

TAWTSM 2010 Preliminary Program

1. EXPERIMENTAL DETERMINATION OF PHASE ENVELOPE DATA FOR SYNTHETIC NATURAL GAS MIXTURES	3
<i>Andrea del Pilar Tibaduiza, Diego E. Cristancho, Ivan Mantilla, Mert Atilhan, Saquid Ejaz, Diego Ortiz-Vega and Kenneth Hall*</i>	3
2. GENERALIZED PHASE BOUNDARY DETERMINATION ALGORITHM FOR MULTICOMPONENT MIXTURES	3
<i>Diego O. Ortiz-Vega, Diego E. Cristancho, Kenneth R. Hall*, Gustavo A. Iglesias-Silva⁺</i>	3
3. TRENDS IN THE ATHERMAL ENTROPY OF MIXING OF POLYMER SOLUTIONS.....	4
<i>Amir Vahid, Neil H. Gray, and J. Richard Elliott[†]</i>	4
4. ON THE ASYMPTOTIC PROPERTIES OF A HARD SPHERE FLUID.....	4
<i>Isaac Sanchez and Jang S. Lee</i>	4
5. APPLICATION OF INTERFACIAL-SAFT (ISAFT) DENSITY FUNCTIONAL THEORY IN MULTISCALE MODELING OF INHOMOGENEOUS SYSTEMS.....	5
<i>Zhengzheng Feng, Christopher Emborsky, Kenneth Cox, Walter Chapman</i>	5
6. SELF-ASSEMBLY OF AMPHIPHILIC MOLECULES OR NANOPARTICLES USING THE I-SAFT DENSITY FUNCTIONAL THEORY	5
<i>Christopher Emborsky, Kenneth Cox, Walter Chapman</i>	5
7. A SYSTEMATIC COARSE-GRAINING METHOD TO PREDICT THE PROPERTIES OF POLYMER NANOCOMPOSITES	6
<i>Youthachack Landry Khounlavong, Venkat Ganesan, Victor Pryamitsyn,</i>	6
8. ATOMISTIC SIMULATIONS OF ALTERNATIVE PROTON EXCHANGE MEMBRANES FOR FUEL CELL APPLICATIONS.....	6
<i>Chetan V. Mahajan, Venkat Ganesan,</i>	6
9. FREE ENERGY FOR SEPARATION OF CELLOBIOSE MOLECULE FROM A LAYER OF CELLOBIOSE	7
<i>Suma Peri, M. N. Karim and Rajesh Khare</i>	7
10. LOCAL CHAIN DYNAMICS IN HIGHLY CROSS-LINKED EPOXY NEAR GLASS TRANSITION	7
<i>Po-Han Lin and Rajesh Khare</i>	7
11. DISPERSION OF POLYMER-GRAFTED NANOPARTICLES IN POLYMER THIN FILMS	8
<i>David M. Trombly, Venkat Ganesan</i>	8
12. COMPOSITION AND CONCENTRATION ANOMALIES FOR STRUCTURE AND DYNAMICS OF GAUSSIAN-CORE MIXTURES	8
<i>Mark J. Pond,¹ William P. Krekelberg,¹ Vincent K. Shen,² Jeffrey R. Errington,³ and Thomas M. Truskett^{1,4*}</i>	8
13. CORRELATING TRACER PARTICLE DIFFUSIVITY WITH EXCESS ENTROPY.....	9
<i>James Carmer, Gaurav Goel, and Thomas Truskett</i>	9
14. CAVITY SIZE DISTRIBUTIONS AND DIFFUSIONS IN POLYIMIDES AND TR POLYMERS BY MOLECULAR SIMULATION.....	9
<i>Yingying JIANG*¹, Franklin Ted WILLMORE¹, and Isaac C. SANCHEZ¹</i>	9

Tentative Program

Plan A	Paper#
1/0/1900 8:30	1
1/0/1900 8:50	2
1/0/1900 9:10	3
1/0/1900 9:30	4
1/0/1900 9:50	5
1/0/1900 10:10	coffee
1/0/1900 10:30	6
1/0/1900 10:50	7
1/0/1900 11:10	8
1/0/1900 11:30	9
1/0/1900 11:50	lunch
1/0/1900 12:10	lunch
1/0/1900 12:30	lunch
1/0/1900 12:50	lunch
1/0/1900 13:10	10
1/0/1900 13:30	11
1/0/1900 13:50	12
1/0/1900 14:10	13
1/0/1900 14:30	14
1/0/1900 14:50	Adjourn

1. Experimental Determination Of Phase Envelope Data For Synthetic Natural Gas Mixtures

Andrea del Pilar Tibaduiza, Diego E. Cristancho, Ivan Mantilla, Mert Atilhan, Saquid Ejaz, Diego Ortiz-Vega and Kenneth Hall*

Thermodynamics Research Group
Texas A&M University
College Station, TX

Abstract

Phase envelope data for four synthetic natural gas mixtures have been determined using isochoric data. The characteristic of the isochoric apparatus and the procedure used for the determination of the saturation temperature and pressure data are described. A new methodology for determining saturation densities from isochoric data is proposed. Finally, the experimental results are compared to some equations of state commonly used in industry. These calculations were performed with a new computational tool developed in our research group for the determination of phase envelopes based upon Gibbs energy minimization.

2. Generalized Phase Boundary Determination Algorithm for Multicomponent Mixtures

Diego O. Ortiz-Vega, Diego E. Cristancho, Kenneth R. Hall*, Gustavo A. Iglesias-Silva[†]

*Artie McFerrin Department of Chemical Engineering
Texas A&M University
College Station, TX 77843-3122

[†]Departamento de Ingeniería Química
Instituto Tecnológico de Celaya
38010 Celaya, Guanajuato
México

Abstract

An improved method to determine phase boundaries for multicomponent mixtures is described. This technique uses procedures based upon Gibbs minimization that leads to a more efficient algorithm that is also able to converge closer to the mixtures critical point than other algorithms (e.g., *K*-value method). Moreover, all the curves reported correspond to stable points according to the stability analysis suggested by Michelsen that implies minimization of the tangent plane distance function. Several examples compare the efficiency of this technique to commercial programs that often fail at certain conditions around the critical point, cricondenbar and/or cricondentherm.

3. Trends in the Athermal Entropy of Mixing of Polymer Solutions

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

¹The University of Akron, Akron OH 44325 USA

²Chemstations Inc., 2901 Wilcrest Dr., Houston TX 77042 USA

Polymeric mixtures of hydrocarbons and alcohols have been simulated with discontinuous potential models to characterize the Helmholtz energy of the repulsive reference fluids. This quantity is equivalent to the athermal mixture entropy. The mixtures included small hydrocarbons with alcohols and n-alkanes, branched hydrocarbons, and aromatics with polymeric molecules of: n-alkanes, ethyl-styrenes, ethyl-propylenes, and isoprenes. We find that the athermal entropy of mixing deviates significantly from ideality, but still follows the van der Waals mixing formula and approach to an asymptote in the long chain limit. This leads to an accurate characterization of the entropic contribution to the χ parameter (χ^S) of Flory-Huggins theory for mixtures of all sizes, shapes, and compositions of molecular structures. A general rule is developed for predicting the athermal entropy of mixing based on knowledge of the volume ratios of the constituent molecules. Combined with the usual approach to characterizing the energetic contribution to the χ parameter, a complete formulation is provided for characterizing the mixture thermodynamics. The simulations are compared to SAFT, and Guggenheim-Staverman (GS) theories of polymer chains.

4. On the Asymptotic Properties of a Hard Sphere Fluid

Isaac Sanchez and Jang S. Lee

University of Texas at Austin

An analysis of the expected divergences in thermodynamic properties at the close-pack density ($\eta_{cp} = \pi 2^{1/2}/6$) along with the known virial coefficients up to 10th order, suggests a weak logarithmic singularity in the excess fluid entropy. The corresponding equation of state (EOS) also possesses a singularity at η_{cp} . The new EOS accurately describes extant molecular dynamics data up to the fluid-solid transition ($\eta \approx 0.494$) with differences of less than 1 part per thousand. This accuracy is maintained into the metastable fluid regime up to $\eta \approx 0.52$. In terms of accuracy, the new EOS is no better than Padé approximants, but the new EOS, unlike the Padé approximants, diverges at η_{cp} . In addition, a new order parameter is defined that enables all system configurations to be classified as either disordered or ordered. Monte Carlo simulations are used to determine this order parameter in the metastable fluid range. Using this new order parameter, evidence is presented to support a thermodynamic glass transition at $\eta_{cp} = 0.54$. With respect to this transition, congruence is found with the traditional ideas espoused by Gibbs & DiMarzio and Adam & Gibbs. It is the rapid disappearance of disordered (random) configurations with increasing density that drives the glass transition and slows the dynamics.

¹ The University of Akron

² Chemstations Inc.

* To whom correspondence should be addressed.

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

E-mail: jelliott@uakron.edu.

5. Application of Interfacial-SAFT (iSAFT) Density Functional Theory in Multiscale Modeling of Inhomogeneous Systems

Zhengzheng Feng, Christopher Emborsky, Kenneth Cox, Walter Chapman

Department of Chemical and Biomolecular Engineering,
Rice University, Houston, TX

Interfacial-SAFT (iSAFT) is a recently developed density functional theory, based on Wertheim's thermodynamic perturbation theory for association, which is computationally simple and thermodynamically consistent in describing structure and thermodynamic properties of polymeric fluids in inhomogeneous environments. In this work, we will present results from iSAFT calculations of the interfacial properties, phase behavior and microstructure of mixtures containing polymer-like molecules and colloidal-like particles. The versatility of the theory allows for a systematic investigation of such physical characteristics as size ratios, polymer chain length, intermolecular interactions, and chain heterogeneity. The results agree qualitatively well with experiments and various theories.

6. Self-Assembly of Amphiphilic Molecules or Nanoparticles Using the i-SAFT Density Functional Theory

Christopher Emborsky, Kenneth Cox, Walter Chapman

Department of Chemical and Biomolecular Engineering,
Rice University, Houston, TX

Abstract: The effects of an amphiphile (surfactant) or nanoparticle on the equilibrium structure and thermodynamic properties of systems containing chemically dissimilar species (e.g., oil and water) are largely governed by the structure of the amphiphile/nanoparticle and physical conditions of the system such as the pressure, temperature, and bulk solubility of the amphiphile/nanoparticle. Following justification of the interfacial statistical associating fluid theory (i-SAFT) density functional theory (DFT) approach against molecular simulation data for a model oil-water-surfactant system, a more extensive systematic study is carried out to analyze the role the amphiphile structure and concentration play in determining the equilibrium microstructure and interfacial tension. In addition, the surfactant-like behavior of different sized nanoparticles is characterized and compared with the surfactant behavior.

7. A Systematic Coarse-Graining Method to Predict the Properties of Polymer Nanocomposites

[Youthachack Landry Khounlavong](#), Venkat Ganesan, Victor Pryamitsyn,

The University of Texas at Austin, Austin, TX

It is well known that the properties of polymeric materials are influenced by multiple length and time scales that are intimately connected. This creates a problem for high molecular weight systems where the size and time requirements for atomistic simulations of such materials are pragmatically impossible to fulfill even for the upper echelon of supercomputers. On top of this, an added layer of complexity is introduced when predicting the properties of polymer nanocomposites (PNCs) due to the multi-component nature of the system. To deal with these issues, we propose a systematic coarse-graining method that extracts the essential atomistic details of a PNC and uses this information in simulations at the mesoscopic level, which have the capability of simulating longer times and larger lengths. This allows for the prediction of experimentally observable PNC properties which are based on an atomistic foundation. In our coarse-graining scheme, molecular dynamics (MD) simulations are performed to ascertain the atomistic information required to be matched at the mesoscopic scale, which information at this scale is obtained through dissipative particle dynamics (DPD) simulations. Our coarse-graining scheme is two-fold: (1) equilibrium coarse-graining is done on polymer-polymer and polymer-particle interactions via the well established iterative Boltzmann inversion method, and (2) dynamic coarse-graining is performed to obtain the parameters for the dissipative forces occurring between polymers as well as polymers and particles that are inherently generated when the resolution of the simulation is lowered. To check our coarse-graining method, rheological properties of the atomistic and mesoscopic scales are compared.

8. Atomistic Simulations of Alternative Proton Exchange Membranes for Fuel Cell Applications

[Chetan V. Mahajan](#), Venkat Ganesan,

Chemical Engineering, University of Texas at Austin, Austin, TX

SPEEK (Sulfonated Poly(ether ether ketone)) membranes constitute promising alternatives to nafion for DMFC(Direct Methanol Fuel Cell) applications. In this talk, the results of extensive all-atom simulations of water and methanol solvated SPEEK membranes are reported. We focus on key features of changes in structure, transport and the corresponding coupling between the structure and transport. Our simulations suggest that the membrane swells appreciably with increasing water and methanol contents. The sizes of water clusters in the membrane are found to be appreciably lower than that reported for nafion in the literature, thus confirming experimental observations of narrower aqueous channels in SPEEK than nafion. The diffusivities of water, hydronium ions and methanol are also found to be lower than those published for nafion earlier, thus complementing experimental findings of lower penetrant mobility in SPEEK than nafion. Structural information pertaining to the relative locations of methanol and hydronium ions is determined.

9. Free Energy for Separation of Cellobiose Molecule from a Layer of Cellobiose

Suma Peri, M. N. Karim and Rajesh Khare

Department of Chemical Engineering
Texas Tech University

Enzymatic hydrolysis is a key step in the production of biofuels using the biochemical platform. The cellulase enzyme complex, which is used in the saccharification process acts synergistically to produce the reaction product, glucose, which can be fermented to ethanol. Cello-oligosaccharides which are the intermediate products formed during the process, are known to attach themselves to the cellulosic surfaces, thus reducing the rate of hydrolysis. In this work, we have investigated the energetics of separation of one cellobiose molecule (repeating unit in cellulose) from a layer of cellobiose molecules.

The umbrella sampling technique combined with the weighted histogram analysis method was employed to determine the free energy required for the separation of a pair of cellobiose molecules in water, as well as for the separation of a cellobiose molecule from the cellobiose layer surface. The potential of mean force (PMF) profile for the separation of a cellobiose pair in water exhibited a single minimum with a non-oscillatory profile; the depth of the free energy well for this process was 1.8 kcal/mol. The PMF profile for the separation of a cellobiose molecule from the cellobiose layer surface exhibited a strong minimum with a well depth larger than 20 kcal/mol. The higher value of the well depth in this case results from the increased number of attractive interactions between the cellobiose molecule being considered and the assembly of cellobiose molecules on the surface. The dynamics of the cellobiose molecule near the cellobiose layer surface was also studied using molecular dynamics simulations.

10. Local Chain Dynamics in Highly Cross-linked Epoxy near Glass Transition

Po-Han Lin and Rajesh Khare

Department of Chemical Engineering, Texas Tech University, Lubbock, TX

Cross-linked epoxy is widely used in aerospace and electronics applications. The highly cross-linked nature of these systems leads to different chain dynamics as compared to the linear polymeric systems. In this work, we have used molecular dynamics (MD) simulations to study the local chain dynamics in cross-linked epoxy near the glass transition temperature. The specific epoxy system studied consisted of diglycidyl ether of bisphenol-A (DGEBA) as the epoxy monomer and trimethylene glycol di-p-aminobenzoate (TMAB) as the cross-linker. Well-relaxed atomistic models of cross-linked epoxy were created using recently developed simulated polymerization approach. The glass transition temperature of these model structures was determined from MD simulation by monitoring their volume-temperature behavior in a stepwise cooling run. The chain dynamics of these systems were characterized by their local translational and orientational mobility. Furthermore, dynamic heterogeneity was studied by analyzing the spatial distribution of the mobile and immobile atoms in the system near the glass transition temperature.

11. Dispersion of Polymer-Grafted Nanoparticles in Polymer Thin Films

David M. Trombly, Venkat Ganesan

Chemical Engineering, University of Texas at Austin, Austin, TX

Effective dispersion of nanoparticles in polymer thin films is important for enhanced material properties, used for applications like organic electronic devices, sensors, and structural materials. Recent experiments on polymer-grafted nanoparticles dispersed in polymer thin films explored the entropically-driven phase behavior of the system as a function of the lengths of the grafted and free chains and the size of the particle compared to the sizes of each chain type. By modeling the interactions between a polymer-grafted particle and the substrate using self-consistent field theory, we capture the essential aspects of the system and report the theoretical phase behavior as a function of the key parameters. Because of the flexibility of our model for varying system parameters, it provides a helpful predictive tool for future experimental work on this system.

12. Composition and concentration anomalies for structure and dynamics of Gaussian-core mixtures

Mark J. Pond,¹ William P. Krekelberg,¹ Vincent K. Shen,² Jeffrey R. Errington,³ and Thomas M. Truskett^{1,4*}

¹Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712, USA

²Chemical and Biochemical Reference Data Division, National Institute of Standards and Technology, Gaithersburg, Maryland 02899-8320, USA

³Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, New York 14260-4200, USA

⁴Institute for Theoretical Chemistry, University of Texas at Austin, Austin, Texas 78712, USA

*Corresponding author – e-mail: truskett@che.utexas.edu

We present molecular dynamics simulation results for two-component fluid mixtures of Gaussian-core particles, focusing on how tracer diffusivities and static pair correlations depend on temperature, particle concentration, and composition. At low particle concentrations, these systems behave like simple atomic mixtures. However, for intermediate concentrations, the single-particle dynamics of the two species largely decouple, giving rise to the following anomalous trends. Increasing either the concentration of the fluid (at fixed composition) or the mole fraction of the larger particles (at fixed particle concentration) enhances the tracer diffusivity of the larger particles but decreases that of the smaller particles. In fact, at sufficiently high particle concentrations, the larger particles exhibit higher mobility than the smaller particles. Each of these dynamic behaviors is accompanied by a corresponding structural trend that characterizes how either concentration or composition affects the strength of the static pair correlations. Specifically, the dynamic trends are consistent with a single empirical scaling law that relates an appropriately normalized tracer diffusivity to its pair-correlation contribution to the excess entropy.

13. Correlating Tracer Particle Diffusivity with Excess Entropy

James Carmer, Gaurav Goel, and Thomas Truskett

Chemical Engineering, University of Texas at Austin

Previous work has shown that bulk dynamics can be correlated with structural and thermodynamic properties of the system. We extend these findings to include the infinite-dilution diffusivity of a single tracer particle. Using computer simulations, we explore how tuning the tracer-solvent interactions affects the dynamics of the tracer. Optimizing the tracer particle two-body contribution to excess entropy results in significant increases in tracer particle diffusivity. Further gains in dynamics were observed when the partial molar excess entropy of the tracer was maximized. While the impact of these optimizations becomes much greater at higher densities, we show that as the particle size is increased there exists a maximum in the relative increase that can be obtained. The potentials obtained through this optimization routine were then approximated by two different types of interaction potentials we see in real systems: Yukawa and polymer brushes. Our simulations show that increases in diffusivity were comparable to the original optimized potentials.

14. Cavity Size Distributions and Diffusions in Polyimides and TR polymers by Molecular Simulation

Yingying JIANG*¹, Franklin Ted WILLMORE¹, and Isaac C. SANCHEZ¹

¹ Dept. Of Chemical Engineering, University of Texas at Austin, Austin, 78751, USA

* Corresponding author. E-mail: sanchez@che.utexas.edu; Tel.: 512-471-5014; Fax: 512-471-5014.

Speaker: Yingying JIANG

Abstract:

The objective of this study is to investigate the cavity size distributions and gas diffusion in polyimides and TR polymers by molecular simulation. The diffusion and the solubility coefficients of small gas molecules (N₂, H₂, CO₂, CH₄) in HAB-6FDA [HAB-6FDA, synthesized from 3, 3'-dihydroxy-4, 4'-diphenylene diamine (HAB) and hexafluoropropane dianhydride (6FDA)] are investigated by experimental techniques. Simulation results are in good agreement with experimental data.

Keywords: cavity, free volume, distribution.

Presentation Preference: Oral Presentation