

## **Conference Program**

(Note: A list of abstracts that have been submitted to date is appended below. These are not listed in order of presentation time yet. Check the schedule on the next page for timing.)

### **Thursday May 25, 2006**

7:15 a.m. Prospective breakfast locations include Starbucks in the student center and McDonalds on Exchange St.

#### **Session 1: 7:55 to 10:10 a.m.**

7:55 Opening remarks (Richard Elliott)

8:00 First speaker, Walter Chapman

#### **Coffee Break: 10:15-10:30am**

#### **Session 2: 10:30 a.m. to 12:33 p.m.**

10:30 Invited Talk: Sohail Murad

#### **Lunch: 12:33pm-1:30pm**

#### **Session 3: 1:30 to 3:45 p.m.**

2:00 Invited Talk: Monica Lamm

#### **Coffee Break: 3:45-4:15**

#### **Session 4: 4:15 to 6:30 p.m.**

4:15 Invited Talk: Claudio Margulis

6:30-6:45: 1min. outlines of Friday's talks.

#### **Conference Banquet: 7:15 p.m.**

**Location, Bulger Penthouse (Bldg 37)**

### **Friday May 26, 2006**

7:15 a.m. Prospective breakfast locations include Starbucks in the student center and McDonalds on Exchange St.

#### **Session 1: 8:00 to 10:15 a.m.**

8:00 First speaker

#### **Coffee Break: 10:15-10:45am**

#### **Session 2: 10:45 a.m. to 2 p.m.**

10:45 Invited Talk: Ernst von Meerwall

#### **Departing comments: 2pm-2:15pm**

Presenter	Advisor	Topic	Session	Len	tStart	SesTot
Chapman	Chapman	dft	Inhomoga1	35	800	
Tang	Tang	DFT	Inhomoga2	18	835	
Talreja	Kusaka	DftPolyInterface	Inhomoga3	18	853	
Nap	Szleifer	polyBrushes	Inhomoga4	15	911	
Zhang	Szleifer	Clustering	Inhomoga5	10	926	
Longo	Szleifer	EntropicLLe	Inhomoga6	10	936	
Taylor	Taylor	SolvationPot	Inhomoga7	18	946	124
Murad	Murad	membranes	Inhomogb1	35	1030	
Malani	Murad	NaClPores	Inhomogb2	10	1105	
Tenney	Lastoskie	Co2Ads	Inhomogb3	18	1115	
Wang	Johnson	SwntDifco	Inhomogb4	15	1133	
Dai	Johnson	qDftCatalyst	Inhomogb5	10	1148	
Semidey	Sholl	qDftMembranes	Inhomogb6	15	1158	
Chen,Haibin	Sholl	Nanotubes	Inhomogb7	10	1213	
Alapati	Sholl	H2alloys	Inhomogb8	10	1223	123
Lamm	Lamm	dendrimers	Inhomogc1	35	130	
Yani	Lamm	Slinterface	Inhomogc2	10	205	
Hassanali	Singer	Slinterface	Inhomogc3	15	215	
Zhang	Singer	MdInterface	Inhomogc4	10	230	
LI	Singer	ProteinHydration	Inhomogc5	10	240	
Knight	Singer	hBondTopology	Inhomogc6	10	250	
Shin	Singer	MdNanofluids	Inhomogc7	10	300	
Cribbin	Kofke	SolidFreeEnergy	Inhomogc8	18	310	
Duff	Lacks	Llinterface	Inhomogc9	18	328	136
Margulis	Margulis	ionic liquids	Ions&Forces1	35	415	
Rear	Lacks	MdIonic	Ions&Forces2	18	450	
Luan	Errington	AqIons	Ions&Forces3	18	508	
Grzelak	Errington	ContactAngle	Ions&Forces4	10	526	
Kamath	Potoff	AminePots	Ions&Forces5	15	536	
Ketko	Potoff	DmePot	Ions&Forces6	10	551	
Bernard-Brunel	Potoff	TorsionalPot	Ions&Forces7	10	601	
Rai	Siepmann	AroPots	Ions&Forces8	18	611	
JRE	JRE	Intro's/guides	Ions&Forces9	15	629	149 Banquet
Sarupria	Garde	proteinMd	SpecTops1	18	800	
Rosch	Errington	proteinMd	SpecTops2	18	818	
Peguin	daRocha	MolecDesign	SpecTops3	18	836	
Shultz	Kofke	VircoCritPt	SpecTops4	18	854	
Lustig	Lustig	FullereneVle	SpecTops5	18	912	
Siderius	Corti	HsSurfaces	SpecTops6	15	930	
Uline	Corti	Nucleation	SpecTops7	10	945	
Novak	Maginn	MdNucleation	SpecTops8	18	955	133 30min snack
VonMeerwall	VonMeerwall	transport/expts	Tests1	35	1045	
Kelkar	Maginn	RNEMDvisco	Tests2	18	1120	
Jutta	Jutta	MixedTcon	Tests3	18	1138	
Asli	Talu	Pore Diffco	Tests11	18	1156	
Krishnamurthy	Murad	MdGasSoly	Tests4	18	1214	
Liu	Tomasko	polysoly	Tests5	13	1232	
Liu	Tomasko	polysolyModel	Tests6	8	1245	
Carri	Carri	PolyProps	Tests7	18	1253	
Vu	Lira	VLeEsters	Tests8	18	111	
Sans	JRE	potentials	Tests9	15	129	
Gerek	JRE	transport corrs	Tests10	15	144	194

# Interfacial Equilibria and Structure of Polyatomic Fluids from Interfacial-SAFT (*i*SAFT) Density Functional Theory

Sandeep Tripathi, Aleksandra Dominik, and Walter G. Chapman  
Chemical and Biomolecular Engineering Dept.  
Rice University  
Houston, TX 77005

A wide range of potential applications such as environmental remediation, biochemical separations, design of biosensors, catalysis, wettability etc. have created significant interest in molecular level studies of systems of complex fluids (e.g. hydrogen bonding fluids, hydrocarbons, proteins, polymers) at solid-fluid and fluid-fluid interfaces. Experimental studies of such systems are challenging due to the small scale of the system. Although computer simulations do help overcome some of these problems, they are computationally expensive; hence the importance of accurate theories cannot be overemphasized.

We have developed a density functional theory (DFT) based on Wertheim's theory of associating fluids that is capable of modeling the adsorption, phase and even chemical equilibria of mixtures of associating and reacting polyatomic fluids near hydrophobic and hydrophilic surfaces [1-5]. The density functional theory is based on a similar formalism to the SAFT model that is widely applied to model bulk phase behavior of associating fluids and polymer solutions. Comparing with experimental data and Monte Carlo simulations, we demonstrate the success of the DFT in capturing the effects of size and shape of the fluid molecules and system parameters such as fluid-fluid and surface-fluid association/interaction strengths and hydrophobicity of the surface, on fluid structure and interfacial properties.

1. Aleksandra Dominik, Sandeep Tripathi and Walter G. Chapman, "Bulk and Interfacial Properties of Polymers from Interfacial SAFT Density Functional Theory," I&EC Research, submitted (2006).
2. Sandeep Tripathi and Walter G. Chapman, "Microstructure and thermodynamics of inhomogeneous polymer blends and solutions," Physical Review Letters, **94**, 087801 (2005).
3. Sandeep Tripathi and Walter G. Chapman, "Microstructure of inhomogeneous polyatomic mixtures from a density functional formalism for atomic mixtures," J. Chem. Phys., **122**, 94506 (2005).
4. Sandeep Tripathi and Walter G. Chapman, "Density-functional theory for polar fluids at functionalized surfaces. I. Fluid wall association," J. Chem. Phys. **119**, 12611-12620 (2003).
5. Sandeep Tripathi and Walter G. Chapman, "Adsorption of associating fluids at active surfaces: a density functional theory," Cond. Matt. Phys., **6**, 523-540 (2003).

# Molecular Simulations of Amphiphilic Dendrimers in Solution

Monica H. Lamm

*Department of Chemical and Biological Engineering  
Iowa State University, Ames, IA 50011*

Dendrimers are large, synthetic macromolecules that have regular and highly branched architectures. A dendrimer has a large number of terminal groups that can be functionalized to tune its properties for use in a wide range of applications, including: medicine, surface science, and catalysis. In this talk, we will discuss our recent molecular simulation studies aimed at making fundamental connections between the macroscopically observed solution phase properties of dendrimers and their molecular architecture. We have performed molecular dynamics simulations on model amphiphilic dendrimers to better understand the conformational changes that variations in terminal group type and arrangement impart to the dendrimer.<sup>1</sup> We will present simulation results for a dendrimer in dilute solution, where the interior monomers are solvophobic and the terminal monomers are varied systematically from all solvophobic to all solvophilic. These results will show how the size, shape, and mobility of the dendrimer and its parts change according to the fraction and arrangement of the two types of terminal monomers.

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<sup>1</sup> Nicholas W. Suek and Monica H. Lamm, *Macromolecules*, in press.

# **Molecular Dynamics and Thermodynamics of Room-Temperature Ionic Liquids**

Claudio Margulis  
Department of Chemistry, University of Iowa

## **Abstract**

We have recently investigated the slow dynamics of 1-butyl-3-methylimidazolium hexafluorophosphate, a very popular room-temperature ionic solvent. Our study predicts the existence of heterogeneity in the liquid and shows that this heterogeneity is the underlying microscopic cause for the recently reported "Red Edge Effect"(REE) observed in the study of fluorescence of the organic probe ANF. Our theoretical work explains in microscopic terms the relation between REE and dynamic heterogeneity in a room-temperature ionic liquid. We have also been able to predict the time- and wavelength- dependent emission spectra of ANF in the same ionic solvent. From the analysis of our simulated data we are able to derive an approximate time scale for reorganization of the solvent around the solute probe.

# **Diffusion Studies by Pulsed-Gradient NMR: Capabilities, Results, and Perspectives**

**Ernst von Meerwall**

Departments of Physics, Chemistry, and Polymer Science, and  
College of Polymer Science and Polymer Engineering  
The University of Akron

## **Abstract**

Since its development in the mid-1960s the pulsed-gradient spin-echo NMR method of measuring molecular self-diffusion has been used to study a variety of systems of increasing complexity. Since 1978 our laboratory has specialized in the application of the high-gradient, non-spectroscopic variant of this method to polymer-based and colloidal systems. Our studies are usually conducted in conjunction with measurements of the NMR spin-spin lattice relaxation time, a sensitive indicator of local molecular mobility. The attributes of this method will be discussed; its main advantages are the first-principles measurement of diffusion rate and its distribution, the absence of a need for chemical labeling, and the unlimited reusability of sample specimens. Multicomponent, restricted, and anomalous (non-Fickian) diffusion is measurable.

Examples of recent work of this laboratory illustrate the range from academic polymer science (transition from unentangled to entangled diffusion of linear polymers) to industrial processes (devulcanization of industrial rubber by intense ultrasound) and to biomedical applications (permeability of bicontinuous microcomposites for controlled drug release). The close relationship among experiment, contemporary theory, and molecular simulations will be emphasized.

The utility of this combination to elucidate details of the diffusion mechanisms operating in complex systems depends on the ability of theory and simulation to make quantitative predictions of absolute diffusion rates as well as of their dependence on sample composition and on environmental variables.

# **Molecular Simulations of Membrane Based Separation Processes**

**S. Murad**

**Chemical Engineering Department**

**University of Illinois at Chicago**

**Chicago IL 60607**

Molecular simulations using a method based on molecular dynamics has been used to study a variety of separation processes. These include reverse osmosis separation of brine, exchange of cations in zeolite membranes, separation of air and N<sub>2</sub>-CO<sub>2</sub> mixtures using zeolite membranes, and pervaporation separation of alcohols. In addition, the effect of external fields such as electric and magnetic on membrane based separation processes has also been explored. This talk will describe the results of our simulations and how we suggest molecular simulations can be use to improve the efficiency of these processes.

# Screening Destabilized Alloys for Hydrogen Storage Applications and Prediction of Thermodynamic Properties using First Principles

Sudhakar V. Alapati<sup>1</sup>, David S. Sholl<sup>1,3</sup> and J. Karl Johnson<sup>2,3</sup>

<sup>1</sup>Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA-15213, USA

<sup>2</sup>Chemical and Petroleum Engineering Department, University of Pittsburgh, Pittsburgh, PA-15213, USA

<sup>3</sup>National Energy Technology Laboratory, Pittsburgh, PA-15236

## *Abstract*

Lack of viable hydrogen storage technology limits the wide-spread use of hydrogen fuel cell powered vehicles. Current DOE targets aim for systems with gravimetric densities >6-9 wt%. The hydrogen storage materials available at present do not achieve this goal. A novel approach has been proposed which obtains hydrogen from the complex metal hydrides such as alanates, amides and borohydrides. The hydrides of period 2 and 3 metals have relatively high hydrogen densities but are thermodynamically very stable meaning high temperatures are needed to dissociate these hydrides. Vajo *et al.*<sup>1</sup> have shown that the thermodynamics of the reaction can be modified by using additives to form compounds in the dehydrogenated state that are stable with respect to the constituents of the initial reaction. The principle underlying this concept is that having a stabilized dehydrogenated state reduces the enthalpy of dehydrogenation and increases the equilibrium partial pressure of the dehydrogenation reaction. Using first principles density functional theory (DFT) approach we have calculated the heats of reaction for over 100 different reactions for various metal hydride systems. We have compared our calculations with experimental and tabulated data where available and find reasonable agreement. Our calculations demonstrate the utility of DFT for screening reactions and for identifying promising materials for further computational and experimental studies. We also discuss calculation of dissociation pressures for the most promising of these materials.

1. J. J. Vajo, F. Mertens, C. C. Alm, R. C. Bowman, B. Fultz, *Journal of Physical Chemistry B* **108**, 13977 (2004).

## Transport Property Prediction by Discontinuous Molecular Dynamics

Z. Nevin Gerek, Neil H. Gray, and J. Richard Elliott, Chemical Engineering Dept., University of Akron

We seek to maximize the predictive value of molecular simulations by leveraging the dynamic derived from discontinuous molecular dynamics (DMD) simulation of repulsive reference fluids based on transferable step potentials. Collectively, we refer to this combined methodology as the step potentials for equilibria and discontinuous molecular dynamics (SPEADMD) model. Although formal derivations of perturbation theories for transport properties exhibit singularities at low density, the success of the Davis-Rice-Sengers (DRS) theory for square-well spheres demonstrates that an analytical theory and hence a viable expansion is possible. At present, we develop perturbation expansions that mimic the form of the DRS theory and take molecular simulations of the reference transferable potential model as their basis. The terms in the perturbation expansion are then treated as empirical coefficients to develop generalized correlations for the mean field effects of attractive forces.

The transport coefficients are evaluated as the long term-limit of the slope of the mean-squared displacement corresponding to the transport property. Predictions of diffusivities are compared with the experimental data and correlations by Zabaloy et al. and Liu et al. We observe that disperse attractions appear to play a major role in diffusivities of longer chains and lower densities. Methane and ethane in the range of 300-500K exhibit diffusivities that are too high to be consistent with the reference fluid simulations, necessitating a correction for the softness of molecular interactions. A new correlation is developed to accurately characterize the diffusivities of tangent sphere chains from  $m = 1-192$ , where  $m$  is the number of segments in the chain. Rouse scaling is obtained in the long chain limit for the new correlation, in contrast to the previous correlation by Yu et al.(2000). The form of the new correlation is extended to n-alkanes and generalized attractive corrections are added as discussed above. The correlation for n-alkanes can also be applied to non-alkanes. The shape parameter ( $m^{eff}$ ) must be treated as a regression variable in order to achieve correlations accurate to ~10%AAD.

Predictions of viscosities are compared with the experimental data and correlations by Chung et al and the TRAPP method. We observe that disperse attractions appear to play a major role in viscosities of longer chains and lower densities. Methane and ethane in the range of 300-500K exhibit viscosities that are too low to be consistent with the reference fluid simulations, necessitating a correction for the softness of molecular interactions. A new correlation is developed to accurately characterize the viscosities of tangent sphere chains from  $m = 1-16$ , where  $m$  is the number of segments in the chain. Rouse scaling is obtained in the long chain limit for the new correlation. The form of the new correlation is extended to n-alkanes and generalized attractive corrections are added as discussed above. The correlation for n-alkanes can also be applied to non-alkanes. The shape parameter ( $m^{eff}$ ) must be treated as a regression variable in order to achieve correlations accurate to ~10%AAD.

Predictions of thermal conductivity are compared with the experimental data and correlations by Chung et al and the TRAPP method. A new correlation is developed to accurately characterize the thermal conductivities of tangent sphere chains from  $m = 1-192$ , where  $m$  is the number of segments in the chain. Rouse scaling is obtained in the long chain limit for the new correlation. The form of the new correlation is extended to n-alkanes and generalized attractive corrections are added as discussed above. The correlation for n-alkanes can also be applied to non-alkanes. The shape parameter ( $m^{eff}$ ) must be treated as a regression variable in order to achieve correlations accurate to ~10%AAD.

## Transport Diffusion of Gases Is Rapid In Flexible Carbon Nanotubes

Haibin Chen<sup>1</sup>, J. Karl Johnson<sup>2,3</sup>, and David S. Sholl<sup>1,3</sup>

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<sup>3</sup>*National Energy Technology Laboratory, Pittsburgh, PA 15236, USA*

### Abstract

Molecular dynamics simulations of rigid, defect-free single walled carbon nanotubes has previously suggested that the transport diffusivity of gases adsorbed in these materials can be orders of magnitude higher than any other nanoporous material (A. I. Skoulidas et al., *Phys. Rev. Lett.* **89** (2002) 185901). These simulations must overestimate the molecular diffusion coefficients because they neglect energy exchange between the diffusing molecules and the nanotube. Recently, Jakobtorweihen et al. have reported careful simulations of molecular self diffusion that allow nanotube flexibility (*Phys. Rev. Lett.* 95 (2005) 044501). We have used the efficient thermostat developed by Jakobtorweihen et al. to examine the influence of nanotube flexibility on the transport diffusion of CH<sub>4</sub> in a (20,0) nanotube. Although inclusion of nanotube flexibility reduces the transport diffusion relative to the rigid nanotube, the resulting transport diffusion coefficients are still extremely large compared to other known materials. We will discuss the implications for these observations for using carbon nanotubes for membrane-based gas separations.

## Transferable Potentials for Perfluorocarbons

Amanda D. Sans and J. Richard Elliott, Chemical Engineering Dept., University of Akron

The Step Potential Equilibria And Discontinuous Molecular Dynamics (SPEADMD) model provides a basis for molecular modeling of thermodynamic and transport properties. It is based on Discontinuous Molecular Dynamics (DMD) and second order Thermodynamic Perturbation Theory (TPT). DMD simulation is applied to the repulsive part of the potential, complete with molecular details like interpenetration of the interaction sites, 110 degree bond angles, branching, and rings.<sup>1,2</sup> The thermodynamic effects of disperse attractions and hydrogen bonding are treated by TPT. This approach accelerates the molecular simulations in general and the parameterization of the transferable potentials in particular. Transferable potentials have been developed and tested for over 200 components comprising 22 families. These families include thiophene, phosphate, fluorocarbon, alcohol, amine, aromatic, and ring compounds to name just a few examples.<sup>3,4</sup>

One advantage of step potentials is that they offer the prospect of setting the step depths without preconceived notions regarding the shape of the potential. For example, the Lennard-Jones potential constrains the potential to reach a minimum at  $1.112\sigma$  and to decay as  $r^{-6}$  with increasing radial distance,  $r$ . In the case of perfluorocarbons, we find that the minimum of the potential is reached at roughly  $1.5\sigma$ , with the range from  $\sigma$  to  $1.5\sigma$  acting as a soft “shoulder” region which is neither repulsive nor attractive. This shoulder region is necessary to explain the unusually high heat of vaporization of perfluorocarbons while maintaining relatively high vapor pressures.

Coincidentally, the zero shoulder also explains the weak mixture interactions between perfluorocarbons and n-alkanes. The potentials for n-alkanes have been found to follow trends more similar to the Lennard-Jones potential.<sup>2</sup> The explanation derives from assuming the Lorentz-Berthelot combining rule to describe site-site interactions between corresponding steps. This leads to  $E_{ijk} \sim \text{SQRT}(E_{iik} * E_{jjk})$ , where  $E_{ijk}$  is the depth of the potential well between sites  $i$  and  $j$  in the  $k$ th step. For steps at short range, the alkane steps are at their deepest, but the perfluorocarbon interactions are zero, making the mixed interaction zero. For steps at long range, the perfluorocarbon steps are deep, but the alkane interactions are weak, making the mixed interaction weak.

The bases for these conclusions are presented with extensive reference to molecular simulations of mixtures and experimental data for vapor pressure of C2-C8 perfluorocarbons and mixed phase vapor-liquid and liquid-liquid equilibria.

### Reference:

- (1) Cui, J.; Elliott, J. R., Jr *J. Chem. Phys.* **2001**, *114*, 7283.
- (2) Unlu, O.; Gray, N. H.; Gerek, Z. N.; Elliott, J. R. *Ind. Eng. Chem. Res.* **2004**, *43*, 1788.
- (3) Gray, N. H.; Gerek, Z. N.; Elliott, J. R. *Fluid Phase Eq.* **2005**, *Vol 228-229C*, 147.
- (4) Baskaya, F. S.; Gray, N. H.; Gerek, Z. N.; Elliott, J. R. *Fluid Phase Eq.* **2005**, *236*, 42.

# Density Functional Theory Calculations for the Comparison of Hydrogen Flux Between Pd-alloy Membranes

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<sup>1</sup>Dept. of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA

<sup>2</sup>National Energy Technology Laboratory, Pittsburgh, PA

## Abstract

The possibility of using hydrogen as a fuel source has attracted widespread attention. Current methods for hydrogen production yield a mixture of gases that must be separated in order to obtain pure hydrogen. Metal membranes are one method to achieve this separation at the high temperatures that are relevant to coal gasification applications. Pd membranes are known to be capable of purifying H<sub>2</sub> from a gas mixture, yet there have also been many problems associated with these membranes. A potential solution to problems associated with pure Pd membranes has been the development of Pd-based alloys. Experimental testing of the many possible Pd-based alloys has been strongly limited by the time and expense associated with these tests. Theoretical methods that can give accurate predictions regarding the properties of these alloys would hence be of considerable value. Density Functional Theory (DFT) calculations using the Vienna *Ab Initio* Software Package (VASP) were performed to investigate the solubility and the diffusion of atomic hydrogen through the bulk of Pd alloys as the initial steps towards the analysis of the flux of hydrogen through alloy membranes. DFT calculations were performed for interstitial H in pure Pd and in AgPd, CuPd, and RhPd alloys. Cluster expansion techniques were used to derive accurate lattice gas descriptions of H site energies and the activation energies associated with site to site hopping from our DFT results. These lattice gas models allow the solubility and diffusion of hydrogen in each material to be predicted as a function of temperature. From this information, it is possible to draw conclusions regarding the performance of these materials as H<sub>2</sub> separation membranes.

# The Influence of Critical Cavities on Homogeneous Bubble Nucleation: A New Picture of Bubble Formation?

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A recent study of cavity formation in model superheated liquids (Punnathanam and Corti, 2003, *J. Chem. Phys.* **119**, 10224) verified the existence of a so-called critical cavity: superheated liquids containing cavities (spherical regions devoid of particle centers) greater than the critical size were found to be thermodynamically unstable. In addition, the size of the critical cavity was found to be a lower bound to the size of the critical bubble (the saddle point on the free energy surface of bubble formation), while the reversible work of forming the critical cavity was found to be a tight upper bound to the reversible work of forming the critical bubble (a crucial quantity appearing in the expression for the rate of bubble nucleation). Taken together, these two bounds plausibly suggest that the free energy surface of bubble formation, characterized by a bubble with a given number of particles  $n$  contained within a given volume  $v$ , should be quite different from the standard description of this surface. For example, one suspects that for any  $n$  each bubble will have its own critical size, larger than both the radius of the critical cavity and the critical radii for smaller  $n$ , beyond which any attempted increase in the volume of the bubble will cause the superheated liquid to become unstable. Consequently, a line of instabilities should appear beyond the bubble nucleation activation barrier. If, in turn, these instabilities are found to reside near the saddle point on the free energy surface, the molecular mechanism of bubble nucleation and growth may be quite different from previous descriptions.

To investigate in more detail the above conjecture, we adapt density functional theory (DFT) to calculate the  $(n, v)$  free energy surface of reversible bubble formation for the pure component superheated Lennard-Jones liquid. The new DFT calculations, which constrain the number of particles located inside the bubble for a fixed radius, confirm that after the free energy barrier has been surmounted the free energy surface abruptly ends along a locus of instabilities. In contrast to the classical picture of bubble nucleation, in which the surface continues indefinitely and describes the rapid, though reversible, growth beyond the barrier, the DFT results suggest that liquid-to-vapor liquid nucleation is more appropriately described by an “activated instability”. We also present molecular simulation results that validate the DFT predictions. Furthermore, the free energy surface reveals that the saddle point, which still corresponds to the critical bubble, is not the only pathway a bubble embryo may take in order to cross the activation barrier. The ridge corresponding to the maximum free energy for each  $n$  that leads to the critical bubble is not steep, suggesting that an embryo will more likely than not surmount the barrier along pathways that do not pass through the saddle point. We discuss the implications of this flat ridge for the mechanism of bubble nucleation near the thermodynamic spinodal.

# First Principles Investigation of Adsorption and Dissociation of Hydrogen on the Mg<sub>2</sub>Si Surface

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<sup>1</sup>Chemical and Petroleum Engineering Department, University of Pittsburgh, Pittsburgh, PA-15261

<sup>2</sup>Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA-15213

<sup>3</sup>National Energy Technology Laboratory, Pittsburgh, PA-15236

## Abstract

MgH<sub>2</sub> is a light-weight metal hydride having a storage capacity of 7.7 wt%. However, the heat of reaction for this hydride is too high so that hydrogen is not released until unacceptably high temperatures. For example MgH<sub>2</sub> has a H<sub>2</sub> vapor pressure of 1 bar at 275 °C. Vajo and coworkers (JPCB, 108, 13977, 2004) have demonstrated that MgH<sub>2</sub> can be destabilized by adding Si, resulting in the reaction  $2\text{MgH}_2 + \text{Si} = \text{Mg}_2\text{Si} + 2\text{H}_2$ . This destabilized reaction has a heat of reaction about one-half that of direct decomposition of MgH<sub>2</sub>, on a per mole of H<sub>2</sub> basis. However, Vajo et al. were unable to observe the reverse reaction,  $\text{Mg}_2\text{Si} + 2\text{H}_2 = 2\text{MgH}_2 + \text{Si}$ , even though the computed thermodynamics indicate that the reaction is favorable. We have used electronic density functional theory (DFT) calculations to investigate the adsorption and dissociation of H<sub>2</sub> on the clean and oxidized Mg<sub>2</sub>Si surfaces as a first step in examining the hydrogenation cycle. The surface energies of different low-index surfaces are examined. It was found that the (-110) surface is the best of all the surfaces tested. The adsorption energies are calculated for H atoms and H<sub>2</sub> molecules on these surfaces to identify the most favorable binding sites and geometries. The energy barriers for hydrogen dissociation on clean surface along two different pathways have been computed, which are 39.8 kJ/mol and 47.2 kJ/mol, respectively, after zero point vibrational energy corrections. The hydrogen dissociation processes are also investigated on different oxygen coverages of Mg<sub>2</sub>Si(-110) surfaces. The energy barrier of hydrogen dissociation on 2/3 ML coverage surface increases to 80.0 kJ/mol. Furthermore, there are no energetic favorable sites for hydrogen atoms at oxygen coverage up to 5/4 ML. The calculation results show that hydrogen decomposition should happen on the clean Mg<sub>2</sub>Si surface at room temperature but that surface oxidation is the probable reason why hydrogen is not observed experimentally.

## Phase Behavior and $T_g$ in CO<sub>2</sub> – Polymer Systems

Dehua Liu, Mike Noon\*, David L Tomasko  
*Department of Chemical and Biomolecular Engineering,  
The Ohio State University, Columbus, OH 43210*

\* Speaker

As an environmentally benign solvent, supercritical CO<sub>2</sub> has found many applications in the polymer industry and fast-growing pharmaceutical and bioengineering fields. However, fundamental knowledge and thermodynamic modeling of CO<sub>2</sub>-polymer binary systems is still far behind the pace of industrial process development. With the goal of supporting ongoing work in CO<sub>2</sub>-aided polymer blending, foaming and bio-impregnation, the CO<sub>2</sub> solubility, PVT properties of CO<sub>2</sub>-polymer mixtures, and CO<sub>2</sub>-induced  $T_g$  depression were investigated with specifically developed techniques. The major polymers of interest include *Polystyrene* (PS), *Poly(methyl methacrylate)* (PMMA), and biodegradable *Poly(DL-lactide-co-glycolide)* (PLGA). Both gravimetric and barometric methods were combined together to obtain the amount of CO<sub>2</sub> sorbed into polymer matrix at various temperatures and CO<sub>2</sub> pressures up to 1500psia. However, the swelling of polymer upon the sorption of CO<sub>2</sub> is always an unknown parameter in most of current CO<sub>2</sub> solubility measurements, which leads to error in the solubility evaluation. In this work, pendant drops of polymer were imaged in a customer-designed high pressure and high temperature view cell and the volumetric changes of drop when exposed to external CO<sub>2</sub> environment was recorded with a CCD digital camera. By conducting Axisymmetric Drop Shape Analysis (ADSA), the real time PVT behavior of binary CO<sub>2</sub>-polymer systems was deduced and further used to correct the CO<sub>2</sub> solubility values.  $T_g$  depression of polymer as a result of CO<sub>2</sub> sorption was also investigated by high pressure DSC. The Sanchez-Lacombe EOS was applied separately in correlating the experimental data of CO<sub>2</sub> solubility, volumetric dilation and  $T_g$  depression, and the interaction parameters between CO<sub>2</sub> and polymer were deduced individually. The applicability and accuracy of S-L EOS in describing CO<sub>2</sub>-polymer binary system are discussed based on the correlation results.

## CO<sub>2</sub>-Induced Surface $T_g$ Reduction of Polymer and Theoretical Modeling

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Currently, CO<sub>2</sub> is experiencing the advances in modifying polymer surface property on nanoscale inspired by its successes in bulk polymer processing, such as interfacial bonding for assembling tissue scaffolds and improving biocompatibility of polymer biomedical devices. A thorough understanding on the effects of CO<sub>2</sub> on surface properties is in a demand and proves to be a tough challenge. Even for pure polymer, the anomalous dynamic behavior of nanoscale surface from bulk phase was not widely recognized until about a decade ago. In this work, we first investigated the surface  $T_g$  behavior of Polystyrene(PS) by the AFM technique we developed. In brief, the gold nanoparticles with uniform size were deposited on polymer surface and then subject to thermal and/or CO<sub>2</sub> treatment. By detecting the embedding depth of particles, the condition where the glass transition occurs could be revealed. In this way, we identified the surface  $T_g$  of pure PS, and its variation as external CO<sub>2</sub> pressure. A thermodynamic model that is capable of profiling the mass density near the surface and mapping the entropy distribution was developed by combining gradient theory, the Gibbs-DiMarzio  $T_g$  criterion and SLEOS. It clearly shows that, even at temperatures lower than bulk  $T_g$ , there is a surface liquid-like layer with reduced density at the scale of 1nm which serves as the origin of dynamic enhancement. The layer is temperature and CO<sub>2</sub> pressure dependent, whose thickness is in good agreement with experimental determinations and molecular simulations. The associated fast mobility could penetrate into the polymer bulk phase at the scale of tens of nanometers via intramolecular chain connection and intermolecular entanglement.

title: Environmental influence on structural properties of polyelectrolyte brushes: effect of geometry, acidity, and salinity.

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Abstract:

Cylindrical weak polyelectrolyte brushes form a model system for the description of the properties of aggrecan, which is one of the main components of cartilage. Likewise they are able to describe polymer coated nanotubes. The structural and thermodynamical properties of these cylindrical weak polyelectrolytes brushes are studied with a molecular density functional theory incorporating the acid-base equilibrium as well as the molecular properties (size and shape) and the dielectric environment. To investigate the effect of geometry also planar and spherical polyelectrolyte brushes are studied. The coupling between geometry, acidity, salinity, and dielectric environment is investigated. The change in dielectric environment in a polymer brush is shown to have negligible effect upon the conformational structure. Changing the salt concentration and pH of the solution has a profound effect on the structural properties of the polymer brush. Moreover, it is demonstrated that these effects are highly dependent upon the geometry of the brush. Planar brushes behave quite differently from cylindrical or spherical brushes.

## Pressure Denaturation of Proteins: A Molecular Dynamics Study

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Studies on the effects of high pressures on biological systems are important from fundamental and applied perspectives. High hydrostatic pressures lead to denaturation of proteins. This behavior is counterintuitive because self-assembled macromolecules like proteins with a well-packed core, in principle, are expected to undergo mechanical compression and further tightening of the core with increasing pressure. Experiments show that the pressure-induced unfolded conformations of proteins are more compact than the thermally denatured proteins and retain elements of secondary structure. The mechanism of this behavior is, however, yet to be determined. Small solute studies indicate that hydrophobic interactions are weakened at high pressures and solvent-separated configurations are stabilized relative to contact configurations. To extend this understanding to realistic systems such as protein-water systems, simulations of solvated proteins at different pressures are required. However, it is not possible to sample the entire folded-to-unfolded trajectory using brute-force molecular dynamics. Thus, we need to develop novel methods to generate pressure-unfolded structures of proteins. To this end, we have developed an algorithm called *forced solvent insertion method* to generate pressure unfolded conformations. To demonstrate the utility of this method, we have applied it to the protein Staphnuclease. Using the unfolded conformations of pressure-denatured Staphnuclease obtained by our method we calculated the structural characteristics of the pressure-unfolded protein (radius of gyration and secondary structure elements) and thermodynamic characteristics of the pressure unfolding process: volume change and the Gibbs free energy change of unfolding. The results are in good agreement with the experimental data, indicating that the methodology developed in the present work captures both the structural and thermodynamic aspects of pressure unfolding of proteins. Our study suggests that the mechanism of pressure unfolding involves penetration of water into the hydrophobic core of protein, which leads to the swelling of the hydrophobic core and subsequent unfolding of the protein. Consequently, pressure-unfolded structures are more compact than thermally denatured proteins. The availability of pressure-unfolded structures from molecular simulations provides insights into the factors that contribute to pressure-stability of proteins as well as protein unfolding pathway.

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**Phase Equilibria of Mixtures of Amines with Alcohols, Ketones and Nitriles**  
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Amines are organic derivatives of ammonia and form structural moieties for a variety of drugs commercially available in the market. The presence of lone pair of electrons on the nitrogen atom makes it a suitable donor of electrons for hydrogen bonding, which influences the thermodynamic properties of amines. Amines have complex phase diagrams with other fluids like alcohols, nitriles and ketones. Diethylamine exhibits binary polyazeotropy with methanol. This phenomena represents a condition for which more than one stable azeotrope exists for a given temperature and pressure. The complexity is compounded when the system shows a temperature dependence on type of azeotropic behavior. This system displays multiple (minimum pressure and maximum pressure) azeotropy at 398 K but only shows a minimum pressure azeotrope at 348 K and 297 K. A variety of hydrogen bonding occurs for this system involving N, O, and H atoms. Diethylamine forms a maximum pressure azeotrope with acetone and also with acetonitrile.

In this work, histogram-reweighting Monte Carlo simulations in the grand canonical ensemble are used to determine the vapor-liquid coexistence curves, vapor pressures and critical points for pure component diethylamine and acetonitrile as well as mixture pressure composition diagrams. The TraPPE force field is used to describe the interactions in diethylamine, acetonitrile, acetone and methanol. Non-bonded interactions are represented by Lennard-Jones (LJ) potentials and partial charges, while harmonic potentials are used to control bond angle bending. The united-atom approach for diethylamine and acetonitrile has small deviations on the prediction of pure component phase diagram compared to the explicit atom representation originally used in the parameterization of the force fields. For acetone and methanol the force field parameters developed under the united-atom scheme was used. The TraPPE force field predicts a maximum pressure azeotrope for diethylamine+methanol for all temperatures studied. This contradicts experimental findings, where a double azeotrope is seen for 398 K, and minimum pressure azeotropes are seen at other temperatures. The TraPPE-UA force field is able to predict the maximum pressure azeotrope for the diethylamine + acetonitrile mixture, while it fails to predict the maximum pressure azeotrope in the diethylamine+acetone system. Simulations in the isobaric-isothermal ensemble were used to determine the microscopic structures predicted by TraPPE at different temperatures and corresponding pressures for the three binary mixtures. Radial distribution functions extracted from the NPT simulations showed evidence of self-association as well as cross association of the molecules by hydrogen bonding. Methods of improving the phase equilibrium predictions are discussed.

# Effect of Partial Charge Parameterization on the Phase Behavior of Dimethyl Ether

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April 21, 2006

## Abstract

Within the petrochemical industry, the conversion of methanol, from coal, to a gasoline additive or as fuel itself has sparked interest. However, the high toxicity and relatively low energy content of methanol have prompted interest in the conversion of methanol to dimethyl ether (DME) for use in automotive fuels. As part of this task, accurate vapor-liquid equilibrium data are required for neat DME as well as mixtures of DME with hydrocarbons and CO<sub>2</sub>.

In this work, the effect of partial charge distribution on the predicted vapor-liquid equilibria of neat DME and DME+CO<sub>2</sub> mixtures is investigated. Starting with parameters given by the Transferable Potentials for Phase Equilibria (TraPPE), new partial charge distributions are derived with guidance from a CHELPG analysis performed on ab initio calculations performed at the HF/6-31+g(d,p) level of theory and basis set. Lennard-Jones parameters are re-optimized such that the deviation of simulation from experimental saturated liquid densities and vapor pressures is minimized. Histogram-reweighting Monte Carlo simulations in the grand canonical ensemble are used to determine the vapor-liquid coexistence curve, critical properties and normal boiling point for DME for a series of partial charge distributions. Similar calculations are used to determine the pressure-composition behavior of DME+CO<sub>2</sub> from 319 K to 360 K. Overall, the results of simulation for our reparameterized force fields are in close agreement with experiment for both the pure component and mixture calculations.

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## Geometric Model of Depletion Forces in Hard-Sphere Colloidal Dispersions Exposed to Various Surfaces

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Colloidal particles exhibit the remarkable ability to self-assemble, suggesting that colloids could be used as templates for complex microstructures, precursors for advanced materials, or even as end products themselves. Precise control of colloidal self-assembly, however, relies upon accurate knowledge of the forces between colloids and between colloids and surfaces, such as electrostatics or hydrodynamic mediated interactions. Another important class of forces, known as depletion forces, is induced by asymmetries in the local arrangement of colloids (or non-adsorbing polymers) about other larger colloidal particles. If the colloids behave in a hard-particle-like manner, i.e., no interaction beyond their impenetrable hard cores, the depletion forces arise solely as a result of entropic considerations. As recently suggested (Dinsmore et al., 1996, *Nature* **383**, 239), passive structures etched into the walls of containers can create entropic potential fields of sufficient range and magnitude such that the motion and position of large colloids can be effectively controlled, thereby offering a straightforward method for the production of novel materials.

Depletion forces between colloids and surfaces, typically flat walls, have been calculated with models spanning from, for example, simple excluded volume arguments (Asakura and Oosawa, 1954, *J. Chem. Phys.* **22**, 1255), to density functional theory (Götzelmann et al., 2003, *Europhys. Lett.* **63**, 233) and to scaled particle theory (Corti and Reiss, 1998, *Mol. Phys.* **95**, 269). The simpler models, while qualitatively useful and easily applied to various surfaces, predict only attractive depletion forces and/or fail to accurately describe complex depletion effects. Conversely, the elaborate methods provide more accurate descriptions of depletion forces but are often limited in application due to the impracticalities that arise when numerically solving their equations.

We therefore present a geometrically-based model of the entropic forces that develop between particles and surfaces in hard-sphere colloidal dispersions that is more descriptive than various simple models while still being solvable for a large variety of surface shapes. In our method, where we utilize a highly accurate approximation first put forth within the successfully updated version of scaled particle theory (Heying and Corti, 2004, *J. Phys. Chem. B* **108**, 19756), the local colloidal arrangement that determines the entropic potential is calculated from the change in the volume of overlap between the smaller particle's equivalent cavity and the larger colloid or surface of interest. Our method is more general than that of Asakura and Oosawa (AO), though it does reduce to the AO approximation in a limiting case. With an appropriately chosen known reference state, our approach yields predictions that agree well with molecular simulation results performed at experimentally relevant conditions (unlike AO). For more complex geometries such as corners and wedges, our method predicts topologically interesting entropic potential force fields that yield a new description of colloidal motion near surfaces. We also input our depletion force predictions into Brownian Dynamics simulations and track the motion of individual colloids to study deposition pathways and structural lifetimes near a geometrically structured surface. The success of our model, given its relatively straightforward nature, suggests that our method could potentially be used in conjunction with the above simulations to engineer surfaces in order to achieve desired colloidal behavior.

Abstract for MTSM 2006:

## **Solvation potentials for polymer chains in solution**

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The conformation of a polymer chain in solution is intrinsically coupled to properties of the solvent. In much of the theoretical work on polymers in dilute solution the effects of solvent are treated in an implicit fashion: thus one studies an isolated chain interacting via an effective site-site potential. Although a formally exact mapping is possible between the chain-in-solvent and corresponding effective-potential-chain, this mapping involves a many-site solvation potential which is not practical to compute. Thus, one generally resorts to a two-site potential approximation. Here we examine the validity of this two-site approximation for short hard-sphere and square-well chain-in-solvent systems. We demonstrate that at least for some systems, the two-site approach is rigorously valid, however a set of two-site potentials (rather than a single effective potential) is required.

## **Solid-liquid Interfacial Energy of the Polymorphs of Paracetamol**

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Polymorphism changes the effectiveness of a drug, and it is often a problem in drug development. Different polymorphs often have different thermodynamic stabilities in a solvent. One method to determine the thermodynamic stability is by observing the solid-liquid interfacial energy of the polymorphs. In this study, the solid-liquid interface of paracetamol (p-Hydroxyacetanilide) crystals in water is investigated using molecular dynamics simulation. Monoclinic (form I) and orthorhombic (form II) are the known polymorphs of paracetamol. The potential energies of the crystal-water interface for these polymorphs are calculated and the interfacial energies of the  $(\bar{1}00)$ ,  $(100)$ ,  $(0\bar{1}0)$ ,  $(010)$ ,  $(00\bar{1})$ , and  $(001)$  faces of each crystal structure are examined to study the relative interaction between the crystal and water at different crystal faces.

# **Extending the transferable potentials for phase equilibria force field to aromatic heterocycles**

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## **Abstract**

The majority of pharmaceutical compounds contain heterocyclic aromatic rings. The ability to accurately model these compounds is essential for predicting important physical properties such as solubilities, octanol/water partitioning coefficients, and melting points for the drug molecules. To this end, transferable potentials for phase equilibria (TraPPE) force field is extended to aromatic compounds containing nitrogen, oxygen, and sulfur hetero atoms. All the atoms are modeled explicitly, and partial atomic charges are obtained using continuum solvation model with octanol as the solvent. Monte Carlo simulations in Gibbs ensemble are carried out to determine the Lennard-Jones parameters that reproduce critical temperature, saturated vapor pressure, and saturated liquid densities. The errors in liquid density, critical temperature, and normal boiling point are less than 2%.

## Phase Equilibria for Bio-derived Chemicals

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Phase equilibria information, particularly vapor-liquid equilibrium (VLE) is critical for reliable distillation process design. Reliable experimental data are desirable, but also a good method to estimate vapor pressure is needed for bio-derived chemicals. This work reports on both experimental and modeling efforts. We report on the development of an apparatus for P-x-y measurements and provide data for the systems: ethyl lactate + water, ethyl lactate + ethanol, oligomerization of lactic acid, ethanol + triethyl citrate. We compare models with experimental data for the system ethanol + ethyl lactate + water + lactic acid + oligomers of lactic acid and esters. A second goal of this work is to use the Step Potential Equilibria and Dynamics (SPEAD) molecular dynamics method for vapor pressure prediction. The compounds of interest involve new functional groups that have not been parametrized for accurate pair potentials. We report on progress to apply SPEAD to molecules with secondary alcohols and esters needed for modeling the compounds.

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## Molecular simulation of the self-assembly of bent-core molecules at water surfaces

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Bent-core (“banana-shaped”) molecules exhibit chiral anti-ferroelectric mesophases, which are promising for a range of applications including light shutters and memory devices. This liquid crystal alignment can be directed by self-assembly at a water surface. To illuminate the self assembly process, molecular dynamics simulations are carried out on systems composed of 4,6-dichloro-1,3-phenylene bis[4-(4-n-subst.-phenyliminomethyl)benzoates] molecules adsorbed on water surfaces. The simulation results elucidate both the intra-molecular and inter-molecular structure and dynamics associated with the self-assembly.

## **Entropy driven liquid-liquid phase separation in a mixed bola-linear lipid layer.**

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Archeobacteria are microorganisms that can survive and proliferate in a variety of extreme habitats, such as high salt concentration environments, anaerobic conditions, and high or low temperatures. A membrane composed of bolaform lipids is what gives the bacteria these unique survival qualities. The nature and composition of this membrane has not yet been elucidated. In this work, the phase stability of a lipid layer that is a mixture of linear and bola lipids is studied using a molecular theory. The effects of changing the fraction of bola lipids, as well as the length of the hydrocarbon chain of the linear lipids are studied. A phase separation between two liquid phases is found in the mixed layer. The two phases are a thin bola-rich lipid layer and a thicker linear-rich membrane. The thin layer is mainly composed by bola molecules whose polar heads are in opposed hydrophilic regions of the membrane (spanning configuration). The phase separation is only present when the hydrocarbon chains of both molecular species have comparable sizes. The driving force for the phase separation is the size matching between the hydrophobic chains of the linear lipid and the spanning bola lipid.

# **Effect of Torsional Potential on the Phase Behavior of Organic Compounds**

Speaker: Damien A. Bernard-Brunel

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In molecular mechanics force fields, the total energy of the system is determined through the summation of all inter- and intra molecular interactions in the system. Intermolecular interactions typically consist of dispersive and Coulombic terms, while intramolecular interactions contain terms for bond stretching, bond bending and rotation around various dihedral angles. These intramolecular potentials are used to control the conformational behavior of the molecule of interest. Although significant research has been performed in the generation of potentials for intramolecular interactions, it is unknown how sensitive thermophysical properties, including phase behavior, are to the parameters used to control the conformation behavior of the molecules.

In this work, configurational-bias Monte Carlo simulations in the grand canonical ensemble are combined with histogram-reweighting techniques to assess the effect of torsional potential parameters on the predicted vapor-liquid equilibria for a variety of organic compounds. Molecules investigated in this work include linear and branched alkanes, alcohols, ketones and ethers. The Transferable Potentials for Phase Equilibria (TraPPE) force field was used as a reference calculation. Using the same non-bonded parameters as defined by the TraPPE force field, new parameters were derived for torsional potentials such that the energy barrier between the various dihedral conformations was lower than the temperature at which the simulations were performed, allowing for a nearly flat distribution of sampled dihedral angles. Additional calculations are performed where dihedral angles are sampled from a Gaussian distribution. Simulations where dihedral angles were sampled from a flat distribution were found to yield results identical to that of the original TraPPE force field. Simulations that sampled from a single Gaussian distribution of dihedral angles resulted in an underprediction of the saturated liquid densities.

# Effect of confinement on the solubility of NaCl in water

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## Abstract

Molecular dynamics simulations have been used to investigate the effect of confinement in a graphite slit pore on the solubility of Sodium Chloride (NaCl) in water. The intermolecular potential used consists of Lennard-Jones and Electrostatic terms, (primitive model) for ions and SPC/E for water. Simulations of NaCl solution at various concentrations (0.31 to 9.76 mole%) with different pore sizes were carried out. Density profiles as well as radial distribution function of water and electrolyte ions were then examined. Our results showed that confinement can significantly affect the solubility of NaCl in water.

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# **Interfacial phenomena and critical region behaviour and of fluids: a common approach by first-order mean spherical approximation**

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Interfacial phenomenon represents the basic transition from vapour to liquid or vice versa, which has been concerned for a long time. Critical behaviour was studied recently for its unusual departure from our classic thermodynamics. Prerequisite for both of them is phase separation and thus there are some microscopic relations between two phenomena. With recent progress in statistical thermodynamics, we can now describe them in molecular level. In the microscopic description, radial distribution function (RDF) takes major role for classical phase equilibria and DCF is responsible for molecular correlation in interfacial properties and fluctuation in phase critical behaviour. To describe two phenomena quantitatively, first-order mean spherical approximation (FMSA) is one very favourable choice. FMSA is developed from an analytical solution to the Ornstein-Zernike equation, in which RDF and DCF are obtained analytically for classic fluids. The FMSA method has been applied to studying both physical phenomena by combining with density function theory. Its quantitative performance is proven by predicting the accurate critical point, surface tension as well as density profile. Additionally, FMSA treats homogeneous and inhomogeneous states as one framework, which is hardly expected from any other theories. Simplicity in FMSA formulation makes its computation as easy as by traditional mean-field theory, in which only qualitative performance can be expected.

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**Molecular Simulation of Carbon Dioxide Adsorption  
in Chemically and Structurally Heterogeneous Porous Carbons**

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2006 Midwest Thermodynamics and Statistical Mechanics Conference

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Capture of carbon dioxide from fossil fuel power plants via adsorption and sequestration of carbon dioxide in unmineable coal seams are achievable near-term methods of reducing atmospheric emissions of this greenhouse gas. To investigate the influence of surface heterogeneity upon predicted adsorption behavior in activated carbons and coal, isotherms were generated via grand canonical Monte Carlo simulation for CO<sub>2</sub> adsorption in slit-shaped pores with underlying graphitic structure and several variations of chemical heterogeneity (oxygen and hydrogen content), pore width and surface functional group orientation. Adsorption generally increased with increasing surface oxygen content, although exceptions to this trend were observed on structurally heterogeneous surfaces with holes or furrows that yield strongly adsorbing preferred binding sites. None of the heterogeneous pore structures investigated adsorb carbon dioxide more strongly than a planar, homogeneous graphitic slit pore.

## On the disappearance of the liquid state for Buckminster Fullerene models

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There has been controversy in the literature whether  $C_{60}$  does condense to a liquid or not. The common belief is it does, based on statistical mechanical studies using both molecular simulation and theory. Since the molecule has the shape of a soccer ball, the accepted model is a  $\infty$  center Lennard-Jones potential, where the interaction sites are smeared over the surface of a super-sphere. This model is known as the Girifalco potential for  $C_{60}$  with a particular radius of the soccer ball. In this work, we consider the entire class of Girifalco-type potentials for a fine grid of reduced radii of the super-spheres, and we determine the vapor-liquid-solid phase equilibria by using second virial coefficients in the gas, thermodynamic perturbation theory in the liquid, and the Lennard-Jones-Devonshire theory in the solid. As a result, the liquid phase disappears at a radius slightly larger than that established for  $C_{60}$ .

## Reverse Non-Equilibrium Molecular Dynamics (RNEMD) for Viscosity Calculation

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Collective transport properties, such as the shear viscosity, are among the most challenging properties to compute with molecular simulation methods. These properties are traditionally calculated using two main methods: equilibrium molecular dynamics (EMD) and non-equilibrium molecular dynamics (NEMD). Estimation of viscosity by EMD usually requires the calculation of the Green-Kubo integral of the off-diagonal elements of a pressure tensor. While rigorous, this technique requires extraordinarily long simulations to obtain reliable results, and the computational burden increases dramatically as viscosity increases. NEMD methods such as the SLLOD algorithm can offer computational advantages over equilibrium methods, but still require long simulations, particularly for large molecules. Also these methods get particularly difficult to apply for charged systems. Recently, in our group we developed a new method to estimate the shear viscosity, called Momentum Impulse Relaxation (MIR). Also, Müller-Plathe *et.al.* have developed a method for estimation of shear viscosity and thermal conductivity, called Reverse Non-Equilibrium Molecular Dynamics (RNEMD). Both of these methods have an advantage that they obtain the viscosity by applying stress to the system and measuring the (easily obtained) velocity profile.

In the RNEMD method, we divide the simulation box into slabs along one of the directions (say 'y' direction). The velocity (say 'x' component of it) of the fastest atom from the bottom slab is exchanged with the velocity of the slowest atom in the middle slab. Thus, the momentum flux is imposed on the system in an unphysical way and the system responds by transporting momentum in the opposite direction. This sets up a velocity profile, the slope of which gives the viscosity.

In this study, we validate this method by applying it Lennard-Jonesium, *n*-hexane, water and molten sodium chloride. After validating this method we use it to compute the viscosity of the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([emim][Tf2N]).

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Title: Cluster Formation and Corralling Effect in Two Dimensional Binary Mixtures

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Abstract: We study the formation of ordered clusters of nanoparticles in binary mixtures in two dimensions using Monte Carlo simulations. The necessary conditions for the formation of highly ordered clusters are: the size mismatch between the two components and a long-range soft repulsions between the large particles. The degree of order of the clusters depends on the concentration of large particles. We show the conditions upon which compression of the layer induces squeezing out of the large particles from the interface. Our findings explain recent experimental observations on poloxamer-lipid mixtures and provide guidelines for how to form ordered clusters of nanoparticles in two dimensions.

# A Molecular Approach for the Design of Surfactants for Hydrofluoroalkane-based Pressurized Metered-Dose Inhalers

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## Abstract

Perhaps the most notable challenge in the transition from CFC- to hydrofluoroalkane (HFA)-based pressurized metered-dose inhalers (pMDIs) is the extremely low solubility of the FDA-approved alkyl-based surfactants in HFAs. Such problem arises due to the mismatch between the hydrogenated tails of the surfactants and the polar and semi-fluorinated nature of the propellants. Amphiphiles are used in most solution and dispersion formulations to improve dosage reproducibility and for valve lubrication. Co-solvents are generally required in order to enhance the solubility of the FDA-approved surfactants. However, co-solvents not only alter the vapor pressure of the mixture, thus affecting the aerosol respirable fraction, but also decrease the overall chemical and physical stability of the formulation. Such problems have sparked a recent surge in the search for new surfactants for pMDIs. In order to overcome the existing reformulation problems, one should be able to quantitatively relate the chemistry of the surfactant tail group to its HFA-philicity, which in turn dictates its solubility and ability to stabilize dispersions in HFAs.

In this work, we propose a general molecular-based approach for the design of solvophiles. Microscopic information obtained from *ab initio* calculations and chemical force microscopy (CFM) is used to address surfactant design for HFAs. Binding energies for HFAs and perhydrogenated, perfluorinated and polar tail chemistries are reported. The same tail moieties are investigated by CFM in 2H,3H-perfluoropentane (HPFP), a model hydrofluoroalkane. The complementary *ab initio* calculations and CFM results provide quantitative information that allows one to discriminate candidate HFA-philic tails based on their chemistry. The results are expected to be applicable to all pMDI-based formulations, which generally require amphiphiles as excipients.

*Keywords:* *ab initio* calculations; chemical force microscopy; hydrofluoroalkanes; inhalers; pressurized metered-dose inhalers (pMDIs); surfactants; drug delivery.

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# **A Molecular Dynamics Investigation of Bubble Nucleation at a Solid Surface**

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NPT and NP<sub>zz</sub>T molecular dynamics simulations of Lennard-Jones atoms were used to compare superheated homogeneous and heterogeneous nucleation on a smooth fcc (100) surface. In the heterogeneous cases, the solid-fluid attraction was varied. Multiple simulations were used to determine nucleation times from which nucleation rates were estimated using a transient nucleation model. Nucleation rates at multiple temperatures were used to estimate free energy changes. We found that the free energy barrier was highest in the homogeneous case as expected. The free energy barrier increased with increasing solid-fluid attraction with limiting behavior in the heterogeneous cases. The temperatures required to get nucleation rates in the homogeneous case similar to the heterogeneous cases were about 10 K higher. The effective free energy change in the homogeneous case was up to a few hundred times higher than heterogeneous cases when scaled to the same temperature using the classical free energy form. Varying the system size, thermostatting method, and barostat time constant affected quantitative results, but not the qualitative trends.

## Diffusion Studies of Water and n-Alkane Molecules in Carbon Nanotubes

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Previous simulations have predicted that the transport rates of light gases in nanotubes are orders of magnitude faster than in any other known porous materials, e.g., zeolites.<sup>[1]</sup> Nanotube membranes are thus predicted to have faster fluxes than crystalline zeolite membranes.

Hinds and coworkers have synthesized multi-walled carbon nanotube/polymer composite membranes.<sup>[2]</sup> Their experimental work has demonstrated that the transport rates of gases and liquids through nanotube membranes are much faster than can be expected from Knudsen or hydrodynamic (Haagen-Poiseuille) flow. Hinds et al. attribute the extraordinarily high fluxes to the nearly frictionless nature of the carbon nanotube walls, thus verifying the predictions made from simulations.

Simulations have been carried out for complex molecules, such as water and alkanes, diffusing through carbon nanotubes. However, all previous simulations of complex molecules in nanotubes have only reported self diffusivities. Three types of diffusivities are important in both experiments and simulations, namely, self, corrected, and transport diffusivities. The transport diffusivity, also known as the Fickian diffusivity, is most useful for real systems, such as pressure driven flow across a membrane. We have calculated all three diffusivities for water, n-hexane, and n-heptane in different SWNTs using equilibrium molecular dynamics simulations. We examine the effects of the nanotube radius, helicity, loading, and temperature on the diffusivities.

Barriers to entry into nanotubes may dominate over diffusion through nanotubes. We have used simulations to probe the mechanism of alkane diffusion from the nanotube surface into the internal sites. Various alkane coverages and SWNT bundle configurations have been considered.

\* Speaker

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## **Estimation of Critical Points from the Virial Equation of State**

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Mayer sampling refers to a collection of methods adapted from applications involving the calculation of free energies, and applied to the calculation of cluster integrals that appear in many theories of statistical mechanics. We have used Mayer sampling to determine virial coefficients (up to  $B_6$ ) for a Lennard Jones fluid, 2-center Lennard Jones plus point quadrupole, water and short square-well chains.

This paper describes our work to use the virial coefficients to calculate the critical point. While the virial equation of state fails at the critical point, in some cases it has been found to provide a useful approximation of the critical temperature. We examine the effect and relative importance of each successive term in the virial series on the predicted critical point for the systems listed above. By considering a wide range of fluids, we address the appropriateness of using a virial series approach to calculating the critical point.

Topic: **Density functional approach for modeling polymer CO<sub>2</sub> interfaces**

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### **Abstract**

Over the past decade supercritical CO<sub>2</sub> has emerged as one of the most significant solvents for polymer processing. The success is attributed to fourfold advantage of scCO<sub>2</sub> solvent system viz. ‘tunability’ to desired temperature and pressure, affinity to organic molecules, low viscosity leading to enhanced mobility, and environment friendly nature. Despite the advances, thorough understanding of polymer CO<sub>2</sub> interfaces has remained an unresolved challenge. The problem becomes more significant considering the recent extension of scCO<sub>2</sub> to nanoscale manufacturing. This study is aimed at bridging the gap between the theoretical and experimental knowledge through molecular level analysis of the system. We analyze the structure of polymer gas interface in the framework of statistical mechanics by using polymer density functional theory (PDFT). The basic rationale of this theory is to calculate the free energy of the binary system and the density profiles of the components at equilibrium. Free energy of the system helps us calculate its equilibrium properties like solubility of polymer in CO<sub>2</sub>, glass transition at polymer gas interface, and T<sub>g</sub> depression by CO<sub>2</sub>. Glass transition calculations will remain the main focus of our study and we will use Gibbs Di-Marzio theory (GDT) for this calculation. According to GDT, configurational entropy of a polymer becomes zero at glass transition. It is interesting to note that the surface T<sub>g</sub> of a polymer is not a fixed quantity, rather there exists a distribution of T<sub>g</sub> in the top layer (few nm). Due to size restrictions it is difficult to analyze such a distribution using experimental techniques. Evaluating the change in configurational entropy in position space will help in overcoming this problem.

Before studying the interfacial properties, it is essential to have a good insight into the phase behavior of the binary system. Hence phase diagram calculation is a vital starting point in our study. Currently we are analyzing the phase behavior to obtain the binodal and spinodal curves, and the vapor-liquid critical point of the binary system. The calculation will also help us validate the interaction parameters and establish bulk system boundaries.

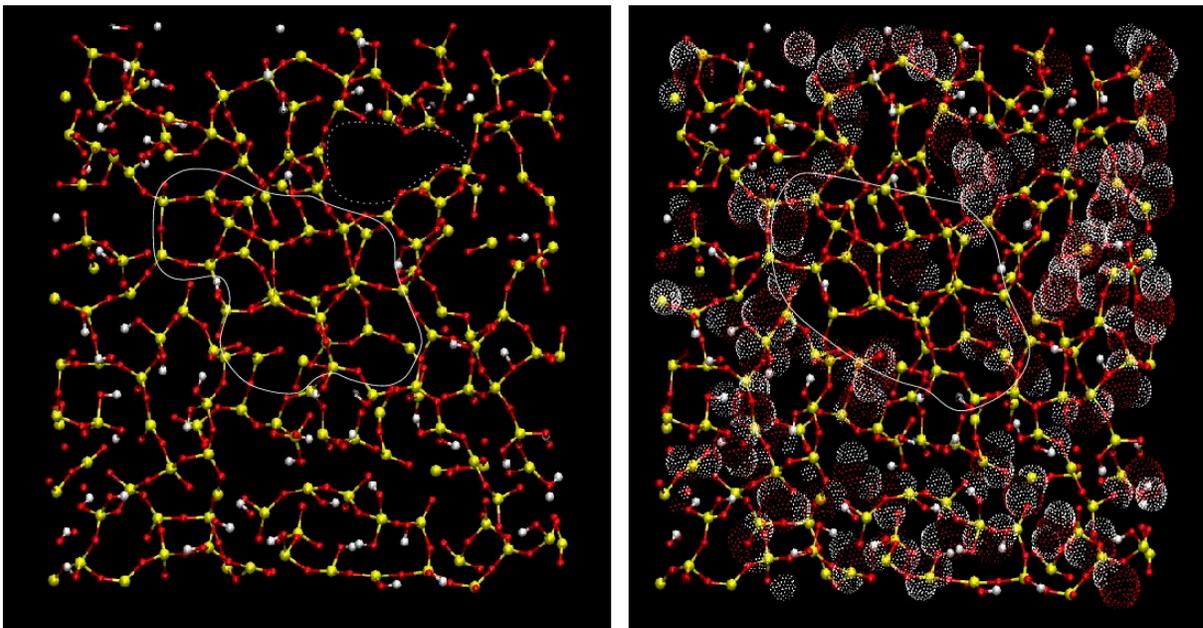
## A Model for the Water-Amorphous Silica Interface

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Amorphous silica-water interfaces are found ubiquitously in nanoscale devices, including devices fabricated from silica as well as from silicon that acquire a surface oxide layer. The surface silanol groups serve as hydrogen-bonding sites for a variety of chemical species, and their reactivity enables convenient chemical modification, making silica surface strategic in bio-sensing applications.

We have taken the popular BKS model for bulk silica and extended it to describe the hydroxylated amorphous silica surface, and its interaction with water. The parameters of our model were determined using *ab initio* quantum chemical studies on small fragments. Our model will be useful in empirical potential studies, and as a starting point for *ab initio* molecular dynamics calculations. We view the model presented here as an initial version to be calibrated and refined by comparison with *ab initio* simulations and experiment. A significant extension of our potential to treat dissociation of silanol groups is currently under development. At this stage, we present a model for the undissociated surface.

Our calculated value for the heat of immersion,  $0.6 \text{ Jm}^{-2}$ , falls within the range of reported experimental values of  $0.2\text{-}0.8 \text{ Jm}^{-2}$ . We also study the perturbation of water properties near the silica-water. The disordered surface is characterized by regions that are hydrophilic and hydrophobic as seen in the figure below where water molecules cluster near regions with higher silanol density (hydrophilic regions). We have also simulated flow of water past an amorphous silica surface in non-equilibrium molecular dynamics simulations.



Solid line shows hydrophobic patch and dotted line shows a void on the surface permitting water accessibility into the surface

# **Hydrogen bond topology, new interpretations of order/disorder transitions in ice, and the behavior of defects in a disordered ice lattice**

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Among the various phases of ice, certain transitions involve ordering or disordering of H-bonds: Ih/XI, III/IX, and VII/VIII, for example. The mechanism of these phase transitions is intimately linked to defects in ice because there is an interplay between defects and the hydrogen bond order/disorder of the water molecules that surround them. For instance, ice Ih transforms to ice XI only when doped with hydroxide ions, but many questions linger about the mechanism, since experiments suggest that ionic defects are not mobile near the transition temperature.

In this talk, theoretical methods are introduced which are capable of treating H-bond order/disorder in various ice phases, and the interaction of the H-bond topology with defects. The theory uses input from periodic electronic density functional calculations for small unit cells to parameterize interactions in terms of the H-bond topology. With the parameterization, statistical mechanical calculations can be done for large simulation cells. We are able to describe the small energy differences among the innumerable H-bond configurations possible in a large simulation cell, either to describe phase transitions in pure water or to elucidate the interaction between defects and the topology of the surrounding ice lattice. Results are presented for ionic and Bjerrum defects in ice Ih, and for the phase transitions listed above. Particular emphasis will be given to the ice III/IX transition, and the behavior of hydroxide in ice Ih. We also present predictions of proton ordering phase transitions for ice V and VI.

# Dynamics Within the Hydration Layer Surrounding a Protein: The Origin of Slow Relaxation Dynamics

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The hydration dynamics of water in the immediate vicinity of a protein surface is critical to understand its structure and biological function. Time-dependent fluorescence Stokes shift experiments have revealed relaxation dynamics following photo-excitation near small molecules in water occurring on a time scale of several picoseconds. In contrast, near proteins the dynamics can take tens of picoseconds or longer. The interpretation of these results is currently a matter of controversy. Bagchi, Zewail and coworkers attribute this several picoseconds to “bound water” in the protein force field. In their model, the observed long time scale for relaxation dynamics is set by the time for exchange of waters between a bound state near the protein and a “quasi-free” state. Halle and Nilsson oppose this model, and propose that the slow relaxation dynamics observed for proteins in aqueous solvents reflects the dynamics of the hydrated protein.

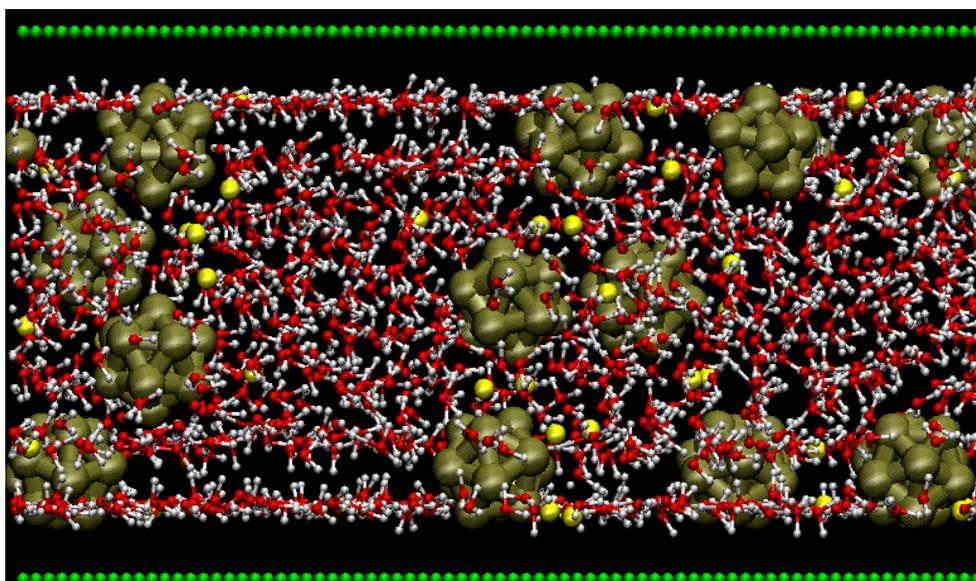
In this work, we theoretically distinguish between the two proposed mechanisms by comparing the relaxation dynamics near myoglobin following photo-excitation of the full dynamical system to the dynamics in which all the protein atoms are frozen. By freezing the protein, we isolate and quantify the inherent dynamics of the aqueous solvent. This allows us to unambiguously decide between the two proposed mechanisms for slow relaxation dynamics. Protein dynamics is found to be essential for slow relaxation dynamics. The slow features of water reorientation dynamics, previously attributed to water immobilization near the protein broken only by limited residence time in the hydration layer, is reinterpreted in terms water polarization near the protein modulated by protein motion and water diffusion within the hydration layer.

# Molecular Simulations of Electrokinetically Driven Nanofluidic Phenomena

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A system consisting of macro-ions, counter-ions and water within a nanochannel was studied by non-equilibrium molecular dynamics methods. Flow in the system was induced by an electric field along the channel direction. The system was simulated with constant temperature and pressure using a Berendsen thermostat and barostat.



We investigated fundamental properties of electrophoretic and electroosmotic transport in nanochannels. Electrophoretic transport is shown to proceed by infrequent hops between the ion atmospheres of oppositely charged particles. We observed electroosmotic flow of an electrically neutral fluid confined by neutral walls, a result that is contrary to the predictions of the classical continuum theory. The effect arises from molecular effects, namely the segregation of macro- and counter-ions near the walls which give rise to an electrical polarization within the fluid. The relationship of this polarization to the  $\zeta$ -potential and to the flow rate is demonstrated. We also observed a “clumping” effect by strong electrostatic correlations between like-charged polyanions.

Preliminary simulations of electrokinetic phenomena in a nanonozzle geometry are presented. These simulations will lay the groundwork for future studies of biomolecular transport in nozzle systems with realistic walls.

# **The Water-Carbon Dioxide Interface Under Sub-Critical Conditions: A Molecular Simulation Study**

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The properties of the interface between water and carbon dioxide are very important in many areas of chemistry and biophysics, such as chromatography, electrochemistry and ion transport across membranes. The principal technological reason to study the water-CO<sub>2</sub> interface is the need to understand the mechanism by which water-CO<sub>2</sub> clathrates are formed, a process of interest because ocean sequestration has been proposed as a means of disposing of carbon dioxide. While the nucleation of clathrate hydrates within the liquid has been examined, the behavior of carbon dioxide near or at the water interface has received less attention. Despite the importance of this interface, knowledge about the structural properties near the interface, such as density profile and molecular orientation, is still very scarce.

In this study, the structural properties of the interface of water and sub-critical CO<sub>2</sub> under different temperatures and pressures were investigated by means of MD simulations, with the SPC model for water and EPM2 model for CO<sub>2</sub>. A capillary wave analysis was used to elucidate properties relative to the true interface. The density profile across the water-CO<sub>2</sub> interface indicates that the interface is highly structured. At higher pressures, a layer of CO<sub>2</sub> close to the liquid-like density is observed. The orientational distribution of water and CO<sub>2</sub> molecules in different layers has been accumulated, indicating that water dipoles and CO<sub>2</sub> molecules tend to lie parallel to the interface.

# **Estimation of Solubility of small gases in polar solvents by molecular dynamics simulations**

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## **Abstract**

Molecular dynamics simulations have been carried out to estimate the Henry's constant and solubilities of a range of small molecules in benzene, ethylene oxide and monoethanolamine, using a scheme that closely mimics experiment. For the solubilities of nonpolar gases in nonpolar solvents and polar gases in polar solvents, our results showed that binary interaction parameters were not needed. Our results also show that the method is reliable for polar-nonpolar systems, which are generally notoriously difficult to investigate using classical methods. However, here the usual Lorentz-Berthelot rules required binary interaction parameters. These were found to be essentially constant for all systems studied here. After validating the results for several systems which experimental data are available, we have also been able to estimate the solubility of systems for which experiments have yet to be carried out. We will present results for four such systems, oxygen in ethylene oxide, and argon, nitrogen, oxygen in monoethanolamine. We have also developed a simple correlation for the dependence of Henry's constants on the binary interaction parameters.

# **Connections between structural, thermodynamic, and kinetic properties of ions in aqueous solution**

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Quantification of local structural order provides an important tool in helping one understand the relationship between the macroscopic thermodynamic and kinetic properties of a system and its underlying microscopic structure. To better understand the physical picture behind ion solvation, we use orientational and translational order metrics that quantitatively describe the organization of water molecules in the vicinity of ions. A series of simulations are performed with varying ion charge and size. Thermodynamic solvation properties are calculated using transition matrix Monte Carlo simulations. Kinetic and structural properties are acquired from molecular dynamics simulations. We present results that show promising connections between macroscopic thermodynamic and kinetic properties and quantitative measures of solution structure.

# Using molecular simulation to explore the phase behavior of a simple model protein

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Many neurological diseases, cataracts, and sickle-cell diseases are linked to protein phase separation and aggregation. At the heart of these phenomena are protein-protein interactions. It is known that these interactions are influenced by numerous physiological factors such as salt concentration, pH, and temperature. Modest variation of any of these factors can lead to significant changes in protein phase stability and behavior. For example, George and Wilson have found that there exists a small range of protein-protein attraction leading to crystallization. It has also been found by ten Wolde and Frenkel that protein crystallization and nucleation may be enhanced by liquid-liquid phase separation. In this work, we take steps to better understand the relationship between the macroscopic phase behavior of a protein solution and its underlying microscopic interactions by studying a simple model for lysozyme introduced by Carlsson et al. The model describes lysozyme as a spherical protein with a hard core, a single spherically-symmetric hydrophobic interaction, and a collection of embedded charge residues. Charge locations are based on information from the protein data bank and the charge values are pH dependent. We will present results that indicate how protein phase behavior evolves with solution conditions based on grand canonical transition matrix Monte Carlo simulations.

## **Determining contact angles from molecular simulation**

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Fluids in contact with attractive surfaces exhibit a wide range of phenomena. Knowledge of these specific behaviors is used to advance technologies ranging from microfluidics to stain defending textiles. For one to describe these phenomena it is necessary to characterize the fluid with its descriptive interfacial tensions and contact angle. Here we propose and validate a new computational technique for determining contact angles and interfacial tensions. Molecular simulations are performed in the grand canonical ensemble with a simulation cell that contains one or two adsorbing surfaces. Transition matrix Monte Carlo methods are used to calculate the grand potential at a given activity, which is compared to the equivalent bulk value to determine the relevant interfacial tension. The contact angle is related to the interfacial tensions through Young's equation. The efficacy of the proposed method is examined by calculating the interfacial properties of a Lennard-Jones fluid in contact with an atomistically-detailed substrate. Good agreement is found between our results and those from a traditional pressure-tensor based technique.

## Efficient Evaluation of Solid-Phase Free Energies

Nancy Cribbin  
Andrew Schultz  
Kenneth M. Benjamin  
David A. Kofke

State University of New York at Buffalo

In order to predict the form of a stable crystalline polymorph, one compares the free energy of each form, and selects the one with the lowest free energy. Although this ignores kinetic influences in crystallization, this procedure provides important information for polymorph prediction. However, current methods take only the potential-energy contribution to the free energy into account, and ignore the entropic contribution. This is done because calculating the entropy is difficult to do rigorously; approximations using lattice dynamics are sometimes applied but the accuracy of these approaches is uncertain. When there is little difference between the potential contributions to the energy, it is hard to distinguish which of the polymorphs is the most stable.

To calculate a free energy, given a reference system of known or easily calculated energy, we calculate the difference in free energy between the system of interest and the reference system, which in effect gives the free energy of the system of interest. For this work, we use a harmonic reference system with spring constants given to match configurational correlations measured in the target system.

We consider two approaches to compute the free energy difference between the target and reference systems. Direct perturbation is not effective, so we examine the performance of overlap sampling approaches, and Bennett's method in particular. Second, we examine the accuracy of the Normal Mode Monte Carlo (NMMC) method, which, is an approximate treatment that assumes that normal mode coordinates are independent not only in the harmonic system, but also in the reference. This technique provides much better sampling accuracy than direct or staged-perturbation methods, but the approximations inherent in its formulation have not been well tested.

We study these approaches as applied to a system of hexane-like molecules modeled with a hard sphere interaction potential. We compare the results of both methods with each other, and with accurate free energies for similar system that were calculated by the Monson group using other methods.

# **Molecular Dynamics Simulation of Molten Silicates at Ultra High Pressures.**

**David B. Rear, Department of Chemical Engineering  
James A. Van Orman, Department of Geological Sciences  
Daniel J. Lacks, Department of Chemical Engineering  
Case Western Reserve University**

Molecular dynamics simulations were performed for the Mg-Si-O system at a variety of high temperatures (~3000K) and pressures (~60 Gpa). Molten silicate systems are known to show a degree of tetrahedral order between the SiO<sub>2</sub> groups (DeBenedetti et al., Physical Review E, 66, 11202, 2002.) resulting in a polymer-like chains at certain temperatures and pressures. This presentation will show what macroscopic conditions produce different degrees of order and affect viscosity and the overall diffusion coefficients of silicon and oxygen in the melt.

# Ludwig-Soret effect in benzene-alkane mixtures

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Thermal diffusion or the Ludwig-Soret effect describes the diffusive mass transport in a liquid mixture subject to a temperature gradient. This mass transport leads to the formation of a concentration gradient whose magnitude and sign is described by the Soret coefficient. Thermal diffusion has long been used as an effective tool for separating mixtures of isotopes in the gas phase. However, the effect is not well understood for liquid mixtures where, in general, it is not even possible to predict which component will be enriched in the colder regions of the fluid (by convention, this component has a positive Soret coefficient).

In this work, we investigate the Soret effect in liquid mixtures of benzene with linear ( $n$ - $C_nH_{2n+2}$  with  $n = 7, 9, 11, 13, 15,$  and  $17$ ), and branched (isomers of heptane and octane) alkanes. Thermal diffusion forced Raleigh scattering experiments were performed on binary benzene-alkane mixtures to determine Soret coefficients for a range of compositions and temperatures. For the linear alkanes the observed Soret coefficients are negative and increase with increasing chain length and benzene concentration. For the branched isomers, the observed Soret coefficients increase with increasing number of methyl side groups. In order to describe the Soret effect in these mixtures, we have extended our recently developed two-chamber lattice model for thermodiffusion and find that both orientation-dependent interactions and packing effects play an important role in the thermodiffusion of benzene-alkane mixtures.

# **A Monte Carlo Simulation Study of the Mechanical, Conformational and Thermodynamic Properties of Networks of Helical Polymers**

By Gustavo A. Carri and Richard Batman

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The main focus of this talk will be the mechanical, conformational and thermodynamic properties of networks made of helical polymers. The results I will present were obtained using a combination of single chain Monte Carlo simulations based on the Wang-Landau algorithm and the Three-chain Model of rubberlike elasticity. We have found that the stress-strain behavior of these networks has novel features not observed in typical networks made of synthetic elastomers. Specifically, the stress-strain relationship is non-monotonic; behavior that correlates with the one of the helical content. This result is rationalized by the elongation-induced formation and melting of the helical structure of the polymer. In addition, a non-monotonic behavior is also observed in the thermo-elastic behavior of the network. The origin of this behavior is traced to the induction and melting of helical beads by the application of a fixed strain and the simultaneous reduction in temperature. We have also studied the thermodynamic behavior of these networks and found that the entropy and heat capacity also display a non-monotonic dependence on temperature and strain. Our study shows that the entropy is controlled by the helical content whenever the latter is significant. Otherwise, the entropy corresponds to the one of a network made of random coils. In addition, the study of the heat capacity shows that strain shifts the helix-coil transition temperature significantly. Other results will also be discussed.