenes, ethyl-propylenes, and isoprenes. The mixing entropy contributions can be accurately characterized by van der Waals mixing rules. Candidates for the interpolation model included the NRTL and Wilson models as well, but the simpler van der Waals model proved quite reliable for characterizing the trends in excess properties with respect to composition. Associative contributions to the Helmholtz energy were attributed to Wertheim's theory in developing the molecular models of the alcohols but were not the object of study in the present investigation. Noting that the Helmholtz energy for the reference contribution is simply related to the athermal entropy, we find that the athermal entropy of mixing deviates significantly from ideality, but still follows the van der Waals mixing formula. This leads to an accurate characterization of the entropic contribution to the χ parameter of Flory-Huggins theory for mixtures of all sizes and shapes. A general rule is developed for predicting the athermal entropy of mixing based on knowledge of the volume ratios of the constituent molecules. Combined with the usual approach to characterizing the energetic contribution to the χ parameter, a complete formulation is provided for characterizing the mixture thermodynamics. The simulations are compared to several theories, including the MCSL theory for hard spheres, the SAFT model, and the Guggenheim-Staverman theory.

¹ The University of Akron

² Chemstations Inc.

* To whom correspondence should be addressed.

Tel: 330-972-7253; Fax: 330-972-5856.

E-mail: jelliott@uakron.edu.

CONSIDERATION OF THE ENTROPY IN THE FREE-ENERGY CALCULATION FOR THE STABLE CRYSTALLINE POLYMORPHS

Tai Boon Tan, Andrew J. Schultz, and David A. Kofke

Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York,
taitan@buffalo.edu

In prediction of a stable form of crystalline polymorph, we can compare the free energy of each polymorph and select the one with the lowest free energy. Most of the current prediction techniques only take into account the energetic contribution to the free energy and have ignored the entropic contribution. This is mainly because determining the entropic contribution is another degree of complication. In order to improve the accuracy of these approximation methods, we have included the neglected entropic term into our free-energy calculation by using the lattice-dynamics approach. This idea is motivated by many previous studies, which have reported that in many cases, the difference between the energies of the most stable polymorphs is relatively small and the stability is believed to be influenced by entropy.

Calculation of true free energy is performed by computing the difference with respect to a known reference. In this work, we use a harmonic reference system with spring constants given to match the configurational correlations measured in the target system. We consider two approaches to compute the free energy difference between the target and reference systems. First, we examine the accuracy of the Normal Mode Monte Carlo method, which is an approximate treatment that assumes that the normal mode coordinates are independent in the harmonic system. Second, we test the performance of overlap-sampling and umbrella-sampling approaches. We have successfully applied this technique to calculate for the free energy of the soft-sphere system, as a simple prototype. These methods are capable of providing accurate free energies up to the melting temperature when applied directly between the harmonic reference and target soft-sphere systems, in cases where the number of degrees of freedom is less than about 300.

Keywords: Molecular crystal, polymorph stability, entropy, free energy calculation, normal modes and perturbation techniques