Société Française
de Génie des Procédés
La science des procédés face
aux enjeux industriels et sociétaux

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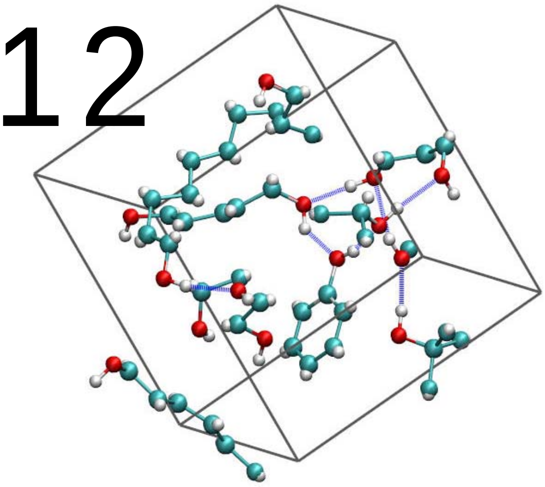
InMoTher 2012



19-20 March 2012 - Lyon, France

Industrial use of Molecular Thermodynamics.

Program and Book of Abstracts

EFCE
Event # 700

Held under the auspices of the:
EFCE Working Party on
Thermodynamics and Transport Properties.

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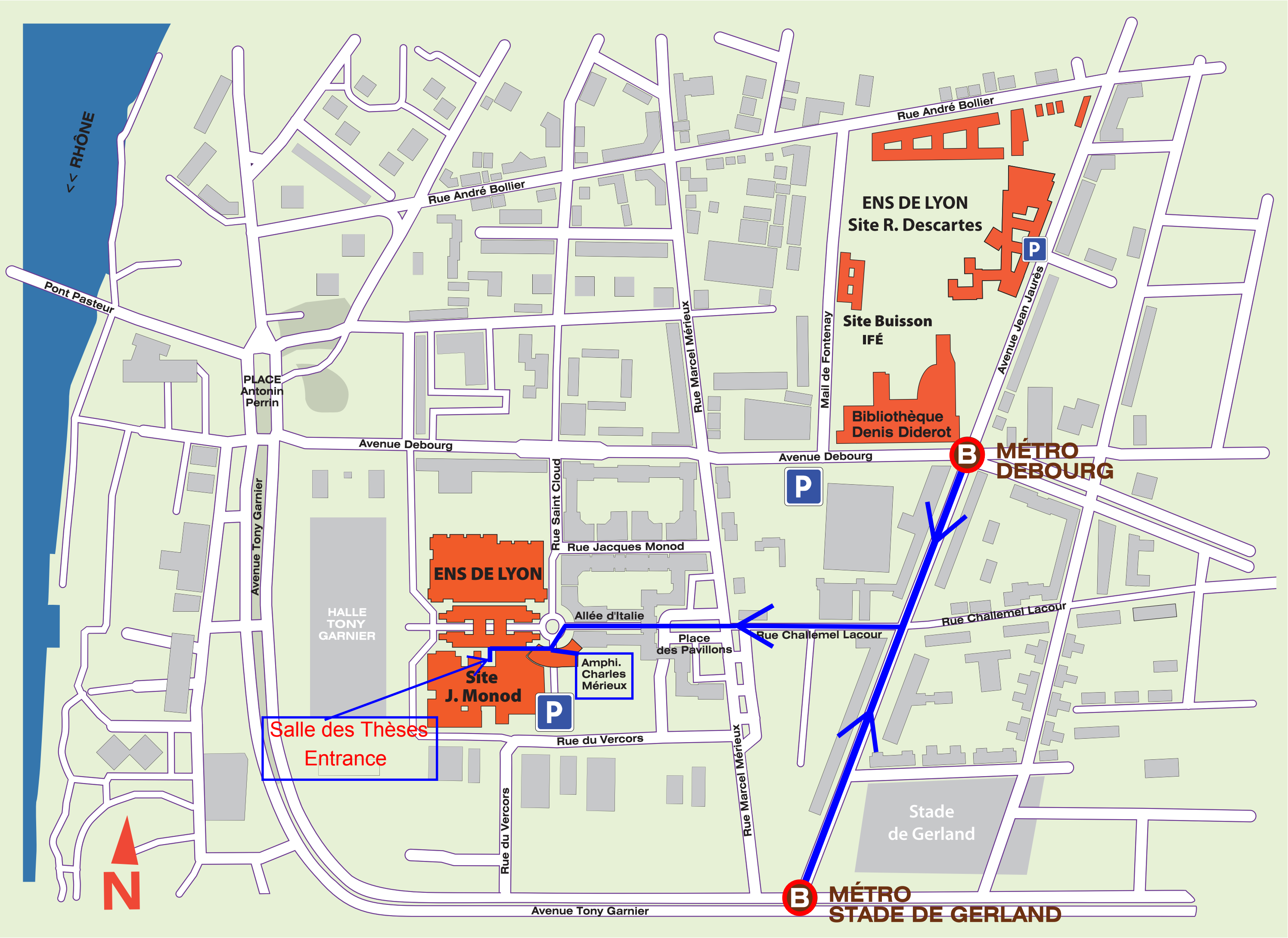

INMOTHER 2012

LYON

19-20, March 2012

FINAL PROGRAM

AND

BOOK OF ABSTRACTS

Editorial

EFCE Working Party on Thermodynamics and Transport Properties

ProcessNet Working Party on Thermodynamics

Dear colleagues and friends,

It is an honor for me to welcome you in Lyon for the Workshop that is initiated by the European Working Party on Thermodynamics and Transport Properties.

The history goes back to a mail that I received from Professor Ioannis Economou, the working party chairman who regrets that he cannot join us today. He asked me to follow up on the successful meeting that was organized jointly by the German ProcessNet working party in Würzburg, in March 2010. Our French national working party that is part of the SFGP (Société Française du Génie des Procédés) was thus recognized for our success in creating a community around the topic of Thermodynamics for the process industry. One major effort that we have tried to realize was to make sure that industrial partners actively participate in our events.

Hence, the way we envisioned this meeting was not as another occasion to share the latest academic developments –such meetings are essential-, but rather as a workshop, that is a place where our industrial colleagues can share their needs and vision and place them in perspective with the new developments that today’s molecular based tools can offer.

This objective has led to a number of proposals that I hope you will appreciate:

- Three academic speakers have been asked to present in plenary session the state of the art of the three main areas that are part of industrial molecular thermodynamics: Molecular and Ab Initio simulation, Molecular equations of state and Tools for Data Management.
- Six invited industrial speakers will show us how the use of molecular thermodynamics is essential in their business, using case-studies and success stories;
- Some industrial participants have chosen to share their opportunities and concerns through industrial booths or software presentations. The booths are located in the atrium and the timing and location of the software presentations is provided in your schedules;
- A round-table discussion, at the end of our workshop, will give the word to a panel of representatives of industrial users, industrial software providers and academic representatives. You will also have the opportunity to share your thoughts, either by taking the word on that occasion, or, time will probably be too short, by completing the sheet that you will be given, and providing your comments in writing.
- The conclusions of this workshop will be written down in a document that will be published in the OGST special issue (Oil & Gas Science & Technology) that will also present all the full length papers of the contributing authors to oral or poster presentations. Please do not forget the deadline for paper submission which is April 1st .

Editorial

I want now to thank the many people that have made this workshop possible. First and before all, Mrs Pascale Bridou-Buffet and Mr David Roig have been behind the scenes from the very beginning, by providing their expertise for all practical aspects. The organizing committee was further composed of Mr Patrice Meheux who represents the SFGP, principal organizer and financial warrant of the event, Prof. Jean-Noel Jaubert who has been a steady and reliable support, both for practical and scientific aspects and Dr. Richard Sass who represents both the European EFCE and the German community who co-organize this event through the ProcessNet working party.

A special thanks goes to Prof. Philippe Sautet who has opened the door of this prestigious research institution that is the ‘Ecole Normale Supérieure’. His contribution is both scientific, as an expert in the practical applications of quantum chemistry, as organizational, together with Anne-Gaelle Villatte, who has made sure that all local details could be solved.

I believe the organizing and scientific committees have worked jointly in very good conditions and, without naming all of them, I want to thank those who have contributed to the selection of papers, search for sponsors, promotion of the event or providing ideas.

The many sponsors that have contributed financially to this event are for us a sign that Molecular Thermodynamics, despite its rather fundamental scientific language, is a subject that industry is concerned with. We have two gold Sponsors, which are TOTAL and the Rhône-Alpes region, through the Axelera competitiveness cluster, and six silver sponsors which are CNRS, Air Liquide, BASF, Linde, Rhodia and, let me thank very specifically IFP Energies Nouvelles, my own company, who has provided me, through the Tuck foundation chair for biofuels thermodynamics, with the opportunity to spend quite some time for the organization of this event.

I want further to thank the organizers of the round-table discussion, Philippe Ricoux (TOTAL) and Mathias Brehelin (Rhodia), all the invited speakers for having accepted our invitation, all session chairs and all of you participants, speakers, poster presenters and attendants. It is thanks to all of you that this workshop can be successful.

Have a good workshop!

Lyon, March 19th, 2012
Jean-Charles de Hemptinne

Summary

InMoTher 2012
19-20 March 2012

Preliminary Program

Sunday, March 18th		
17:00	*19:00*	***Registration***
		Welcome reception

Monday, March 19th (AM)			
8:30	*9:00*	***Registration***	
9:00	*9:10*	***Opening***	
9:10	10:00	***Plenary Lecture*** ***Molecular Simulation of Phase Equilibria: Progress and Challenges.*** Prof. Athanassios Z. PANAGIOTOPOULOS - Princeton University **Chairperson**: Philippe UNGERER - Materials Design	
10:00	*10:30*	***Coffee break***	
		Session 1A (Amphithéâtre Mérieux) **Chairperson**: Maurizio FERMEGLIA - University Of Trieste	**Session 1B (Salle des Thèses)** **Chairperson**: Karel AIM - Institute of Chemical Process Fundamentals of the ASCR
10:30	11:00	***Invited Lecture*** ***Application of COSMO-RS in the Design of Ionic Systems.*** Steve LUSTIG - Du Pont	***Invited Lecture*** ***Are there Ways to Improve the Accuracy of predictive Methods in the field of Thermodynamic Properties?*** Rob MEIER - DSM
11:00	11:20	***Non-equilibrium Molecular Dynamics Simulation of real Fluids in Nanoporous Materials.*** Martin Thomas HORSCH (ref. 32)	***Molecular Thermodynamics of Quantum Fluids using the SAFT-VR approach with Quantum Corrections.*** Alejandro GIL-VILLEGAS (ref. 22)
11:20	11:40	***Heat and Mass Transport through Surfaces.*** Jean-Marc SIMON (ref. 108)	***Modelling of Electrolytes with ePPC-SAFT.*** Justyna ROZMUS (ref. 73)
11:40	12:00	***Prediction of physical Properties of*** CO_2 ***in ionic Mea/Aqueous Solutions by Molecular Simulation.*** Carlos NIETO DRAGHI (ref. 86)	***gSAFT: Application of the SAFT-g MIE Group Contribution EOS in the Oil/Gas Industry- from academic Research to Industrial Deployment.*** Claire ADJIMAN (ref. 124)
12:00	12:20	***Comparison of predicted pKa Values for some Amino-Acids, Dipeptides and Tripeptides, using Cosmo-rs, Chemaxon and Acd/Labs Methods.*** Oumar TOURE (ref. 25)	***Comparison of Performance of the PC-SAFT, Soave-Redlich-Kwong and Peng-Robinson Equations of State in Modelling Vapour-Liquid Equilibria of Binary*** CO_2 ***' 1-Alkanol Mixtures.*** Luis Antonio ROMAN RAMIREZ (ref. 105)
12:20	12:40	***Molecular Simulation of Ions in aqueous Solutions.*** Stephan DEUBLEIN (ref. 70)	***Recent Advances in Modelling the Viscosity of Dense Fluids.*** Velisa VESOVIC (ref. 74)
12:40	*13:40*	***Lunch (buffet)***	

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Monday, March 19th (PM)			
13:40	14:30	*Plenary Lecture* ***Equations of state for complex fluids.*** Joachim GROSS - Stuttgart University **Chairperson**: Georgios KONTOGEORGIS - Technical University Of Denmark	
14:30	*14:40*	***Change of room***	
		Session 2A1 ((Amphithéâtre Mérieux) **Chairperson**: Alejandro GIL-VILLEGAS - University of Guanajuato	**Session 2B1 (Salle des Thèses)** **Chairperson:** Carlos NIETO-DRAGHI - IFPEN
14:40	15:10	*Invited Lecture* ***Advanced Models in industrial Praxis: from Process Design to Process Optimization.*** Georgios FOLAS - Satoil	*Invited Lecture* ***Molecular Thermodynamics- Industrial Applications with Focus on Screening and Extrapolation.*** Manfred HEILIG - BASF
15:10	15:30	***Solubility of Pharmaceuticals: a Comparison between a PC-SAFT-Based Approach and NRTL-SAC.*** Theodora SPYRIOUNI (ref. 101)	***Molecular Dynamics Investigation of Triethylene Glycol in hydrated LTA Zeolite ' Emphasis on Evaluation of Potential Models.*** Bjørnar JENSEN (ref. 44)
15:30	15:50	***Predicting Phase Equilibria of Oxygenated Compounds Using Molecular Models: Results from the MEMOBIOL Project.*** Rafael LUGO (ref. 82)	***Chemical Potential Calculations in Molecular Dynamics Simulations of Adsorption in Zeolites.*** Charlles ABREU (ref. 59)
15:50	16:10	***Nano Tools for Macro Problems: Multiscale Molecular Modeling of Life and Material Sciences.*** Maurizio FERMEGLIA (ref. 92)	***Hydrate Formation in Pipelines and Maximum permittable Water Content in Gas.*** Bjørn KVAMME (ref. 34)
16:10	*16:40*	***Coffee Break***	
		Session 2A2 ((Amphithéâtre Mérieux) **Chairperson**: Ilya POLYSHUK - Ariel University of Toronto	**Session 2B2 (Salle des Thèses)** **Chairperson:** Velisa VESOVIC - Imperial College of London
16:40	17:00	***About unexpected Solid-Liquid Phase Diagrams obtained with most of SAFT-like Equations of State.*** Romain PRIVAT (ref. 123)	***Improving the Modeling of compositional Grading in Petroleum Reservoirs: a Molecular Dynamic Approach.*** Guillaume GALLIERO (ref. 122)
17:00	17:20	***Efficient Calculation of Fluid Phase Equilibria with Equations of State.*** Ulrich DEITERS (ref. 35)	***Multiphase Equilibrium of Fluids confined in heterogeneous porous Solids.*** Marcelo CASTIER (ref. 107)
17:20	17:40	***Application of Lattice Cluster Theory Equation of State for pure Compounds.*** Kai LANGENBACH (ref. 50)	***Improving Molecular Simulation Models of Adsorption in porous Materials: Interdependence between Domains.*** Joel PUIBASSET (ref. 121)
17:40	18:00	***Make your Thermodynamic Models available in most Process Simulators.*** Michel PONS (ref. 80)	***Strategy for Multiscaled Micro-emulsion Design with Application in chemical Enhanced Oil Recovery.*** Johannes FRAAIJE (ref. 52)
18:00	*20:00*	***Poster session with Cocktail***	
20:00		***Departure to the Dinner***	

Software Demonstration	**15:10 to 16:10** (In two paralell Sessions) *- Culgi (Ruben Serral Gracia)* *- ProSim (Olivier Baudouin)*	**18:10 to 19:10 :** *InModelia (Patrice Kiener)*

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Preliminary Program

Tuesday, March 20th			
9:00	9:50	***Plenary Lecture*** ***NIST ThermoData Engine: Increasing Value, Preventing "Pollution", Broadening Scope, and Providing Communications for Thermodynamic Property Information.*** Michael FRENKEL - NIST **Chairperson**: Christophe COQUELET - Mines ParisTech	
9:50	*10:20*	***Coffee break***	
		Session 3A (Amphithéâtre Mérieux) **Chairperson**: Philippe ROUSSEAU - Processium Lyon	**Session 3B (Salle des Thèses)** **Chairperson**: Guillaume GALLIERO - University of Pau
10:20	10:50	***Invited Lecture*** ***Use of Data in Engineering Company.*** Michael KLEIBER - Uhde GmbH	***Invited Lecture*** ***Ab initio Thermochemistry of Industrial Materials for Energy.*** Pascal RAYBAUD - IFPEN
10:50	11:10	**CO_2 *Mixture Properties using Equations of States and Molecular Simulations.*** Dimitrios TSANGARIS (ref. 58)	***Coupling Microscopic and Mesoscopic Scales to Calculate Thermodynamic Properties of heterogeneous Fluid Systems including Nanometric Carbon Clusters.*** Emeric BOURASSEAU (ref. 24)
11:10	11:30	***Experimental and computational Study on the Liquid - Liquid Equilibrium of Thiophene with ionic Liquids.*** Marta BATISTA (ref. 43)	***Molecular Dynamics Determination of Water-Nanorugged Surfaces Interfacial free Energies.*** Frédéric LEROY (ref. 42)
11:30	11:50	***Mesoscopic Simulation of Polyelectrolyte Brushes under Shear.*** Florent GOUJON (ref. 109)	***Prediction of the Surface Tension of Alkane/acid Gases Mixtures with Monte Carlo Molecular Simulations.*** Jean-Claude NEYT (ref. 41)
11:50	12:10	***Development of Property Models with uncertainty estimate for Eliable Product-Process Design.*** Amol HUKKERIKAR (ref. 79)	***Solid - Liquid Phase Behavior of Polymer - Solvent Mixtures.*** Michael FISCHLSCHWEIGER (ref. 51)
12:10	12:30	***Generalization of SAFT + Cubic Equation of State for predicting and correlating Thermodynamic Properties of heavy organic Substances.*** Ilya POLISHUK (ref. 126)	***Multiscale Modelling of Polymer-Filler Interaction.*** Gaëtan MAUREL (ref. 64)
12:30	12:50	***Guiding the Design of ionic Liquids as Substitutes of volatile Organic Solvents: PLS-DA Models for Ecotoxicity (V. Fischeri) Discrimination.*** Manuel ALVAREZ-GUERRA (ref. 85)	***A Stochastic Multi-Scale Modelling Approach of Polymerization Processes.*** Dimitrios MEIMAROGLOU (ref. 69)
12:50	*14:00*	***Lunch (buffet)***	
14:00	16:00	***Round-Table discussion*** ***How to improve technology transfer for a faster innovation in molecular thermodynamics*** Moderated by Philippe RICOUX - Total and Mathias BREHELIN - Rhodia	
16:00	16:15	**Conference closing**	

PLENARY LECTURE

(Abstracts)

Ref PL-132

Molecular Simulation of Phase Equilibria and Self-Assembly: Progress and Challenges.

Athanassios Z. Panagiotopoulos

Department of Chemical and Biological Engineering, Princeton University, USA

This lecture provides a review of molecular simulation methods for modeling phase equilibria and self-assembly. The Gibbs ensemble [1] is a direct approach proposed over twenty years ago that is suitable for calculations of moderate accuracy. The Grand Equilibrium method [2] is based on isothermal-isobaric and pseudo grand canonical simulations in the liquid and vapor phases, respectively. Combined with Kofke's Gibbs-Duhem integration [3], these methods allow the relatively routine calculation of phase diagrams for given intermolecular potentials. Alternative methods, in particular histogram reweighting Monte Carlo (reviewed in Ref. 4) provide good accuracy near critical points and provide paths for overcoming hysteresis and long time scales inherent in self-assembly of surfactants and polymers. In recent years, with the advent of fast, scalable, open-source packages for molecular dynamics calculations [e.g. 6,7] the time scales over which self-assembly and microphase separation can be studied have been extended to μs, even for realistic potential models with explicit solvent. However, there is still a significant need for development of coarse-grained models that correctly capture structure and thermodynamics in order to extend the time and length scales of systems that can be modeled.

References:

*[1].A.Z. Panagiotopoulos, Molec. Phys., **61**: 813-826 (1987).*
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*[3] D.A. Kofke, J. Chem. Phys., **98**: 4149 (1993).*
*[4] A. Z. Panagiotopoulos, J. Phys. Condens. Matt., **12**: R25-R52 (2000).*
*[6] B. Hess, et al., J. Chem. Theory Comp., **4**: 435-447 (2008).*
*[7] P. J. in't Veld, S.J. Plimpton, and G.S. Grest, Comp. Phys. Comm., **179**: 320-329 (2008).*

Ref PL-136

SAFT Equations of State for Complex Fluids Model Development and Applications.

Joachim Gross

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Stuttgart, Germany

Thermodynamicists are faced with the mandate to provide methods and models for increasingly complex mixtures. Analytic equations of state based on the Statistical Associating Fluid Theory (SAFT) [1,2] allow to model complex systems. The term ‚complex' here refers to strongly asymmetric mixtures, such as in polymer solvent mixtures, or to fluids with anisotropic interactions, such as associating and polar substances, or to structurally anisotropic fluids like liquid crystalline materials. Also mixtures with charged species require models with a sufficiently detailed molecular model. This contribution highlights some recent developments in modeling complex mixtures.

It is remarkable, that SAFT models serve in various new application domains: They are used for integrated solvent and process design [3,4]. When applied with the classical density functional theory, these models provide a powerful framework to predict interfacial properties [5,6]. SAFT-models are also used to speed up molecular simulations, for example by estimating vapor-liquid bias potentials in the grand canonical ensemble or they are used to very efficiently adjust force field parameters [7]. A review and discussion of some recent applications is given.

***References**:*

[1] W.G. Chapman, G. Jackson, K.E. Gubbins, Phase equilibria of associating fluids: Chain molecules with multiple bonding sites. Molec. Phys. 1988, 65, 1057.

[2] L.F. Vega, G. Jackson, 20 Years of the SAFT equation of state—Recent advances and challenges. Fluid Phase Equilib. 2011, 306, 1-3.

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[5] C.P. Emborsky, Z. Feng, K.R. Cox, W.G. Chapman. Recent advances in classical density functional theory for associating and polyatomic molecules. Fluid Phase Equilib. 2011, 306, 15-30.

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Ref PL-063

NIST ThermoData Engine: Increasing Value, preventing “pollution”, broadering scope, and providing communications for thermodynamic property information.

Michael Frenkel

Thermodynamics Research Center (TRC), Thermophysical Properties Division
National Institute of Standards and Technology (NIST), Colorado, USA

The NIST ThermoData Engine (TDE) [1] represents the first full-scale software implementation of the dynamic data evaluation concept for thermophysical and thermochemical property data. This concept requires the development of large electronic databases capable of storing essentially *all* relevant experimental data known to date with detailed descriptions of relevant metadata and uncertainties. The combination of these electronic databases with artificial intellectual (expert-system) software, designed to automatically generate recommended data based on available experimental and predicted data, leads to the ability to produce critically evaluated data dynamically or ‘to order’. The scope of the TDE includes pure compounds, binary mixtures, ternary mixtures, and chemical reactions.

TDE is a critical component of the Global Information System in Science and Engineering (GISSE) in application to the field of thermodynamics (ThermoGlobe) [2].

Role and feasibility of use of a variety of molecular tools (such as chemical system identifiers InChI) and property prediction methods (group contributions, QSPR with SVM technology, Monte Carlo and *ab initio*) in critical data evaluation, as well as in global data validation process, involving major journals in the field and supported by TDE, will be discussed.

Various options for “bundling” TDE with engineering software applications, including chemical process design engines, will be illustrated.

TDE technology is incorporated into online software to aid the process of experimental planning for property measurements. The software is to be used by experimentalists through open domain free Web access worldwide.

References:

[1] Frenkel, M. et al. NIST ThermoData Engine : NIST Standard Reference Database 103b (Pure Compounds, Binary Mixtures, Ternary Mixtures, and Chemical Reactions, *www.nist.gov/srd/nist103b.htm*
[2] Frenkel, M. J. Chem. Eng. Data, ***2009****, 54, 2411; Comp. Chem. Eng.,* ***2011****, 35, 393*

Keywords: dynamic data evaluation, ThermoData Engine.

INVITED LECTURE

(by order of references)

Ref O-077

Molecular Thermodynamics - industrial Applications with Focus on Screening and Extrapolation.

Manfred Heilig

BASF SE, Chemical and Process Engineering, Ludwigshafen, Germany

Physical Property Data and Thermodynamics are the fundamental basis for process development and chemical engineering applications. The point of origin are and remain in foreseeable future experimental data. A comprehensive physical property database is therefore essential. In addition validated and by traditional fitting equations parameterised data allow a quick access to process relevant data and also to process ideas and concepts.

Industrial applications of “Molecular Thermodynamics” are focused on physical property data that require molecular insight or a high effort for an experimental determination. Two aspects will be highlighted: thermodynamic screening applications and extrapolation of physical property data.

Thermodynamic screening methods can be applied for the selection of process and functional solvents. Converting the process idea or the functional application to physical property criteria the available data from databases have to be supplemented by predictive modeling for a multitude of components. Here, in addition to group contribution methods, the quantumchemical continuum solvation model Cosmo-RS is very useful.

Extrapolation means the prediction of data in wide ranges of temperature, pressure and concentration as well as the prediction of higher systems, based on pure component and binary data. Here CPA and PCSAFT-type equations of state enable a physically more sound extrapolation. However a complex pure component parameterization is required.

With quite high time and effort the Molecular Simulation, based on intermolecular potentials obtained from few thermodynamic data, is so far only feasible for important systems. Besides a nearly complete set of physical property data Molecular Simulation enables access to structural information of fluids and fluid mixtures.

Ref O-120

AB initio Thermochemistry of industrial Materials for Energy.

Pascal Raybaud

IFP Energies nouvelles, Solaize, France

The environmental context prompts the chemical community to propose innovative approaches for improving the prediction of properties of materials used in new energy applications such as cleaner and renewable fuels. For that purpose, rational and quantified concepts on bulk and surface properties of materials are needed for the improvement of existing materials or the discovery of new ones.

This lecture illustrates how ab initio molecular modelling within density functional theory (DFT), has brought insights into the understanding and property prediction of three important classes of materials in the field of new energies: 1/ hydride solids for hydrogen storage, 2/ photocatalytic TiO_2 materials, 3/ metallic catalyst surfaces. We highlight how the thermodynamic phase diagrams are determined by ab initio calculations as a function of the (T, P) working conditions expressed by the chemical potential of the reactant/adsorbate.

Considering the properties of bulk materials, hydride solids represent a first relevant example. The DFT evaluation of their thermodynamic stabilities and enthalpies of hydrogenation has revealed the limits and potentialities of alanates [1] and KSi-hydride, respectively [2]. Then, regarding nitrogen-doped TiO_2 materials, a recent DFT study has explained the origin of their enhanced visible light absorption as a function of the chemical potential of nitrogen [3]. Finally, the surface thermochemistry of a metallic catalyst in the presence of hydrogen pressure is illustrated [4,5]. Moreover, these theoretical results provide rational guides for new experiments. Beyond molecular thermodynamics, a brief opening on molecular kinetic challenges will be given.

***References**:*

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Key words: hydride solids, TiO_2 photocatalyst, metallic catalysts, hydrogen.

Ref O-131

Are there ways to improve the accuracy of predictive methods in the field of thermodynamic properties?

Robert J. Meier

DSM, Geleen, The Netherlands

Thermodynamic data are key in the understanding and design of chemical processes. There are various ways to obtain such data. Next to the experimental determination, computational methods are extremely valuable in the design of new chemical routes involving new chemical species, and sometimes indispensable tools in obtaining, e.g., heats of formation and Gibbs free energies, but also many other quantities. It is meanwhile becoming recognised that the accuracy of the predictive tools is often not sufficient. We have noticed for instance that boiling points can be very much off. 'Chemical accuracy' for (free) energies required is about 1-4 kJ/mol. Regarding heats of formation and Gibbs free energies the major toolboxes to obtain such quantities by computation are quantum mechanical methods and group contribution methods. The group contribution methods are common in industrial context. On the other hand, quantum chemical calculations can essentially treat any species, whether it can be broken down into useful groups or not. However, although a lot of progress was made in quantum calculations over the last decade, for the majority of chemical species we are still quite a bit away from what is often referred to as chemical accuracy, i.e. '1 kcal/mol'[1].

Following a state of the art overview, propositions will be presented how to improve the state of the art.

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Ref O-133

Thermophysical Properties from the Engineering Point of View.

Michael Kleiber

ThyssenKrupp Uhde GmbH, Dortmund, Germany

In an industrial company, many people are concerned with physical properties. They usually have different backgrounds which makes it difficult for them to even communicate with each other. There is a wide range from the specialist for physical properties, who is more or less focused on getting the correct values for a given problem on demand, to the layout engineer, who hardly knows the meaning of the particular properties but has to ensure that every piece of information is transferred correctly. One can easily imagine that many people do not relate the success of a company, becoming manifested in the successful startup of a built plant or the fulfilling of production plans, to the careful preparation of the physical properties by the specialist. On the other hand, physical property specialists must not restrict themselves to the determination of physical properties but should get involved in the processes as much as possible, as they might be the only people which are able to detect and solve the various problems encountered by the engineers who are less familiar with the thermodynamic issues.

Taking the focus on a typical engineering company like Uhde, the presentation refers to some of the everyday problems of a process simulation engineer, e.g. the problem with derived properties like c_p^{liq}, the model change in a process simulation or the behavior of substances at extreme conditions. It is referred what the preferences are when a model has to be chosen and what the demands are when a new model is established in a company. It is pointed out what the real gaps in the physical property description are. The roles of estimations and the accuracy requirements in process simulation is discussed, in fact, the application of estimation methods is not a matter of accuracy but of responsibility. The often performed comparison between the φ-φ- and the γ-φ-approach is done from the industrial point of view.

Finally, a perspective is given what the role of molecular thermodynamics in an engineering company might be in the future. Although the importance of estimations will probably not increase, molecular thermodynamics can contribute in the development of new correlation approaches. As far as the author can judge it, the application of molecular thermodynamics will be restricted to specialists. In process simulation, the correlation models will not be replaced by molecular thermodynamics; the additional calculation effort to use predictive methods does not give an advantage. However, the current empirical estimation methods will certainly be replaced.

Ref O-134

Advanced models in industrial praxis from process design to process optimization.

Folas Georgios

Statoil ASA, Oslo, Norway

Statoil, as many other companies, is mostly using commercial simulators for design, optimization and troubleshooting of production facilities. Initial phases of a project may be executed internally, and by the time that the design concept is frozen, the design is further detailed by engineering companies. The general philosophy is to use standard commercial, widely used, tools to the maximum extent.

In order to enhance the capabilities of the company and overcome shortcomings of commercial simulators, either CAPE-OPEN packages or stand alone tools (developed either internally or in collaboration with universities) are being utilized for specific applications. This work presents examples of the application of advanced models in process design and process optimization. A range of applications such as the confidence in the calculation of water content of natural gas on the design of processing facilities, evaluation of corrosion risk in production pipelines, gas hydrate inhibition, evaluation of freezing risk in low temperature gas processes, and the use of models such as CPA and SAFT are discussed.

Ref O-135

Application of COSMO-RS in the Design of Ionic Systems.

Steve Lustig (Du Pont) , Andreas Klamt (CosmoLogic)

COSMO-RS is a broadly applicable theory used to predict accurately a wide range of properties in complex liquid mixtures. Applying first principles quantum chemistry, an empirical contact Hamiltonian and statistical thermodynamics, COSMO-RS predicts equilibrium pure substance properties: vapor pressure, boiling temperature, enthalpy of vaporization; and mixture properties: partial vapor pressures, activities, gas solubilities, liquid solubilities, fluid phase diagrams, pK_a, and more. While classical forcefield based molecular dynamics and Monte Carlo methods can be used to predict these properties, implementations of COSMO-RS are much faster and more accurate. The basic theoretical approach was originally developed for neutral molecular systems and more recent works illustrate successful applications with complex ionic liquids.

This seminar summarizes the fundamental underpinnings of COSMO-RS theory and explores its application to both property prediction benchmarks as well as design of practical ionic liquid systems. A central question for benchmark studies is whether COSMO-RS property predictions are more accurate when molecular ions are treated quantum mechanically as either separate ions or paired ions or both. Here we compare benchmarks involving infinite dilution activity coefficients and finite-concentration Henry's Law coefficients. Two application studies are considered: the design of an optimal ionic liquid for absorption cooling processes and design of solvents for lithium ion batteries. In both cases the COSMOtherm application is implemented as a subroutine within an overall algorithm that optimizes a thermodynamic design criterion. For the absorption cooling study we consider how to select cation-anion pairs to optimize the thermodynamic coefficient of performance while minimizing thermal and hydrolysis degradation chemistries. For the lithium ion battery study we consider the prediction of temperature-dependent solubility of $LiPF_6$ and ionic speciation profiles in two very different classes of organic solvents. Here the thermodynamic criterion is minimization of the system Gibbs free energy subject to mass action balance, charge balance and solid-liquid equilibrium constraints. Both applications require accurate prediction of thermodynamic properties over a range of temperature and finite concentrations. However even the qualitative results in both cases provide physical understanding that enables a chemical engineer to understand these complex systems and design useful systems.

ORAL PRESENTATIONS

(by order of references)

Ref O-022

Molecular Thermodynamics of Quantum Fluids using the SAFT-VR approach with Quantum Corrections.

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We present an extension of the SAFT-VR approach [1] that takes into account quantum corrections (SAFT-VRQ), based on the methods developed by Green [2] and Kim *et al.* [3]. The Helmholtz free energy A for a fluid comprised of N particles at temperature T is given by:

$$\frac{A}{NkT} = \frac{A^c}{NkT} + \frac{A^Q}{NkT} \qquad (1)$$

where k is the Boltzmann's constant, A^c is the free energy for a classical fluid obtained by the SAFT-VR method, and A^Q is the quantum correction. For a single-monomer fluid of density ρ, A^Q is given by [2,3]:

$$\frac{A^Q}{NkT} = \frac{\rho}{24m}\left(\frac{h}{\pi kT}\right)^2 \int_0^\infty \nabla^2 u(r) g(r) r^2 \, dr \qquad (2)$$

where h is the Planck's constant, m is the mass per particle, $u(r)$ is the interparticle pair potential and $g(r)$ is the pair radial distribution function. Alternatively, this result can be deduced from the Wentzel-Kramers-Brillouin (WKB) approximation of $g(r)$, which implies an effective pair-potential $u^e(r)$ for quantum fluids obtained from $u(r)$ [4]:

$$u^e(r) = u(r) + D\nabla^2 u(r) + \frac{9}{10} D^2 \nabla^2 \nabla^2 u(r) + \cdots \qquad (3)$$

Where $D = \lambda_B^2/24\pi$ and λ_B is the de Broglie's wavelength. By using the standard SAFT-VR approach with the pair potential given in Eq. (3), we recover expressions (1) and (2). Predictions for the phase diagram and other thermodynamic properties, like the Joule-Thomson coefficient, are presented. In the case of hydrogen, we found that quantum corrections are important for the *global* behavior of the properties and not only for the low-temperature regime. Predictions obtained by SAFT-VRQ compares very good with respect to cubic equations of state developed for hydrogen [5]. We also present a semi-classical simulation method of quantum fluids described by Eq. (3), using the Gibbs Ensemble method [6].

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Keywords: Quantum fluids, SAFT-VR, Joule-Thomson coefficient, WKB approximation.

Ref O-024

Coupling Microscopic and Mesoscopic Scales to Calculate Thermodynamic Properties of heterogeneous Fluid Systems including Nanometric Carbon Clusters.

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One of the key points of the understanding of detonation phenomena is the determination of equation of state and thermodynamic properties of the detonation products mixture. Concerning carbon rich explosives, detonation products mixtures are composed of solid carbon nano-clusters immersed in a high density fluid phase. The study of such systems where both chemical and phase equilibriums occur simultaneously represents an important challenge in the detonation community, and molecular simulation methods appear to be the only way to obtain some answers at the moment.

In recent years, we have developed original methods and models to study those systems [1]. Expensive Molecular Dynamic simulations have been performed using a complex bond order dependant potential (LCBOPII) to study carbon clusters at the atomic level in order to build an accurate phase diagram of such nanometric objects. A mesoscopic model has also been developed to replace all atoms carbon clusters by meso-particles presenting the same properties. Then, the Reaction Ensemble Monte Carlo method (RxMC), which allows determining the chemical equilibrium of a molecular fluid mixture, has been adapted to calculate properties of fluid systems with mesoparticles at chemical equilibrium. By applying those methods to real detonation products mixtures, we have shown that the heterogeneity of such systems can not be neglected [2].

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Keywords: Reaction Ensemble Monte Carlo, Mesoparticle, Carbon Clusters, Detonation Products.

Ref O-025

Comparison of predicted pKa Values for some Amino-Acids, Dipeptides and Tripeptides, using Cosmo-rs, Chemaxon and Acd/Labs Methods.

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Liquid-phase pKa values play a key role in food science. Chemical properties of molecules depend largely on whether they are ionized or not. Most organic molecules are capable of gaining and/or losing a proton in aqueous solutions. Proton transfer most frequently occurs between water and any ionizable atom of the organic molecule. The molecule's response to protonation or deprotonation depends significantly on the site that was disturbed by proton transfer. Partial charge distribution in the molecule also varies with protonation of the acid/base active sites. Since the partial charge distribution is very sensitive to the protonation-deprotonation process (both near and far from the disturbed site), it can be used to determine the pKa of a molecule.

First, we use the COSMO-RS method, a combination of the quantum chemical dielectric continuum solvation model COSMO with a statistical thermodynamics treatment for more realistic solvation (RS) simulations, for the direct prediction of pK_a constants of about 50 molecules (amino-acids, dipeptides and tripeptides). Then we compare our results with experimental data and the pKa values predicted using two other methods. We used respectively the ChemAxon method using a program based on the calculation of partial charge of atoms in the molecule and the ACD/Labs method that enables to calculate single pKa values for all possible dissociation centers when the rest of the molecule is considered neutral, using an internal database containing chemical structures. The averaged RMS of the predicted pKa values for each method compared to experimental results were respectively 0.53 for COSMO-RS, 0.38 for ChemAxon and 0.41 for ACD/Labs. Regarding these results, COSMO-RS appears as a promising method to predict the pKa values of molecules of interest in food science with scarce available pKa values such as peptides. The final goal of this study is to use the pKa values in a predictive thermodynamics model for products of interest in food industry.

Key words: pKa prediction, COSMO-RS, amino-acids, dipeptides, tripeptides, food science.

Ref O-032

Non-equilibrium Molecular Dynamics Simulation of real Fluids in Nanoporous Materials.

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Fluid flow in a slit pore can be decomposed into diffusion (caused by a chemical potential gradient) and a convective contribution which is proportional to the pressure gradient [1]. Experimentally, these two mechanisms cannot be clearly distinguished, since a chemical potential gradient induces a corresponding pressure gradient and vice versa.

The present work applies molecular dynamics to Poiseuille flow of real fluids through nanopores and combines several methods to isolate convective, diffusive, and entrance effects. With a massively parallel simulation engine, pore diameters up to 100 nm (and down to 1 nm) are considered. This includes the transition from the microscopic regime, where boundary slip is of minor importance, to extremely narrow pores where the slip length can exceed the channel diameter. Self-diffusion under confinement is simulated by implementing Avendaño's dæmon [2] which pushes two differently «coloured» sets of otherwise identical molecules against each other.

The TIP4P/2010 model [3] and the truncated-shifted Lennard-Jones potential are used to represent water and methane, respectively, and the magnitude of the driving force as well as the surface polarity are varied. Regarding channel diameters down to the molecular length scale, the pressure drop inside the membrane is found to be approximately proportional to the flow velocity and inversely proportional to the cross-sectional area, in agreement with Darcy's law.

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Ref O-034

Hydrate Formation in Pipelines and Maximum permittable Water Content in Gas.

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Transport of carbon dioxide in offshore pipelines often involves conditions where hydrate may form from residual water in carbon dioxide or hydrocarbon gas. The critical question is whether the water will drop out as liquid droplets first, and then form hydrates, or alternatively, adsorb on the pipeline surfaces, and then form hydrates. In this work we have used different Quantum Mechanical approximations to estimate the charge distribution of hematite crystals. These rust particles were embedded in water and chemical potential for adsorbed water molecules were estimated through thermodynamic integration and compared to similar estimates for same size water cluster. Values obtained for chemical potential of water in different surrondings indicated that it would be thermodynamically favorable for water to adsorb on hematite, and that evaluation of potential carbon dioxide hydrate formation conditions and kinetics should be based on this formation mechanism. The behavior of water outside the immediate vicinity of hematite (beyond 3 - 4 diameters) closely resembled that of bulk liquid and can form hydrates with readily available carbon dioxide (if inside stability region). An example of estimated water limits for liquid drop out versus adsorption is given in fig. 1.

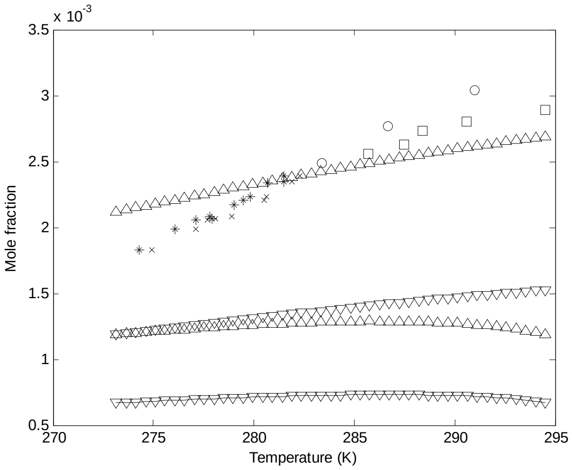

Fig. 1. Limits for water content in CO2 when liquid water drop-out is considered (upward triangles) and when adsorption is considered (downward triangles). Upper set of curves is for 61 bar and lower set is for 101 bar. All results calculated according to Kvamme & Tanaka [1] with adsorption data from Kvamme et.al. [2]. Stars and circles are experimental data from Seo et.al. [3] at 101 bar, with similar results for 61 bar as plus and square.

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Keywords: Gas transport, water condensation, adsorption, hydrate.

Ref O-035

Efficient Calculation of Fluid Phase Equilibria with Equations of State.

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While many physical properties of fluids, including phase equilibria, can be obtained from computer simulations directly, the numerical effort is huge. For many applications, equations of state — perhaps fitted to simulation data or based on molecular theory — are a better way to determine properties. But even with such equations, the calculation of phase equilibria or stability limits, if done with conventional methods, can run into problems.

Instead of characterizing mixtures by their molar volumes and mole fractions, *isochoric thermodynamics* uses the amounts of substance ("mole numbers") in a fixed reference volume. This is equivalent to using molar densities (concentrations) for all components. Using then the Helmholtz energy density as thermodynamic potential function, particularly elegant formulations of equilibrium and stability criteria can be obtained, with identical criteria for pure fluids and mixtures [1].

Application of differential geometry leads to a new, highly efficient algorithm for phase equilibrium calculations that does not require the computation of phase volumes at each iteration step. Consequently, the CPU times for phase equilibrium calculations with noncubic equations of state (reference equations, advanced theoretical models) are significantly reduced. As a byproduct, a very useful method for the estimation of initial values is obtained. Furthermore, the calculation of stability limits and critical points of mixtures is simplified considerably [2, 3].

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Keywords: phase equilibria, thermodynamic stability, algorithm, equation of state.

Ref O-041

Prediction of the Surface Tension of Alkane/acid Gases Mixtures with Monte Carlo Molecular Simulations.

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The knowledge of thermodynamic properties of mixtures of alkane with multipolar molecules such as carbon dioxide or hydrogen sulfide is important for the petrochemical industry. Accessing to those properties is experimentally difficult in geological conditions, or in the case of poisonous substance like hydrogen sulfide.

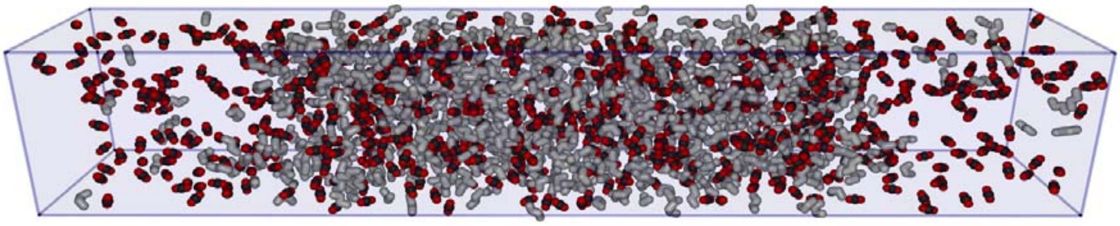
Since a few years, molecular simulation is commonly used to predict those properties. In this work, Monte Carlo methods are used to simulate liquid-vapour coexistence of three different mixtures: CO_2-butane, CO_2-decane and H_2S-pentane. The systems were simulated at 344K, and under different pressures.

The force field used for alkanes is AUA-4, a United Atoms force field in which force centers are not on the atoms. For acid gases, rigid force fields were chosen.

Thermodynamic properties such as phase diagrams, composition mixture diagrams and also surface tension are predicted from these simulations.

The results were compared to models results and experimental data. A good agreement with the experimental data let us to imagine a quantitative prediction for comparable mixtures.

In the case of miscible gases, specifics effects of absorption or molecular organisation at the interface have been observed. These structural insights at the interface and its effects on the surface tension are very important. They represent a way of understanding the evolutions of the thermodynamical properties for such mixtures and of providing a microscopic interpretation of the macroscopic properties.



CO_2-C_4 simulation box with two interfaces

Keywords: surface tension, mixture, alkane, acid gas, molecular simulation.

Ref: O-042

Molecular Dynamics Determination of Water-Nanorugged Surfaces Interfacial free Energies.

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We address the question of what is necessary to enhance the wetting properties of a surface intrinsically hydrophobic or hydrophilic. In particular we aim to understand at the molecular level under what condition nanoscale roughness (i.e. roughness in the range of 1-10nm) can amplify the wetting properties of a given surface.

For that purpose, we perform molecular dynamics calculations dealing with water in contact with model rugged graphite-based surfaces whose roughness stretches from a few Angströms to a few nanometers. We introduce a thermodynamic integration algorithm to determine the solid-liquid interfacial excess Gibbs free energy of the systems in either suspended or collapsed wetting states [1,2].

Our results are compared with the predictions of the Cassie-Baxter and Wenzel macroscopic theories.[3,4] While we confirm that the Cassie-Baxter theory is likely to be applicable at the nanoscale, we discuss why Wenzel's macroscopic approach reaches its limit when atomistic details are taken into account and when roughness dimensions are comparable to the range of intermolecular interactions. We show that a generalized Wenzel's surface free energy equation that includes Cassie-Baxter concepts may prove useful to understand why an apparently hydrophilic flat surface can be turned into a hydrophobic surface by means of roughness. This yields us to describe general prescriptions on how to build surfaces in order to control the static wetting properties of rugged surfaces [5].

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Keywords: solid-liquid interfaces, surface free energy, nanoscale rugged surfaces, superhydrophobic surfaces.

Ref O-043

Experimental and computational study on the liquid-liquid equilibrium of thiophene with ionic liquids.

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Ionic liquids (ILs) are a new class of compounds with unique physical and chemical properties that have captured the attention from researchers who have been studying them in a wide range of applications. Their unique solvation ability along with the capacity for task-specific design by combining different cations and anions, is of great interest for liquid-liquid extractions [1].

During the past few years, environmental regulations imposed the reduction of hazardous emissions in refineries by removing organic sulfur content in fuels, what is conventionally accomplished through a hydrodesulphurization process.[1-2] This process has high operation costs due to high consumption of energy and hydrogen, and new desulphurization technologies are being investigated. Imidazolium based ionic liquids appear as alternatives to act as extraction solvents in the separation of sulphur-containing compound from hydrocarbons.[1-2] It has been observed that systems composed by ILs and thiophene present different liquid-liquid equilibria depending on the IL anion. In some cases, they show upper critical solution temperature (UCST) while others have a lower critical solution temperature (LCST) [3].

Aiming at better understanding the interactions between ILs and thiophene that generate the various types of phase diagrams observed, and evaluate their impact upon the extraction processes, the systems of thiophene with [BMIM][NTf_2] and [BMIM][SCN] were studied using ^{1}H, ^{13}C and ^{19}F NMR spectroscopy, excess volumes measurements and computer simulations. By analyzing the experimentally determined chemical shift deviation (δ) and the excess volumes (V^E) and the calculated radial distribution functions, it was possible to evaluate the interactions between the species composing the mixtures. A full picture of the molecular interactions between the ionic liquids and thiophene was drawn allowing understanding the formation of the two types of phase diagrams (UCST and LCST) observed.

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Keywords: ionic liquids, thiophene, solution behavior.

Ref O-044

Molecular Dynamics Investigation of Triethylene Glycol in hydrated LTA Zeolite ' Emphasis on Evaluation of Potential Models.

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Trace components are common in various amounts in oil and gas reservoirs and processing. These trace components often have to be removed to meet transport specifications and ensure safe and reliable gas processing.

Zeolites are widely used in industrial applications as molecular sieves for separation through adsorption. Despite their industrial importance, we are still facing large knowledge gaps. Significant challenges are experienced in understanding molecular kinetics of adsorption, the mutual impact of simultaneous diffusion processes of different components, their interactions, and the influence of zeolite lattice.

Statoil has long experience in deep water removal using molecular sieves on a number of gas processing plants. An important operational problem is pollution of the adsorbent by triethylene glycol following the natural gas. Due to lack of theoretical understanding, high costs are incurred because the revision stops are increased in order to replace the polluted adsorbent. It is therefore crucial to have a better understanding of mechanisms that govern adsorption in zeolites.

The previous research focused on the Monte Carlo techniques simulations of alcohols in hydrated zeolites, with no molecular dynamics simulations carried out on similar systems [1,2]. While Monte Carlo techniques easily yield chemical potentials and allow to locate favorable adsorption sites, they are not particularly suitable for study of process kinetics. They do not show the complete path of molecules from bulk to adsorbed state.

The focus of this work was to model a zeolite system involving a mixture of methane, triethylene glycol and water. We investigated the impact of different potential models to determine their inherent suitability for industrial applications. Potentials selected in this study were developed by Jackson and Catlow [3], and have been used in several studies employing Monte Carlo methods. Comparison with Lennard-Jones 12-6 potentials [2] has also been carried out.

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Keywords: Zeolite; TEG; water; molecular dynamics; potentials.

Ref O-050

Application of Lattice Cluster Theory Equation of State for Pure Compounds.

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During the last years there have been great advances in the calculation of phase diagrams with physically based equations of state (e.g. PC-SAFT [1]). In their development the occurring energetic effects caused by interactions between different or similar functional groups where in the main focus. These equations of state are in principle applicable to the description of molecules not differing in chemical composition but in isomerism. This however, demands the adjustment of pure component parameters for every isomer.

On the other hand Freed an co-workers developed the Lattice Cluster Theory[2], which allows the description of a molecule's architecture directly in the thermodynamic potentials. This theory admitted the description of the demixing equilibria of hyper-branched polymers in water[3]. In this application; however, the lattice is introduced incompressible. Following a proposal by Freed et al.[4], the lattice can be made compressible by the introduction of void lattice sites, thereby allowing the derivation of an equation of state. This course of action allows the development of an equation of state (LCT-EOS) with two adjustable parameters for a pure substance, i.e. the size of a lattice site and the interaction energy between two non-void sites. It can be shown that the LCT-EOS is capable of calculating small differences between the vapor pressures of isomers (e.g. n-heptane and 2,3-dimethyl pentane) with the same set of pure-component parameters.

This contribution deals with the presentation of the new LCT-EOS, with the calculation of the architectural coefficients and with the adjustment of the two pure component parameters. Furthermore, the calculated vapor pressures, the saturation densities, the isobaric heat capacities, the surface tensions, the speeds of sound, and heats of vaporization for several alkanes, differing in chain length and in isomerism, are discussed and compared with experimental data from literature.

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Keywords: equation of state, lattice cluster theory, pure components,
physical properties prediction.

Ref O-051

Solid - Liquid Phase Behavior of Polymer - Solvent Mixtures.

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The chemical composition of semicrystalline ethylene polymers, e.g., molecular weight distribution, stereoregularity and short-chain branching distributions play the dominant role for the material properties and therefore for product design. Temperature rising elution fractionation (TREF) is used to control the short-chain branching distributions. TREF involves dissolving the polymer in a suitable solvent at high temperature and loading the resulting solution onto a fractionation column. The column is slowly cooled, allowing the polymer molecules to crystallize out of solution. Polymer fractions with lower average short-chain branching content form thicker crystals at higher temperatures [1]. For the optimization of the fractionation methods, based on phase equilibrium calculations, can be developed[2].
The solid-liquid equilibrium (SLE) of a polymer solution, where the structure of the polymer in terms of molecular weight, stereoregularity and short-chain branching has to taken into account, forms the background of this fractionation method.
Recently, the lattice cluster theory (LCT) [3] was applied to the description of the architecture of hyperbranched polymers and liquid-liquid equilibria in solvents[4] and solvent mixtures[5] were calculated. The basic idea of this contribution is the application of the LCT to the calculations of the SLE of ethylene copolymers in a solvent, where the melting enthalpy and the melting temperature are taken from our own DSC-measurements. The theoretical framework leads to the solubility of the copolymer in the selected solvent as function temperature, of molecular weight and short-chain branching at constant pressure. A comparison between the calculated phase equilibria using LCT and the own experimental data is discussed.

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Keywords: solid-liquid phase behavior, polymer crystallization, lattice cluster theory.

Ref O-052

Strategy for Multiscaled Micro-emulsion Design with Application in Chemical Enhanced Oil Recovery.

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The use of surfactants to create an ultra-low oil-water interfacial tension (micro-emulsion) is a rapidly growing application in the area of enhanced oil recovery. A practical numerical tool to simulate the interface and model the surfactant activity can be a great help in screening and optimizing suitable surfactant systems. In general, interfacial stability is key to many industrial applications and methods for rational design of soft interface structures are much desired in industry. One may think of colloidal protection in coatings, polymer blend stability, liposomal drug delivery, or, as we discuss in more detail in this paper, complex emulsions in oil recovery.

The complex and highly curved interfacial structure and low interfacial energies of micro-emulsions, is a significant challenge for most currently available molecular modelling techniques. We have developed an effective strategy to model interfacial tension and micro-emulsion stability. The principle of the newly developed theory rests on the novel observation that one can readily determine the so-called surface torque density from molecular stress profiles across an oil/surfactant/water interface. The modelling strategy is relatively simple and requires only the simulation of a flat interface. It is therefore possible to calculate within one day whether such interface will stabilise a micro-emulsion, and also what type of micro-emulsion that would be (water-rich, oil-rich or equal water and oil volumes).

We use the general purpose multiscale modelling library CULGI (**C**hemistry **U**nified **L**anguage **I**nterface), to develop scripts for the interfacial modelling. These simulations can include ionic interactions (salt), the influence of co-surfactants and a variable oil composition. Depending on the accuracy required, the calculations can be performed on either free energy level (minutes simulation time), coarse grained particle level (Dissipative Particle Dynamics, hours simulation time) or molecular dynamics level (days simulation time). Combination of these methods make this a practical and efficient screening tool for surfactant selection.

In this paper, we discuss the relevance of micro-emulsions for chemical enhanced oil recovery, the mathematical background of the interfacial thermodynamics, the coupling with the simulation methods, the method of scripting in the CULGI library, and the connection with simplified formulation approaches such as Winsors “R” theory and quantitative structure activity relations. The used software library will be discussed in a different presentation.

Keywords: Multiscaled modelling, Interface, Microemulsion, Enhanced Oil recovery, Chemical EOR.

Ref O-058

CO_2 mixture properties using Equations of states and Molecular Simulations.

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The increasing use of fossil fuels requires the development of new technologies to reduce the accumulation of greenhouse gases in the atmosphere. Storage of carbon dioxide in underground cavities is a promising technology. In order to define a proper guideline of CO_2 purity and impure components in accordance with technical, safety and environmental requirements, a better understanding of the thermodynamic properties of CO_2 mixtures is needed. One possible solution is the generation of experimental data at conditions inside the operating window. Here, a less expensive approach to physical properties prediction is proposed based on molecular based models and traditional equations of state.

In this work, the available experimental data were collected and tabulated. Based on the required thermodynamic properties (i.e. volumetric and phase equilibria properties, derivative properties namely specific heat capacity at constant volume and pressure, speed of sound and Joule-Thomson coefficient) the applicability of those data was assessed and knowledge gaps were identified. Existing models were retuned or new models were developed in order to fill the gaps with acceptable accuracy. Classical cubic equation of state (SRK, PR, and SRK), empirical equations of state (Span and Wagner), complex semi-empirical equations of state (SAFT/PC-SAFT) and atomistic molecular simulations using realistic force fields were considered. Finally, the underlying models were compared and used to study the effect of impurities on CCS processes.

Vapour-liquid equilibrium of CO_2 was studied with a newly developed method by combining the Gibbs Ensemble Monte Carlo (GEMC) method and the multiple histogram method. The new method is a simple and accurate way to predict fluid phase equilibrium close to and away from the critical point. By performing a number of discrete GEMC simulations over the range of interest, multiple histograms were used to provide a continuous function that can be used in engineering calculations (i.e. CFD, flowsheeting). For the simulation of the CO_2 molecule a model with three Lennard-Jones sites with charges centered at each atom was used.

Our study showed that both predictions and correlations can be achieved with different degree of accuracy by the EoS. On the other hand, molecular simulation methods have evolved into a very useful tool for filling the gaps. The underlying models greatly improved the understanding of CO_2 mixture behaviour and can be used to guide the design of CCS processes. As our study indicates for example, as the mole fraction of non-condensable gases increases then purification, compression and condensation becomes more difficult. Also, if the formation of multiple phases is to be avoided non-condensable impurities concentration must be kept low.

Acknowledgments:
Financial support from the European Commission through project "Quantitative Failure Consequence Hazard Assessment for Next Generation CO_2 Pipelines" (project no. 241346-2; FP7-ENERGY-2009-1) is gratefully acknowledged.

Ref O-059

Chemical Potential Calculations in Molecular Dynamics Simulations of Adsorption in Zeolites.

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Adsorption of small molecules in nanostructured materials such as zeolites is recognized as a possible alternative to conventional industrial processes. In the oil industry, it can possibly substitute some of the energetically demanding processes of gas separation. Zeolites can also be used as adsorbents in gas storage devices and as ion-exchangers in the treatment of industrial wastes. The choice of the right material and process conditions for each application requires reliable knowledge of phase equilibrium and transport properties of the systems of interest. In this context, molecular simulation with detailed atomistic description arises as a valuable tool in the study of adsorption. The availability of highly efficient Molecular Dynamics (MD) software makes it relatively straightforward to simulate these systems for the calculations of transport properties. Nevertheless, phase equilibrium calculations are more conveniently performed using Monte Carlo methods, which usually requires more effort to be put into practice. In this paper, we show how one can employ MD to calculate chemical potentials of both neutral and charged molecules adsorbed in zeolites, thus enabling the study of phase equilibrium by using efficient, free-source MD software packages. For this, we use a coupling parameter strategy and employ an Expanded Ensemble method[1] to calculate free-energy variations obtained by reversibly decoupling a tagged molecule from the system or by reversibly changing its identity, which is related to the chemical potential of the corresponding species. The method, implemented with LAMMPS,[2] allowed us to study adsorption isotherms of gases and to investigate ion-exchanging characteristics of acid zeolites. By presenting the obtained results, we intend to foment discussions about further applications of the methodology.

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Keywords: Adsorption, Zeolites, Molecular Dynamics, Chemical Potential.

Ref O-064

Multiscale Modelling of Polymer-Filler Interaction.

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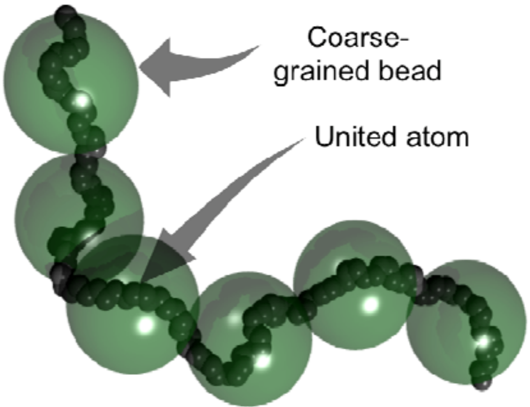
Fillers are particles of nanometric size, which can be dispersed in a polymer matrix to form composite materials. These fillers allow an enhancement of the mechanical properties of the polymer matrix; this enhancement is often called reinforcement. In spite of visible changes in macroscopic properties, as an increase in the shear modulus, an accurate description of the associated mechanisms is still missing. The structure of matter can be probed accurately thanks to the current molecular simulation tools despite some restrictions. Indeed, mechanical properties like viscosity or shear modulus (in the rubber state), require a large exploration of the configuration space and cannot be calculated from atomistic simulations.

In order to study both of the microscopic structure of the reinforced matrix and its mechanical properties, a multiscale approach is needed. This method involves the combination of molecular and mesoscopic description of the matter to combine accuracy over a wide range of time. Data from microscopic simulations (Molecular Dynamic) are used for the development of new interaction potentials at the mesoscopic scale (Dissipative Particle Dynamic), whose aim is to conserve the chemical aspect of the polymer.

The study was initially performed on a *cis*-1,4-polybutadiene bulk matrix to develop the transition method between the microscopic and the mesoscopic level. The way the potentials are developped (i.e. at constant pressure using the iterative Boltzmann inversion method[i]) is one of the stakes of this work. Various simulation data, like density or end-to-end vector, are then compared with the experimental data in order to validate this method. It will be applied to polymer-filler systems for prospective and predictive uses.



Levelling process during the transition between microscopic and mesoscale.

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Keywords: multiscale modelling, dissipative particle dynamics, shear modulus, polymer-filler interaction.

Ref O-069

A Stochastic Multi-Scale Modelling Approach of Polymerization Processes.

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With a view towards the production of polymer products with more stringent and better defined quality specifications, a vast amount of research activity has been directed to the accurate prediction and control of the "polymer quality". This term includes a series of polymer molecular (e.g., molecular weight/copolymer composition/branching distributions, etc.) and morphological (e.g., particle/pore size distributions, etc.) properties, which directly affect the end-use properties of the produced polymers [1]. Extensive research work, which has been carried out over the last decades mainly on the fields of mathematical modeling and computer-based simulation of polymerization processes, has produced remarkable results in terms of the accurate prediction of the above properties and their correlation with the various process characteristics and operating conditions [1,2].

Nevertheless, these results have not been proven adequate to interpret the connection between the process conditions and the final, end-use properties of the polymeric products. In this respect, additional information is required in terms of the nano-scale, exact architectural characteristics of the polymer chains which is strongly related to the system kinetics and, thus, to the physical and thermodynamic characteristics of the process. A typical example of this claim is the dependence of the rheological behavior of polymer melts on the topological properties of highly-branched polymer chains [3,4].

In this work, an attempt towards the elucidation of this connection is presented, via the implementation of a holistic, multi-scale modeling approach on the basis of a stochastic Monte Carlo (MC) algorithm. Through this approach, it becomes possible to calculate molecular polymer properties on different length-scales of the same system and to predict the effect of the process conditions on the values of these properties. In addition, the calculated analytical topological information can be further exploited in terms of the prediction of spatial and rheological polymer properties. An industrial process (i.e., the production of low density polyethylene, LDPE, in high pressure tubular reactors) is utilized as representative paradigm [5].

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Keywords: Multi-scale modeling, polymer properties, stochastic simulations.

Ref O-070

Molecular Simulation of ions and aqueous Solutions.

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Aqueous electrolyte solutions play an important role in many industrial applications, understanding these solutions is of prime interest. In the present work, we apply molecular modeling and simulation on the basis of classical force fields with explicit solvent and ion models to determine the thermodynamic properties of aqueous electrolyte solutions. The focus lies on alkali and earth-alkali metal cations, and anions from the halide group. Each ion is modeled as one Lennard-Jones (LJ) sphere with one or two point elementary charges in its center of mass. Water is modeled using force fields of the LJ + partial charge type from the literature, like SPC/E and TIP4P.

In the present study, a comprehensive set of new force fields for the ions of the groups specified above was developed. They are optimized for describing basic thermodynamic data. The size parameter was adjusted to the reduced solution density, whereas the energy parameter (which does not significantly influence the density) was fitted to activity data. A global fitting approach was used. The new models perform well for all combinations of the cations with the anions, over a wide range of ionic strength and predict well structural properties like the radial distribution function, dynamic properties like the self-diffusion coefficient and properties of solution like the electric conductivity.

The simulations were performed with the molecular simulation program ms2. The long range interactions of the charges were considered by Ewald summation.

Keywords: monovalent ions, divalent ions, molecular simulation.

Ref O-073

Modelling of Electrolytes with ePPC-SAFT.

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Accurate predictions of phase behaviour and thermophysical properties are crucial in design and optimization of numerous industrial processes. Classical process simulators contain numerous models able to characterize complex systems. However, most of them fail when electrolytes are present.

It is well-known that dissolved salts strongly affect the phase equilibria of aqueous solutions, modifying their boiling temperatures and resulting in salting out of gases, and that a description of these systems requires precise and specially adapted models. As electrolyte-containing mixtures are of widespread interest in many industrial fields, we have extended the PPC-SAFT equation of state, which was adapted to model water + hydrocarbon systems by Nguyen-Huynh *et al.* [1], to electrolytes. For this purpose two additional electrolyte terms have been included: long-range Coulombic interactions are taken into account using the mean spherical approximation (MSA) for a primitive model of the electrolyte solution and the solvation energy of the ions is described using the Born term [2]. The dielectric constant of the solvent varies with salt concentration according to the predictive Pottel rule.

We have developed ion-specific, temperature-independent intermolecular model parameters, which cover the most important monovalent salts (20 alkali halides). The ion diameters used by the model are those of Pauling. In this SAFT framework, we consider that the dispersive energy can be neglected and all interactions can be described using association, thus only the association parameters are required.

ePPC-SAFT is able to predict accurately the mean ionic activity coefficient (MIAC), density, vapour pressure and gas solubility (salting out) in water over a wide temperature and molality range (25-200°C and 0-6 molal). An overall AAD of 6.8% was obtained for the MIAC. The results of the model, in the context of possible industrial applications, will be presented.

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Keywords: electrolytes, phase behaviour, ePPC-SAFT, equation of state.

Ref O-074

Recent Advances in Modelling the Viscosity of Dense Fluids.

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Industrial process design creates a considerable demand for reliable values of the viscosity of a wide variety of fluid mixtures over extensive ranges of density and temperature. The economic case for improving the accuracy with which viscosity is determined is strong; however, the wide range of possible fluid mixtures and of conditions of interest precludes obtaining the relevant data by experimental means alone. There is, therefore, a clear need for predictive methods that are accurate, reliable and internally consistent. Kinetic theory forms a very useful starting point for the development of methods to predict the viscosity of a fluid. Although for dilute gases the accurate calculations of the viscosity are now possible from the realistic intermolecular potential surface [1], for dense fluids the situation is less satisfactory. At present no rigorous theory exists for an exact evaluation of the viscosity of a dense fluid.

Here, we present the VW method [2]. It makes use of the Enskog-Thorne rigid-sphere theory, modified recently [3-4] to deal with chain-like molecules in a self-consistent manner. The model is fully predictive and has no adjustable parameters pertaining to dense fluid mixtures. We discuss the recent advances achieved with the VW method, drawing analogues with the SAFT framework for the equilibrium thermophysical properties and present the results of comparisons with a large range of experimental data. The deviations observed for binary and multicomponent liquid alkane mixtures are within approximately 5-7%. We further illustrate the versatility of VW model by successfully predicting the viscosity of petroleum fluids, which we characterized in terms of pseudo components.

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Keywords: Viscosity, VW model, petroleum fluids.

Ref O-079

Development of Property Models with uncertainty estimate for Eliable Product-Process Design.

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Physical and thermodynamic properties of pure components are vital pre-requisites for performing tasks such as, process design, computer aided molecular product design among others. While use of experimentally measured values for the needed properties is desirable, the experimental data for the properties of interest may not be available in many cases. Also, product-process design involving new molecules require property models to be predictive. In such cases, predictive property estimation methods such as group-contribution$^+$ (GC$^+$) approach are generally suitable to obtain the needed property values. Also, in addition to the accuracy of the property estimates, the design engineer requires to consider uncertainties in the estimated property values in order to assess the quality and reliability of the final design. As a consequence, development of efficient and reliable property prediction methods and tools that can also provide estimates of uncertainties in predictions of properties becomes necessary.

The objective of this work is to develop a systematic methodology to provide more reliable predictions with a new and improved sets of model parameters for GC$^+$ approach (combined GC models with atom connectivity index (CI) based models) together with the results of uncertainty analysis such as covariance matrix needed to quantify the uncertainties in the estimated property values. In total 21 properties of pure components, which include normal boiling point, critical constants, normal melting point, standard Gibbs energy among others have been modeled and analysed. The statistical analysis of the model performance for these properties is highlighted through several illustrative examples. Important issues related to property modeling such as thermodynamic consistency of the predicted properties (relation of normal boiling point versus critical temperature etc.) have also been analysed. The developed methodology is simple, yet sound and effective and provides not only the estimated property values using the GC$^+$ approach but also the uncertainties in the estimated property values. This feature allows one to evaluate the effects of these uncertainties on the product-process design calculations thereby contributing to better-informed and reliable engineering solutions.

Ref O-080

Make your Thermodynamic Models available in most Process Simulators.

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Advanced thermodynamic models need to be put to use in process simulators in order to provide the industry with the benefits they have been targeted at providing. Implementation of advanced models is a major issue for industrial users as reported by Hendriks et al. [1]. Each major process simulator proposes its proprietary solution for incorporating a user-defined thermodynamic model.

A more economical solution is to develop only once the interface between the thermodynamic model and any process simulator by using the CAPE-OPEN interface standards. Since most commercial process simulators are implementing the CAPE-OPEN interfaces, the CAPE-OPEN approach ensures a large and immediate usage of research results when these, implemented as thermodynamic models, are adhering to CAPE-OPEN. Already many thermodynamic software components have been brought to the CAPE-OPEN standards.

Transforming an existing thermodynamic model into a CAPE-OPEN compliant thermodynamic model requires wrapping the existing code using some programming language. In order to facilitate this task, which calls for some specific programming knowledge especially of Microsoft COM middleware, CO-LaN, the organization acting as the CAPE-OPEN standardization body, has released working examples of CAPE-OPEN thermodynamic software components: the source code in Microsoft Visual Basic 6 and in Microsoft C++ is made available together with their corresponding binaries. That way developers may build their solution from existing code, minimizing the learning curve needed.

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Keyword: CAPE-OPEN.

Ref O-082

Predicting Phase Equilibria of Oxygenated Compounds Using Molecular Models: Results from the MEMOBIOL Project.

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The MEMOBIOL (*Modélisation à l'Echelle MOléculaire pour les BIOraffineries Lignocellulosiques* - Molecular Scale Modeling for Lignocellulosic Biorefineries) project, led by IFP Energies nouvelles (IFPEN), focusing on molecular modeling applied to lignocellulosic biomass (wood residues, cereal straw, forestry waste) has been selected by the ANR (French National Research Agency) as part of its 2009 "Chemistry and Processes for Sustainable Development" call for projects. In addition to IFPEN, the project brings together six partners from the academic world (Armines -*École des Mines de Paris CEP/TEP*-, ENSTA-ParisTech -*École nationale supérieure des techniques avancées*- and LSMP - *Laboratoire des sciences des procédés et des matériaux*), and the industry (Materials Design and ProSim).

The MEMOBIOL project has provided the framework for achieving the evaluation of different predictive molecular models in the context of VLE/LLE phase equilibria calculations.

The models investigated within the MEMOBIOL project are:

- The GC-PPC-SAFT EOS [1] (LSPM)
- Monte Carlo molecular simulation using the AUA4 force field [2] (IFPEN)
- The COSMO-SAC and COSMO-RS approaches [3] (Ensta-Paristech)

Phase equilibrium data from the literature as well as data measured at the CEP-TEP laboratories (Armines) have been used to evaluate the predictability of these models. The results are generally in good agreement, as shown in figure 1 for the VLE diagram of the binary furan-hexane.

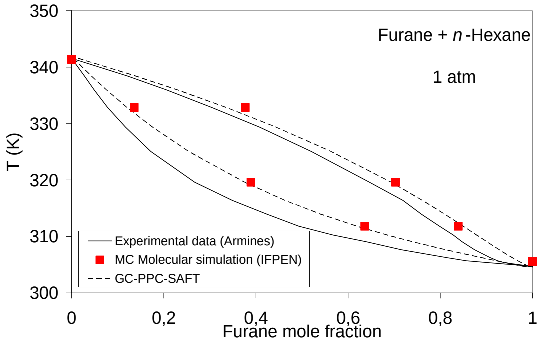

Fig.1: Prediction of VLE of furan+hexane using MC molecular simulation and the GC-PPC-SAFT EOS

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Keywords: Phase Equilibria, oxygenated compounds, biomass, model.

Ref O-085

Guiding the Design of ionic Liquids as Substitutes of volatile Organic Solvents: PLS-DA Models for Ecotoxicity (V. Fischeri) Discrimination.

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In the last decades, ionic liquids (ILs) have received rising attention in multiple fields of chemical technologies due to their unique properties and the possibility of designing them to fulfil a specific task, earning the accolade “designer solvents”. Particularly, ILs are frequently considered possible substitutes of volatile organic solvents because their negligible vapour pressure eliminates the problems associated with toxic emissions to air. However, ILs have at least some solubility in water, so their potential aquatic toxicity should not be disregarded. The lack of knowledge about the aquatic environmental risks of ILs is a major drawback to a wider adoption of these substances by industry, but the huge number of potential ionic liquids that may be synthesised makes their experimental assessment unfeasible. Accordingly, there is a growing need of scientific tools to predict the toxicity of these compounds, minimising the experimental efforts, and helping to assess “a priori” their ecotoxicity in relation to the solvents that they may replace, in order to ensure that ILs are also in this sense safer alternatives.

This contribution presents a new approach to aid the initial steps of the design process of ILs based on ecotoxicity discrimination. PLS-DA (Partial Least Squares-Discriminant Analysis) was used to develop models that, simply considering the combination of 30 anions and 64 cations included, allowed the discrimination of ILs based on their expected ecotoxicity (bacterium *Vibrio fischeri* assay) with respect to solvents traditionally used in industrial applications. A sequential approach is proposed, which involves a PLS-DA discriminant model using toluene as reference, followed by an additional PLS-DA model based on chloroform that can serve as complement to achieve a more refined discrimination. The predictive ability of the models was successfully validated by reserving test sets that were not used during model training. The successful results obtained in the external validation of the models reveal that this approach can be useful as a discriminating tool for screening purposes and prioritising ILs on the basis of their expected aquatic ecotoxicity, in order to easily guide design efforts, from the early steps of the process, along paths that could result in aquatic environmentally friendly ILs that would lead to lower ecotoxicity than conventional solvents they may replace.

Keywords: ionic liquids, ecotoxicity, PLS-DA, solvent design, screening.

Ref O-086

Prediction of physical Properties of CO2 in ionic Mea/Aqueous Solutions by Molecular Simulation.

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The present work has been carried out on the amine-based CO_2 capture process [1]. The solvent used in our application is an aqueous solution of mono ethanolamine (MEA). Two main properties such as mass diffusion and solubility of molecular CO_2 in MEA aqueous solutions have been calculated. The all atoms OPLS force field for mono ethanolamine (MEA) has been optimised in order to better reproduce pure component and mixture experimental properties of this molecule. The impact of the charged species (resulting from the equilibrium reaction of CO_2 with the MEA) on the diffusion coefficient have been studied at different temperatures. Our results are in agreement with the predictions of correlative models that implicitly considers the ionic concentration[2] as can be seen in Fig 1. The good agreement obtained between simulations/experimental data for viscosity in this ionic system allows an indirect verification of our predicted diffusion of CO_2. We have also estimated the solubility of carbon dioxide in the aqueous MEA solution using Monte Carlo (MC) molecular simulation. Two methods have been used in order to calculate solubilities at infinite dilution [3]: 1) thermodynamic integration, which provides the solvation energy of CO_2 in the solvent ; and 2) Widom insertion tests, which provides an estimation of the Henry's constant. This methodology can be used to estimate the physical absorption capacity of a solvent without the problem of the coupled chemical reaction. Further work can be carried out by using reactive MC in order to take into account the chemical reaction taking place in this process.

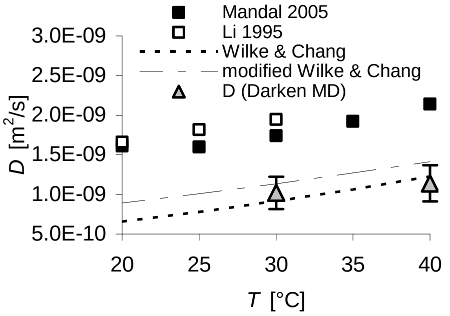

Fig 1: Variation of D_{CO2} for an ionic aqueous solutions of CO_2/MEA/MEA-H^+/MEA-COO^-/H_20.
The molar ration of CO_2/MEA is 0.5.

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Keywords: Molecular diffusion, gas solubility, MEA, CO2, post-combustion capture, process design.

Ref O-092

Nano Tools for Macro Problems: Multiscale Molecular Modeling of Life and Material Sciences.

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A current challenge of physical, chemical and engineering sciences is to develop theoretical tools for predicting structure and physical properties of complex systems at nano-scale from the knowledge of a few input parameters. However, despite all efforts, progress in the prediction of macroscopic physical properties from structure has been slow. Major difficulties relate to the fact that (a) the microstructural elements in multiphase material are not shaped or oriented as in the idealizations of computer simulations, and more than one type can coexist; (b) multiple length and time scales are generally involved and must be taken into account, when overall thermodynamic and mechanical properties wish to be determined, and finally (c) the effect of the interphases/interfaces on the physical properties is often not well understood and characterized. As a consequence, their role is often neglected in the development of new theoretical tools or they are treated in a very empirical way. In this work, we focused on issues (b) and (c) in a multiscale molecular simulation framework, with the ultimate goal of developing a computationally-based nanocomposite designing tool to be applied to a large number of systems. In particular, we apply a general multiscale simulation methodology [1] to some examples of industrial relevance both in material science and in life science.

The first example is of general importance for the polymer industry and is related to the enhancement of mechanical and barrier properties if a nanofiller is dispersed into a polymer matrix: the role of multiscale modeling for the development of the material in the stage of screening the best design is evidenced. [2] The second example, important for the opto electronic industry, is related to the prediction of the dispersion of gold nanoparticles into a diblock copolymer system forming different nanostructures (lamelles, cylindres,…). In this case it is relevant to understand how it is possible to influence the self-assembly of the nanoparticles in different regions of the diblock copolymer structure. The third and fourth examples focuses on drug delivery systems of new generation, based on polymers able to transport drugs or DNA towards target cells. Micellar formation and drug capacities are investigated using multiscale simulation for diblock biopolymers and for dendrons.

In all the examples, evidenced and emphasis will be given to the applicability of multiscale molecular modelling for the design of systems of industrial interest.

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Keywords: Multiscale molecular modeling, nanocomposites, in silico material design.

Ref O-101

Solubility of Pharmaceuticals: a Comparison between a PC-SAFT-Based Approach and NRTL-SAC.

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Thermodynamic models are increasingly used by the pharmaceutical industry at different stages of the product and process development and optimization processes. At the product development and formulation stage, various solvents are screened for new pharmaceutical molecules. At the later stage of process development and optimization, appropriate selection of a solvent or a mixture of solvents is critical for the crystallization and other processes.

In this work, we show the performance of two models in calculating the solubility of active pharmaceutical ingredients in different solvents and mixtures. The first model uses PC-SAFT in the context of a workflow integrated in the MAPS platform of Scienomics [1]. The second model is the NRTL-SAC model [2]. In a previous work [3] NRTL-SAC was compared against other thermodynamic models like COSMO-SAC and UNIFAC. In this work the comparison of the PC-SAFT-based model and NRTL-SAC is performed on the following molecules: paracetamol, ibuprofen, naproxen, salicylic acid, benzoic acid, p-aminobenzoic acid, anthracene, and temazepam. Both models have been parameterized on the same number of solvents. Results of solubility in different pure solvents, also as a function of temperature, and solubility in binary mixtures are presented.

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Keywords: Pharmaceuticals, Solubility, PC-SAFT, NRTL-SAC.

Ref O-105

Comparison of Performance of the PC-SAFT, Soave-Redlich-Kwong and Peng-Robinson Equations of State in Modelling Vapour-Liquid Equilibria of Binary CO2 ' 1-Alkanol Mixtures.

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Comparisons of the performances in modelling the Vapour-Liquid Equilibria (VLE) of CO_2-1-alkanols systems (from methanol to 1-nonanol) between 230 K and 453 K with the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) equation of state (EoS) and the cubic equations of state of Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) were made. Different versions of the PC-SAFT equation were considered: to account only for the dipolar moment of alcohols (named in this work as PCP-SAFT-D); to account only for the quadrupolar moment of CO_2 (PCP-SAFT-Q); the non-polar version of the equation (PC-SAFT); and the polar and non-polar versions of the equation but considering the recently proposed induced association (I) approach (PCP-SAFT-ID, PCP-SAFT-IQ and PC-SAFT-I). The association term was taking into account in all versions. For the SRK and PR EoS, classical mixing rules were considered. In all cases, a single binary interaction parameter (k_{ij}) was adjusted for each isotherm.

Comparisons between the equations were made by computing the Average Relative Deviation (*%ARD*) in pressure and vapour composition. Results showed that the induced association approach improved the representation of these systems compared when polar interactions are taken into account solely. Surprisingly, results with the SRK and PR EoS are similar than those obtained with PCP-SAFT-Q, even with a better performance over the dipolar and association versions with or without induced association. Best results for all systems were obtained with the PCP-SAFT-IQ equation, which also generated a lower k_{ij} for most of the temperature cases.

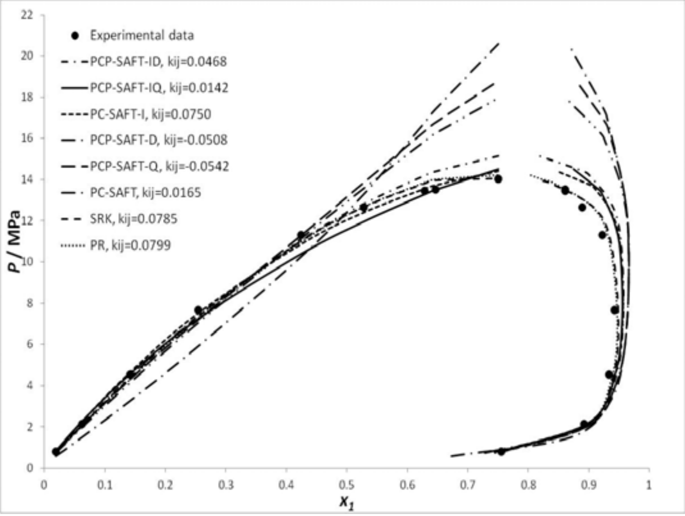

Figure 1. Phase diagram for the CO_2 (1) + methanol (2) system at 352.6 K.

Keywords: VLE, PC-SAFT, SRK, PR, CO_2, 1-alkanols.

Ref O-107

Multiphase Equilibrium of Fluids confined in heterogeneous porous Solids.

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Proximity to walls affects the behaviour of fluids confined in small pores. This is relevant in many situations of practical interest, such as in adsorption in porous solids and the recovery of petroleum from oil rocks. Fluid confinement can be modelled in various levels of detail, including molecular simulations. However, the computational effort for molecular simulations is still too large for many applications. A relatively simple model, as an equation of state (EOS), which captures the underlying physics of confinement with small computational load is of much value. Also, for being similar to EOS for bulk fluids, it is possible to model adsorption equilibrium by including EOS for confined fluids in procedures for phase equilibrium in bulk phases. Our group has recently developed an extended van der Waals EOS for fluids confined in cylindrical pores [1]. In the limit of non-attractive pores of large diameter, the predicted fluid behaviour tends to that of a bulk fluid. This model can predict several types of adsorption isotherms, correlate data of many pure adsorbates, and predict the adsorption behaviour of several mixtures. It also predicts shifts in critical properties as result of confinement [2]. Despite these results, a drawback to using this model is that is that the van der Waals EOS is not accurate enough for chemical process design. With this motivation, this paper shows results of an extended Peng-Robinson EOS developed using a similar methodology. Also, this EOS is used to model fluid behaviour in heterogeneous adsorbents, modelled as solids with cylindrical pores of different diameters and characteristic interaction energies between the molecules of the fluid and the pore walls. The equilibrium conditions are formulated as a multiphase equilibrium problem in which the specifications are the temperature, amount of each component, and total volume available for the bulk phase and for each type of pore. The problem is solved by minimizing the Helmholtz energy of the system. Possible pore condensation is considered by executing the global phase stability test to decide whether to include additional bulk or confined phases.

References:

[1] Travalloni, L., Castier, M., Tavares, F.W., Sandler, S.I., Chem. Eng. Sci. 65, 3088–3099, 2010.
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Keywords: porous media, confined fluids, equations of state.

Ref O-108

Heat and Mass Transport through Surfaces.

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In order to describe the transport of mass and heat through surfaces, irreversible thermodynamics theory (IRT) has been extended to heterogeneous systems [1]. It gives the possibility to describe within the same framework, i.e. thermodynamics, the transport processes in bulk systems and at their boundaries, at interfaces.

Little direct evidence of the validity of this theory and its limits are however available. The molecular dynamics (MD) simulations give the possibility to directly see what is happening locally at the heterogeneities, at surfaces, at equilibrium and out of equilibrium. It was used to validate the theory and to improve the way to express it as to be convenient for applications.

We simulated different surface systems from the most simple, a liquid-vapour interface of argon, to complex porous solid (zeolithe) in contact with molecular adsorbents (alkanes). Large mass and heat fluxes were applied across the surfaces. In all case we could verify that the transport phenomena obeyed the laws of IRT. We particularly validated the local equilibrium hypothesis, which is one of the key concepts of IRT. This principle is very strong and it applies even for extreme conditions like temperature gradients up to those present in flames (100 K/Å).

From the simulations the interface transport resistivity to mass and heat were calculated. Compared to the neighbouring bulks the resistivities are larger, which indicates that the surface acts as a barrier to heat and mass transfer.

The coupling between heat and mass, i.e. the Soret effect, is particularly important. In terms of heat of transfer, q*, it is of the same order of magnitude as the heat of evaporation, see Fig. 1. In the case of the adsorption of n-alkanes in zeolite systems we showed that it could originate large non-isothermal kinetics effects [2]. It means that a model of transfer of heat and mass through surface should include explicitly this effect in order to better model experimental results.

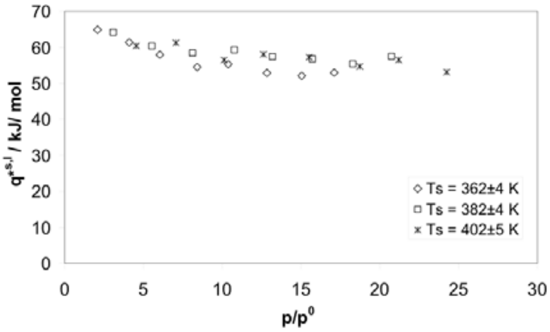

Figure 1 Measurable heat of transfer as a function of the gas pressure at constant surface temperature for n-butane/silicalite system [2]. The heat of desorption is about 55 kJ/mol.

References:

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*[2] Inzoli, I. et al. MMM, **125** 112 (2009)*

Ref O-109

Mesoscopic Simulation of Polyelectrolyte Brushes under Shear.

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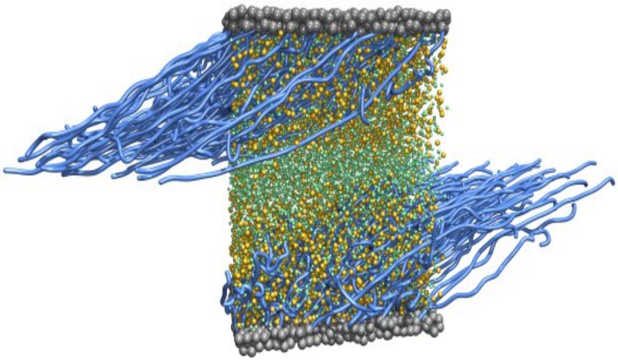
Polymer coated onto solid surfaces have many applications in wetting, adhesion, lubrication, colloid stabilization and biocompatibility. The use of polyelectrolytes introduces electrostatic repulsion between polymer chains, thus modifies the properties of the brush. Additionally, the inclusion of counterions inside the brush changes the rheological properties of these systems, decreasing the friction coefficient between two grafted surfaces.

This study is based on mesoscopic simulations using the dissipative particle dynamics (DPD) method with electrostatics. The use of smooth conservative potentials, dissipative and random forces allows to model the polymer chains and explicit solvent and counterions with large distance and time scales. It is then possible to simulate the structure and rheology of such complex systems.

We present here the results of our simulations of grafted polyelectrolytes brushes under shear. The shear rate, the solvent quality, the concentration of added salt have a notable influence on the brush structure (density profile, length and tilt distribution). The friction and viscosity of the overlap region is governed by the brush interpenetration and the charge fraction in the polymer chain.

It appears that the use of polyelectrolytes increases repulsions between chains and consequently has the same influence than good solvents. However, the long range of the electrostatic interactions induces a whole new range of structural behaviours, which have to be understood to do the link with the intereseting rheological properties of these systems.



Snapshot of a typical configuration of two polyelectrolyte brushes under shear with counterions and solvent particles.

Keywords: polymer brushes, friction, polyelectrolytes, mesoscopic simulation.

Ref O-121

Improving Molecular Simulation Models of Adsorption in porous Materials: Interdependence between Domains.

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Fluid confinement is ubiquitous in nature and industry, and is the most widely used technique to characterize porous materials. The main characterization tool consists in measuring the so-called adsorption / desorption isotherms, i.e. the amount of gas adsorbed by the porous substrate as a function of the fluid chemical potential (or relative pressure). The models used to analyse the data are generally quite simple, leading to inaccurate characterization of the porous materials. In particular, ignoring the interdependence between the elemental pores or domains leads to inappropriate conclusions. Our approach proposes to cure this problem in the molecular simulation approaches.

Molecular simulation is a powerful tool to study fluid adsorption in elemental nanoscale cavities or domain, since the relevant fluid/fluid and fluid/substrate interactions are described at molecular level. However, due to computer limitations, it is not possible to take into account the complex network of interconnections between the various domains or heterogeneities which span up to micrometer scale. As a consequence, molecular simulation generally provides good description of fluid adsorption at low coverage where the domains are approximately independent, but it is ineffective in the hysteresis region because the large scale spatial distribution of heterogeneities in the pore network is beyond the computer capabilities. In this work, a multiscale approach is introduced, allowing both a molecular description of fluid/fluid and fluid/substrate interactions, and simultaneously taking into account the connectivity between the various domains constituting the porous material.

The case of argon confined in heterogeneous tubular silica mesopores (MCM-41 or oxidized porous silicon) is considered. In this simple case, the topology of the domain network reduces to one dimension. However, comparison with the simple Independent Domain Theory shows the strong influence of the disorder produced by the distribution of domains along the pore. It is also shown that the independent pore model significantly overestimates the hysteresis width. The effect of the pore being open at only one or at both ends is addressed, and results are compared to experiments.

Ref O-122

Improving the Modeling of compositional Grading in Petroleum Reservoirs: a Molecular Dynamic Approach.

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An accurate knowledge of the initial state of a petroleum reservoir is crucial to optimize its development plan. Such knowledge relies on a precise description of the spatial distribution of the fluid components within the reservoir which is mainly influenced by gravitational segregation and thermo-diffusion phenomena [1-2].

Usually, a good estimation of the steady state spatial distribution of the components is obtained by thermodynamic modeling based on a cubic Equation of State (EoS). Nevertheless, this heuristic approach is unable to yield any knowledge on the time required to establish a segregated profile and it needs an ad hoc correlation to take into account thermodiffusion which is not readily available. One way to provide additional information both on the thermodiffusion effect and on the dynamic of the thermo-gravitational phenomena is to use Non-Equilibrium Molecular Dynamics simulations on systems representing an idealized 1D reservoir fluid column [3].

We will show during the presentation how such a molecular based approach can be employed to test the usual (EoS) methods and can shed light on some the underlying physical mechanism (evolution/stability) of the thermo-gravitational process in idealized situations. In particular, using Molecular Dynamics simulations, it will be shown that the thermodiffusion effect can affects the vertical distribution of the different compounds as much as segregation [4] and can even lead to an unstable (i.e. convective) situation in a CO2 rich reservoir.

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*[2] F. Montel, J. Bickaert, A. Lagisquet, G. Galliéro, **J. of Petroleum Sci. and Eng.** 58, 391-402, 2007.*
*[3] G. Galliéro, F. Montel, **Phys. Rev. E** 78, 041203-1/10, 2008.*
*[4] M. Touzet, G. Galliéro, V. Lazzeri, Z. Saghir, F. Montel, **C.R. Meca.** 339, 318-323, 2011*

Keywords: Molecular Dynamics, Petroleum Fluids, Thermogravitation.

Ref O-123

About unexpected solid-liquid phase diagrams obtained with most of SAFT-like equations of state.

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Actual representation of fluid phase behaviour is an important issue in chemical engineering. Since the pioneering work of Van der Waals, many equations of state (EoS) for fluids have emerged. They are capable of accounting for both liquid and vapour phases and allow to represent the thermodynamic behaviour of pure components and mixtures. The quality of such models is generally assessed through their ability to describe physical phenomena (changes of state, criticality, azeotropy and so on) as well as their capacity to accurately calculate PVT properties and phase equilibria. However, beyond qualitative and quantitative efficiency, the knowledge of the limitations of the models is of major importance and must be necessarily taken into account to avoid erroneous calculations.

In this study, the fugacities of components in the liquid phase are estimated using the non-associating PC-SAFT equation of state. The solid phase is assumed to be pure and its fugacity is calculated from a basic model requiring the knowledge of both the enthalpy of fusion of the pure compound and its melting temperature. Then, the influence of the binary-interaction parameter (k_{ij}) value of the PC-SAFT EoS on the shape of solid-liquid phase diagrams is qualitatively assessed. It is shown on a well-illustrative system that a range of reasonable k_{ij} values leads to strongly surprising diagrams exhibiting non-feasible phenomena such as liquid-liquid azeotropy.
These unusual predictions can be ascribed to the potential existence of five roots when solving the PC-SAFT EoS (and more generally, most of SAFT-like EoS) at a fixed temperature and pressure, whereas from a physical point of view, only three roots should be obtained.

Ref O-124

gSAFT:
Application of the SAFT-g MIE Group Contribution EOS in the Oil/Gas Industry- from academic Research to Industrial Deployment.

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SAFT-γ Mie is a new equation of state recently developed by the Molecular Systems Engineering group at Imperial College London. It is an advanced group-contribution form of the SAFT equation of state making use of the Mie potential for a more accurate and flexible description of the dispersive/repulsive interactions between segments. One of its key characteristics is the accurate description of vapour/liquid phase equilibria, including the region of the critical point, as well as the second-derivative thermodynamic properties such as the thermal expansivity, isothermal compressibility, heat capacity, Joule-Thomson coefficient, and speed of sound.

In 2009, Process Systems Enterprise (PSE) acquired the exclusive intellectual property rights associated with SAFT-γ Mie and related work, for the purpose of incorporating these developments within its gSAFT advanced thermodynamics technology for process modelling. In late 2010, TOTAL, PSE and Imperial College embarked on a joint project aimed at exploring in detail the applicability, benefits and limitations of this technology on a wide range of mixtures of interest to the oil & gas industry. The current phase of the project is primarily focused on mixtures of hydrocarbons (alkanes and aromatics), carbon dioxide, water and methanol. The main output is a single, consistent set of group parameters capable of accurately describing the behaviour of these generic mixtures within the SAFT-γ Mie framework.

Starting with a brief overview of the SAFT-γ Mie equation of state, this paper primarily focuses on the systematic methodology employed in developing the corresponding like and unlike group parameters. This comprises a sequence of steps including the choice of representative components and mixtures, the definition of an appropriate set of groups required to describe them, the collection of the necessary experimental data, a streamlined set of software tools and workflows employed for the accurate, efficient and error-free estimation of the relevant parameters, and ultimately the deployment of the gSAFT software within process modelling tools. Results illustrating the predictive accuracy of gSAFT for the above mixtures are presented, including representative examples of the simultaneous description of vapour-liquid and liquid-liquid equilibria, the densities of the coexisting phases, and excess properties of mixing.

Keywords: SAFT, group contribution, process modeling.

Ref O-126

Generalization of SAFT + Cubic Equation of State for predicting and correlating thermodynamic properties of heavy organic substances.

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The current presentation discusses a scheme for generalizing parameters of SAFT + Cubic EoS (GSAFT + Cubic) for predicting and correlating thermodynamic properties of heavy (18 and more carbon atoms) organic substances and of ionic liquids. The accuracy of this approach might usually be compared with the multi-parameter empirical Tait equation. However, unlike the latter one, it has a predictive character. In the cases of the substances included in the databanks such as DIPPR, GSAFT + Cubic requires input of a single experimental density datum point. In the cases of complex fluids, such as the heavy oils, the ionic liquids or the ester lubricants, the proposed approach requires input of two experimental points of density and estimation of the ideal gas heat capacity for predicting various auxiliary properties in wide *PVT* range. A major advantage of GSAFT + Cubic over the empirical correlations is its applicability for estimating phase equilibria and other thermodynamic properties of mixtures while using the one-fluid approach. In particular, it has been demonstrated that GSAFT + Cubic yields accurate predictions of the available VLE and LLE data of mixtures of the heavy *n*-alkanes and the ionic liquids.

POSTERS PRESENTATIONS

(by order of references)

Ref P-002

Numerical Simulation of the Elimination of Copper (II), Cadmium (II) and Zinc (II) from phosphoric Acid.

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In this paper a numerical study of the adsorption phenomenon of copper, cadmium and zinc present in phosphoric acid is presented. The process is carried out batchwise using bentonite and activated carbon as solid supports.

The governing equations for the adsorption phenomenon are discretisized by finite differences method using the explicit scheme where the conditions of stability are checked and solved by Gauss Seidel method.

A computing code was developed to determine all the structures of diffusion of heavy metals solutions into the pores of adsorption particles.

In order to examine the code reliability, the obtained results were compared to the values reported in the literature and a maximum deviation of 1.49 per cent was shown.

The application of the program code for the case of the adsorption of copper, cadmium and zinc onto the two supports and using our experimental data enables the calculation of the superficial intraparticule diffusion coefficient Ds, as well as the mass transfer coefficient K_f.

Key words: Superficial Diffusion; Mass transfer coefficient; Adsorption; Cations; Bentonite.

Ref P-003

Experimental and numerical study of adsorption of dibutyl phthalate from phosphoric acid purification.

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The present study concerns the experimental elimination of an organic, the dibutyl phthalate (DBP), by means of adsorption onto three different solid supports: activated carbon, bentonite and olive stones, in a batch reactor. The effects of different parameters on the retention capacity of the three adsorbents, such as the contacting time, the shaking velocity, the pollutant initial concentration, were investigated. The determination of the equilibrium isotherms as well as a kinetic study was also included. The obtained results confirmed the good performance of activated carbon, comparatively to bentonite, olive stones and other adsorbents such as sawdust and cereal by-products, previously considered. The results also showed that the equilibrium adsorption capacities for the three adsorbents followed best the Langmuir model for the activated carbon but poorly for bentonite and olive stones. The kinetic study has shown that the adsorption process is of second order and the rate constants have been determined for the activated carbon and bentonite. For the olive stones the correlation factors for 1st and 2nd order kinetics were far from unity, indicating a poor representation.

Keywords: Phosphoric acid, Dibutyl phthalate, adsorption process.

Ref P-019

What can Cosmo-RS do for Crystal Engineering.

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During the past decade the Conductorlike-Screeing Model for Realistic Solvation (COSMO-RS) has been established as a reliable predictive tool for fluid phase thermodynamics. Although not being able to treat molecules in their solid crystalline form, COSMO-RS can nevertheless also be of great value for some aspects of crystal engineering. Different aspects will be discussed:

- Solvent screening and interaction analysis for finding interesting and diverse solvents for crystallization,
- Estimate of ΔG_{fus} based on COSMO-RS descriptors,
- COSMOhkl for morphology engineering: σ-profiles of crystal faces and their free energy in solution,
- Cocrystal Screening based on excess mixing enthalpy.

Key words: solubility, morphology, cocrystals.

Ref P-026

Prediction of physical Properties of Non-Electrolyte organic Compounds by Modified Group Contribution Method.

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Predictive techniques are widely used for estimating physical properties of pharmaceutical and bio-compounds. In fact, the high reactivity and the tendency to decompose of these compounds render difficult the experimental determination of their properties. The estimations of these properties by traditional group contribution methods (GCM) are not reliable due to the size and the complexity of the molecules. Group contribution methods are quick tools to obtain physical properties, but their accuracy is strongly dependent on the amount of compounds with each structural group and group combination included in the GCM training database. The combination of structural groups of pharmaceutical and bio-compounds are often insufficiently characterized in the databases of GCMs. As an alternative, molecular modeling (MM) simulation could be used for obtaining the required properties, but it is usually time consuming and the accuracy of these predictions is questionable.

In this work, we present a modification of the group contribution approach for calculating non-electrolyte organic compound properties. This new technique exploits the concept of chemical similarity. Structural similarities among compounds are taken into account in the optimization of the group contribution coefficients by means of weighting factors. The group contribution coefficients are optimized for each estimation task. When experimental data is not available for rare groups or group combinations, the training database can be supplemented with MM calculated data for the specific class of compounds. In this way, the experimental data and MM results are combined to ensure the quality of the estimated properties. The use of MM results in form of a weighted group contribution method provides a sufficient level of generalization and reliability of the derived coefficient. In addition, this methodology is a time efficient way to use available MM calculation results.

The new methodology was tested on the prediction of the normal boiling point (NBP) for 400 non-electrolyte compounds using the most known group contribution method, i.e. the method of Joback [1]. The new method reduced the absolute average error (AAE) in NBP from 15.7K for the JR method to 8.9K.

References:

[1] K.G. Joback, R.C. Reid. Estimation of pure-component properties from group contributions. Chem. Eng. Commun. 57 (1987) 233-243.

Keywords: Group contribution methods, distance weighting, boiling point.

Ref P-027

Ab-initio Calculations – a Source of PC-SAFT Parameters.

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We report on highly accurate ab initio calculations of binding enthalpies and entropies of gas phase clusters of alcohols and amines and demonstrate how they can be used to obtain association parameters for PC-SAFT. The accuracy necessary for this requires modern quantum chemical post-SCF methods for energy calculations as well as analysis of topological symmetry and hindered rotor effects for reliable entropies. This approach goes beyond the rigid rotor + harmonic oscillator method implemented in standard quantum mechanics software tools. The results demonstrate that (1) thermochemical cluster properties can nowadays be obtained by ab initio methods with accuracy comparable to or even better than that of the experimental data of most species. (2) Cooperativity effects and state dependent cluster distributions cause a strongly varying average enthalpy and entropy per bond as function of temperature and density for some substances. In contrast to this, the two association parameters of PC-SAFT lead to density independent bond enthalpy and entropy and are thus effective parameters. Therefore, we choose to compute the cluster distribution at 60% of the critical temperature at dew density and show that the thus obtained association parameters can be used to reduce the number of adjustable parameters from 5 to 3 with only a marginal loss of accuracy for the studied systems.

Keywords: Predictive; PC-SAFT, Association, Quantum Mechanics,
Statistical Thermodynamics.

Ref P-028

Application of CPA to Mixtures containing Acid Gases.

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Aim of the study is to suggest the optimum approach in modeling the phase behavior of CO_2 and H_2S containing mixtures with the CPA equation of state. In this direction, many modeling approaches were used. Firstly, acid gases were modeled as non-associating (inert) compounds. In a second step, cross-association interactions between H_2S or CO_2 and water, alcohol and glycols were assumed. Finally, the potential of modeling acid gases as self-associating fluids was investigated. In the last two approaches, effort has been made in order to incorporate in the model experimental and theoretical values for the strength of cross-association interactions between acid gases and water or alcohols. Binary, ternary and multicomponent mixtures with water, alcohols, glycols and hydrocarbons were considered. Binary parameters were adopted from the corresponding binary systems and the model was applied to predict the phase behavior of several ternary and multicomponent mixtures [1,2].

Using interaction parameters obtained solely from binary systems, CPA can predict satisfactorily the phase equilibria of multicomponent H_2S or CO_2 containing systems. For H_2S systems, the best results are obtained when cross association between H_2S and water or methanol is explicitly accounted for, especially when the cross-association energy is taken from experimental studies. However, equally good results are obtained when a self-associating H_2S molecule is assumed (using the 3B association scheme), when the cross-association energy, which characterizes its interactions with polar molecules, is taken from experimental spectroscopic studies. For CO_2 systems, one of the best approaches is to consider CO_2 as self associating fluid using the 3B or 4C association scheme. However, often equally good results are obtained by considering that CO_2 is not self – associating fluid and accounting for cross-associating interactions with water and alcohols (solvation).

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Keywords: Acid Gases, CPA, Multicomponent mixtures.

Ref P-030

Optimization of Proten Stability during Freeze-Dring Process.

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Stabilization and storage of biological materials, in particular proteins, are the principal goals of the pharmaceutical industry. To improve their stability, the proteins must be stored in solid form (powder). The most commonly used method for preparing solid protein is the freeze-drying [1] [2].This process consists to remove water from frozen sample by sublimation and desorption [3]. The process of freeze-drying can be visualized in terms of three steps: i) initial freezing, ii) Primary drying and iii) Secondary drying [4]. However, the freezing stress, changed pH and drying stress affect the protein stability during the process [5]. To protect the protein structure during the process, excipients (PVP, Trehalose, and Sucrose) can be added to the protein solution [6].

Raman microspectroscopy is used to monitor structural changes of the protein and the physical mechanisms of bioprotection, during freeze-drying. The spectra of amide I, II and III bands between 800 and 1800 cm^{-1}, probe the α-helix and β-sheets structures of the protein and their transformation.

The aim of the study is determination of the nature of stress responsible for protein denaturation and analysis of mechanisms of stabilization of co-solvents, during freeze-drying.

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Keywords: Stability, Protein, Freezedrying, Raman microspectroscopy.

Ref P-031

CO_2 Capture on Carbon Fibers Activated with supercritical Fluids.

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The impact caused by the burning of fossil fuels is driving increased efforts to preserve the environment. Within this context a global solution has been propounded: the reduction of CO_2 emissions. Most of the alternatives posed involve CO_2 capture during the processes where it is generated and later storage. Although adsorption on solid materials is not an efficient method for large scale storage, it may, however, be used for CO_2 capture.

In this work, several series of activated carbon fibers (ACFs) have been prepared with supercritical fluids -water and CO_2- for CO_2 capture. A model is proposed for analyze and predicting the adsorption depending on the textural characteristics of activated carbon fibers. This work is completed by the determination of several thermodynamic parameters.

The adsorption capacity of the different fibers was calculated using the adsorption isotherms of CO_2 at 258K, 273K, 288 y 303K. The maximum amount of CO_2 storaged in these *ACFs* has been 17%wt. This value is significantly better than the values found in bibliography, under the same experimental conditions [1]. The parameters -small micropore volume (smaller than 0.7 nm) and large size micropore volume (between 0.7 and 2.0 nm)- have been chosen for determining how the fibers´ textural characteristics effect their capacity for CO_2 storage. The results indicate that micropore size is closely related to the amount of CO_2 adsorbed. In view of these, it possible to propose an adsorption model based on two centres of adsorption with different interaction energies.

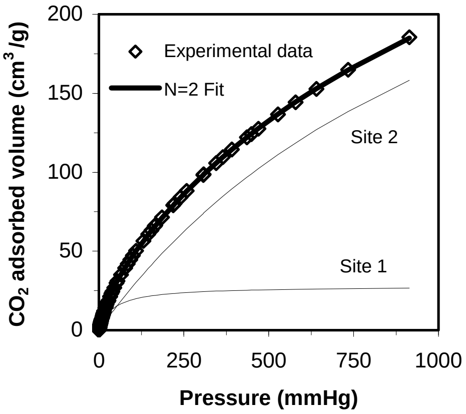

Figure 1 shows the fitting of an isotherm data to a model in which two energetically different centres are considered.

Figura 1.- Fitting of the isotherm to two centres model with the contribution of each centre.

The model also allows us to determine the adsoprtion constants of each centre. Through its evolution with the temperature, we have determined the enthalpy adsorption of the process using the Van´t Hoff equation.

The value of the enthalpy decrease with the burn off. These values correspond to the expected in a process of physisorption [2].

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Keywords: CO_2 capture, activated carbon fibers, supercritical fluids.

Ref P-033

Application of the UNIFAC-CI Models for Phase Equilibria Predictions of organic Chemical Systems.

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Prediction of properties is important in chemical process-product design. Reliable property models are needed for increasingly complex and wider range of chemicals. Group-contribution (GC) methods provide a useful tool but there is a need to validate them and improve their accuracy when complex chemicals are present in the mixtures. In accordance with that, a combined GC and atom connectivity approach that is able to extend the application range of property models has been developed for mixture properties [1,2,3]. This so-called GC^{Plus} approach is a hybrid model which combines GC and molecular descriptor theories such as connectivity indices. Connectivity indices (CI) are formalisms defined via graph theoretical concepts intended to describe the topological characteristics of molecular structures. The main idea is the use of connectivity indices to describe the molecular fragmentation that relates properties which are the molecular interactions with the molecular structures. One established GC method is the UNIFAC model, used to predict activity coefficients for mixtures. The values required for the group interaction parameters (GIPs) are obtained by fitting phase equilibrium data. There are, however many gaps in the UNIFAC parameter table due to lack of data. Alternative to performing measurements, which may be time consuming and not always feasible, values of the missing GIPs, can be predicted through the GC^{Plus} approach and used in the UNIFAC model to calculate activity coefficients. In this work, the application of this hybrid model, called UNIFAC-CI, is highlighted in two industrial case studies. The first one involves pharmaceutical systems where the solubility of complex drug-like molecules in different solvents are investigated. The second case study involves lipid systems where the phase equilibria of a multicomponent system in the deodorization process of oil and fats which also include extraction and refining of high-value commercial by-products are investigated. In each case study, a parameter table that contains all the needed fine tuned binary interaction parameters is developed. In addition, other interesting examples of systems involving the application of the hybrid model will be presented.

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Keywords: Connectivity Index, Property Prediction, UNIFAC, Organic Systems.

Ref P-037

Ethylene Vinyl Acetate Copolymer'Solvent Interaction Parameters from inverse Gas Chromatography.

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Flory–Huggins polymer solvent interaction parameter at infinity dilution (X^{∞}_{12}) of an ethylene vinyl acetate copolymer (EVA) containing 33 wt % vinyl acetate, with nine volatile solvents has been calculated from the retention time values measured by inverse gas chromatography technique (IGC) [1], at 30, 40 and 50 ºC. The X^{∞}_{12} parameters are shown in Figure 1. These indicate that p-xylene, toluene, tetrahydrofuran and cyclohexane were the most compatible solvents for this kind of polymers, with X^{∞}_{12} values below 0.5, while the worst solvents were ethanol and methanol, with X^{∞}_{12} values up to 2.0. In addition, the EVA solubility parameter (δ_2) was calculated according to the Hildebrand and Guillet procedures [2], from the values of the solubility parameter of the solvents, as shown in Figure 2. The results were 17.36 MPa$^{1/2}$ at 30 ºC, 17.03 MPa$^{1/2}$ at 40 ºC and 16.77 MPa$^{1/2}$ at 50 ºC. Compared with bibliographic data of similar materials [3] these last results are optimal. Consequently the primary X^{∞}_{12} estimated values are reliable for the subsequent estimation of thermodynamic parameters for the simulation of EVA-solvent separation process.

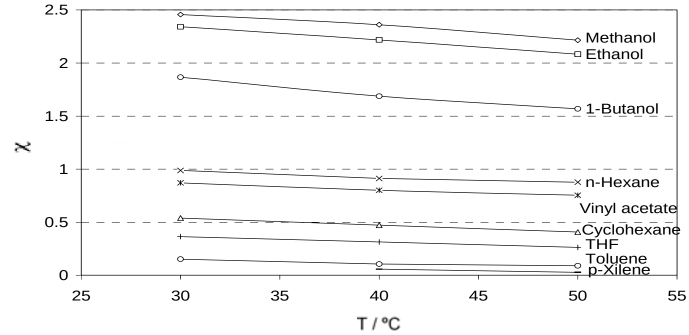

Fig.1. Flory–Huggins interaction parameter (X^{∞}_{12}) of EVA 33% wt VA with different solvents

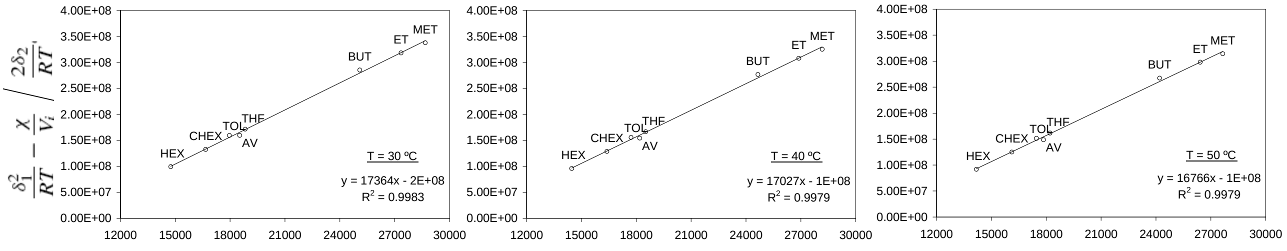

Fig.2. Calculation of solubility parameter (δ) of EVA 33% wt VA with different solvents

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Keywords: EVA copolymer, Inverse Gas Chromatography, Flory Huggins.

Ref P-038

Thermodynamics of PVA'Solvent Systems.

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Nowadays polymer-type materials are widely used in many different fields. For this reason it is crucial to study their thermodynamic properties along with the properties of their mixtures with solvents. Among all these materials, poly-vinylalcohol (PVA) is one of the most important mainly due to its applications in paper coatings, as thickener or as a modifier in poly-vinylacetate glues [1].

In this work we have calculated, by means of Inverse Gas Chromatography technique [2], the weight-based infinite dilution solvent activity coefficient of several binary PVA-solvent mixtures, employing a PVA material with a viscous number-average molecular weight of 47300. The results are summarized in Table 1 and, as it could be expected, the value of this parameter decreased with the temperature.

Table 1. Weight-based infinite dilution solvent activity coefficient of several PVA-solvent mixtures

T (ºC)	**Weight-based solvent activity coefficients (Ω_s^∞)**							
	MetOH	EtOH	1-PropOH	1-ButOH	1-PentOH	1-HexOH	1-HeptOH	1-OctOH
90	27.22	45.89	64.43	101.5	139.2	204.6	211.3	217.4
100	19.35	34.14	49.04	77.66	108.8	157.9	182.6	244.7
110	13.19	24.58	36.99	57.24	78.07	119.2	n/d	n/d

From these values we calculated the NRTL binary interaction parameters, following a procedure already described in literature [3], with an algorithm written in Excel. Finally, the obtained parameters were employed to simulate, with ASPEN PLUS® software, a polymer-solvent steam stripping separation step. The simulation results indicated that a two-staged stripping process allows obtaining PVA with purity higher than 99.5%.

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Keywords: Polyvinyl alcohol; Inverse Gas Chromatography; Simulation; Stripping.

Ref P-039

Calcium Mediated Polyelectrolyte Adsorption on like-charged Surfaces.

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One of the most widespread example of a polymerically stabilized colloidal system is concrete. In this context, anionic comb polymers with a charged backbone, mostly polycarboxylate esters, have been found to adsorb on the highly negatively charged cement nano-hydrates at conditions of high pH and high calcium concentration. Grafted to the backbones are hydrophilic sidechains (PEG) which are thought to provide the required entropy (steric hindrance) to overcome ion correlation forces which otherwise cause the cement to aggregate[1]. The result is a high performance concrete with enhanced workability, durability and mechanical properties.

In this contribution, our aim is to rationalize the mechanisms of the polymer adsorption in such systems. To do so we have performed Monte Carlo simulations of linear and branched polyelectrolytes in contact with like-charged surfaces and divalent counterions[5]. By fitting experimental titration data[3,4] of polyacrylic acid in various salt solutions, the polymer model parameters and the ion-pairing between calcium ions and charged monomers were determined. The adsorption was shown to occur as a result of surface overcharging by the calcium ions and ion pairing between charged monomers and calcium. In agreement with experimental observations[5], the simulations predict a non-Langmuir adsorption isotherm, i.e, we observe an adsorption maximum as the calcium or the polymer content is increased. The non-Langmuir isotherms were rationalized in terms of charge-charge correlations. Moreover, the effect on the adsorption when varying the sidechain grafting density, surface charge density and the degree of polymerization of the polymer backbone and sidechains has been studied.

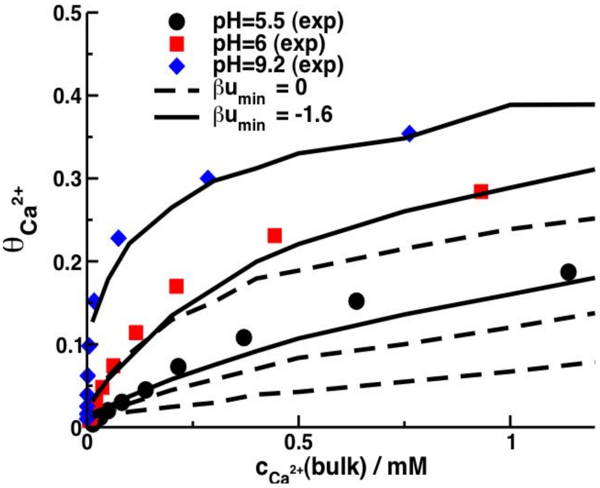

Figure 1: Comparison between simulations (lines) and experiments (symbols) of calcium binding to polyacrylic acid.

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Keywords: Polyelectrolytes, adsorption, ion-pairing.

Ref P-040

Alkanolamines Force Field.

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Aqueous solutions of amines are commonly used in postcombustion carbon dioxide capture processes. The dissolution of the gas in aqueous solutions depends on the molecular interactions in {water-amine-CO_2} systems.

Molecular simulation is a promising tool for predicting thermodynamic properties and establishing structure-properties relationships essential to the development of predictive models. The main objective of this work is to develop a force field adapted to describe alkanolamines containing the NCCO basic structure (Figure 1).

Monoethanolamine (MEA) is the simplest amine containing this structure. It is also the reference absorbent for CO_2 capture processes [i]. We propose a methodology to determine the parameters needed for the molecular simulation of such amines. This methodology will be first tested for pure amines and then applied to aqueous solutions. In both situations, the amines are considered in a polar solvation environment, dominated by hydrogen bonding interactions. Thus, polarization effects were taken into account by calculating the electrostatic charges distribution in presence of solvent molecules. The densities and vaporization enthalpies of pure amines were calculated by molecular simulation and compared to experimental values.

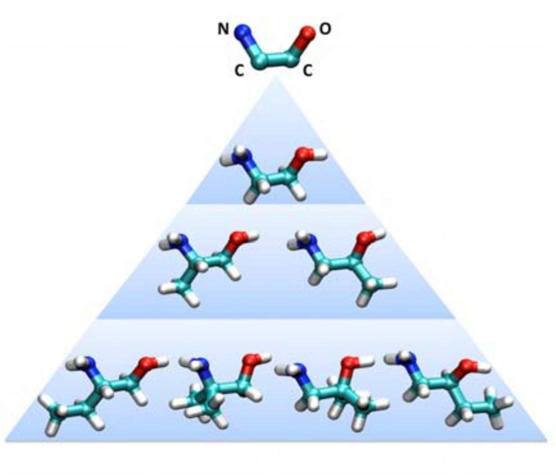

Figure 1: Alkanolamine Studied

References:
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Keywords: Alkanolamines, force field, vaporization enthalpy.

Ref P-045

Merging CAMD with Model Driven Architecture for Multiscale Formulation of Molecules.

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Under the incentive of regulations (REACh or new VOC directives), of opportunities (green is marketable) or of social awareness towards lower Energy, Environment, Health and Safety (EEHS) impact, the substitution of molecules, like bio-solvents is a major issue in chemistry, pharmaceutics, energy supplier, food, aeronautics, car makers…. Beneath that problem, lies the need for any end-user products to satisfy not only primary and functional properties but also EEHS related properties and other secondary properties like flavor, etc.

If the trial and error method had some success, its inefficiency is well known. Such a bottom-up approach first selects a few high potential molecules, alters chemically their structure and tests *a posteriori* their ability to match desired properties. The primary property is usually matched but unmatched secondary properties can often kill the market potential of the molecule.

The alternative approach, reverse engineering started in the 70's among the chemical engineering community and led to the building of Computer Aided Molecular Design (CAMD) tools: identify all desired properties, select property models and target values, aggregate them in an objective function and search for molecules matching these properties. Deterministic method or genetic algorithms build molecules from chemical fragments.

Within the accuracy of the property models, finding candidate molecules matching the properties by CAMD is easy, but they are often ruled out by chemists because their synthesis is too expensive or unfeasible.

We improve the success of reverse engineering by designing a CAMD tool with a model-driven architecture. Business rule models help manage the decision processes among all actors: manager (we substitute a molecule), market engineer (green is better), process engineer (CAMD tool & thermodynamics), chemists (set synthesis rules; select building blocks from renewable resources).

Within the CAMD tool, molecular graph representation of molecules allows a multilevel search[1]: at level 1 many candidates are proposed, matching properties evaluated by simple models like correlations, QSAR or first-order group contribution models (GCM). Higher levels reduce candidates and use more complex and accurate models: second and third-order GCM, knowledge-based models (eg SLE, …) and ultimately produce inputs for molecular simulation (COSMO-RS, quantum chemistry, Monte Carlo or molecular dynamic).

Reference:

[1] Harper et al. Fluid Phase Equil. 1999, 158-160, 337-347.

Keywords: CAMD, Business Rule Models, Multi-scale Property Models,
Product Formulation.

Ref P-046

Physico-Chemical Study and Modeling of the CO2-Glycerol System: Vapour-Liquid Equilibrium.

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Glycerol has attracted increasing attention in recent years for its bio-based origin as a byproduct in biodiesel fabrication, currently 1.2 million tons in 2010.

The use of glycerol as a sustainable catalytic reaction solvent for organic synthesis has attracted a lot of attention[1]. However, one of the drawbacks in the utilization of non-volatile solvents such as glycerol in catalytic reactive systems is the recovery of reaction products and recycling of the catalysts.

In this context, biphasic systems employing supercritical CO_2 ($scCO_2$) as a second phase can be envisaged. In that case, reaction products can be selectively extracted thanks to $scCO_2$ with the catalyst remaining in the glycerol phase. The effective design and control of a biphasic reactor containing $scCO_2$ requires the knowledge of the physical state of the mixture and the understanding of the influence of CO_2 on the physicochemical properties of the second phase. L-V equilibrium experimental data concerning biphasic systems including CO_2 and glycerol are scarce and prediction of phase behavior of systems such as CO_2-glycerol is not an easy task: classical cubic equations of state don't consider the strong associating behavior of molecules such as glycerol.

In this study the liquid-vapor equilibrium of the CO_2+glycerol system is measured and modeled. Phase equilibrium experimental points have been determined in a high-pressure view cell at 40, 50 and 60°C at pressures up to 400 bar. Modeling has been achieved by employing a group contribution method combined with a perturbed polar chain-statistical associating fluid theory equation of state (GC-PPC-SAFT)[2] to take into account glycerol-glycerol auto-association and glycerol-CO_2 cross-association interactions generated by hydrogen bonds of glycerol hydroxyl groups.

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Keywords: supercritical CO_2, glycerol, phase equilibrium, biosolvents, SAFT.

Ref P-048

On the Interactions between ionic Liquids and amino Acids in aqueous Solutions: Molecular Dynamics Simulation Studies.

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Processes such as the separation and recovery of bioproducts from natural sources and fermentation media, enzyme activity and stability, kinetic resolution of racemates and biosynthesis, are topics of utmost importance in biotechnology. The search for efficient and safe approaches to these procedures and the recognition of advantageous properties in ionic liquids (ILs) has led to a growing interest in the use of these compounds as *green* alternatives to conventional solvents. For the improvement and optimization of biotechnological processes through the design of adequate ILs, a deep knowledge of the factors that influence the solvation of biocompounds in ILs and aqueous phases, as well as of their underlying molecular mechanisms, is essential. In this respect, liquid-liquid equilibrium data for aqueous solutions of ILs and amino acids (taken as model systems) have been precious sources of information and have enabled the establishment of correlations between the chemical structure and properties of the biomolecules and the magnitude of the solubility effects observed. In order to get further insight into the molecular mechanisms governing the behaviour of (IL + amino acids+ water) systems and develop a well-supported molecular picture of the phenomena occurring in these systems,complementary microscopic information is crucial. Therefore, in this work, molecular dynamics (MD) simulations were performed for aqueous solutions of (1-butyl-3-methylimidazoliumbis (trifluoromethyl) sulfonyl imide) in the presence of five amino acids (glycine, alanine, valine, isoleucine and glutamic acid). The amino acids chosen span the different solubility behaviours – from salting-in, to negligible, to salting-out effect on the IL aqueous solubility. By analyzing the radial distribution functions of the various groups and moieties, and calculating their respective energies of interaction, insight into the molecular interactions established in solution will be provided.

Keywords: ionic liquids, amino acids interactions, molecular dynamics simulations.

Ref P-049

The Cation Effect on the aqueous Solubility of amino Acids in the Presence of Salts: experimental and molecular Dynamics Simulation Studies.

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The study of the solubility behavior of amino acids and proteins in aqueous electrolyte solutions is of utmost importance to understand the biochemistry of natural systems, develop medical and pharmaceutical responses to diseases induced by biochemical disorders and improve the efficiency of biotechnological processes. Although the effect of common salts on the aqueous solubility of amino acids and proteins is phenomenologically well described [1], the underlying molecular-level mechanisms are far from being elucidated and consensual, in spite of the several explanations proposed during the past century. In order to contribute to the interpretation of the solubility behaviour of (amino acids+salts +water) ternary mixtures, we have previously studied the anion effect on the aqueous solubilities of amino acids using molecular dynamics (MD) simulation methods [2]. Aiming at further understanding the molecular interactions governing the behavior of these systems, experimental and MD studies were performed in this work for aqueous solutions of three amino acids, taken as model systems – alanine, valine and isoleucine – in the presence of salts such as $MgCl_2$, $MgSO_4$, NH_4Cl and $(NH_4)_2SO_4$, at T=298.15 K and different concentrations. The ions were selected in order to evaluate the cation effect on the aqueous solubility of the amino acids. The combined analysis of the thermodynamic data and of the radial distribution functions of the various groups and moieties, as well as of their respective energy of interaction, insight into the molecular interactions established in solution will be provided.

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Keywords: amino acids, salts, interactions, molecular dynamics simulations.

Ref P-055

Removal of Dyes form colored Textile Wastewater by Poly (TtEGDMA-cross-2-HPMA) Hydrogels Adsorbent: Equilibrium and Kinetic Studies.

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Poly tetra (ethyleneglycol) dimethacrylate crosslinked withe 2-hydroxypropyl methacrylate (Poly (TtEGDMA-cross-2-HPMA)) hydrogels were used as sorbent to remove bemacid red (ET_2) from aquous solution under various operating conditions. The effects of the expermental parameters such as dye concentration and crosslinked agent concentration. The sorption kinetic uptake for ET_2 by Poly (TtEGDMA-cross-2-HPMA) at various initial dye concentrations was analysed by pseudo-first and pseudo-second models. Two sorption isotherms namely the Langmuir and Freundlish isotherms were applied to the sorption equilibrium data. The sorption kinetics of ET_2 onto the hydrogels followed pseudo second-order kinetics and the adsorption equilibrium data obeyed Langmuir isotherm.

Keywords: tetra (ethyleneglycol) dimethacrylate, 2-hydroxypropyl methacrylate, bemacid red, pseudo-second model, Langmuir isotherm.

Ref P-057

Thermodynamic Excess Properties for binary Mixtures of Alkanone + Chloroalkanes.

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We are interested in the study of the thermodynamic behaviour of alkanone- chloroalkane. The purpose of this work is the determination of the vapors liquid equilibria, VLE, excess molar enthalpies ,H^E,of 2-heptanone + polychloroethane with view to study the effect of specific interaction (carbonyl-chlorogroups) on the thermodynamic excess proportes. Carbon atom of polychloroalcanes are know to act as proton donors in hydrogen bonds in mixtures with oxygenated solvents.

In this paper, we report excess molar enthalpies, H^E, and molar excess Gibbs energies, G^E, for Binary mixture of 2-heptanone + 1,2 - dichloroethane, 1,1,2 - trichloroetrhane, 1,1,2,2-tetrachloroethane, these measurements were performed in order to complement the data on VLE and excess molar properties of mixtures containing polychloroethane [1,4]

The vapour pressur of the pure compounds and the binary mixture were measured by means of a static apparatus [5], at temperatures between 263,15K and 343,15K. From these data, isothermal molar excess gibbs energies, G^E, were calculated. The excess molar enthalpies of the binary mixtures have been measured at 303,15K and atmospheric pressure, using a C80 SETARAM CALORIMETER;

The data on excess molar enthalpies and Gibbs energies have been examined on the basis of the DISQUAC groupe contribution Model.

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Ref P-060

Vapour pressures and Thermodynamic Excess Properties of 3,5- ; 2,6-dimethylpyridine and methylpyrazine with cyclohexane.

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The vapour pressures of liquid (3,5; 2,6)-dimethylpyridine and methylpyrazine with cyclohexane mixtures were measured by a static method in the range of 283.15–353.15 K. The pure components vapour pressures data and those of the mixtures were correlated with the Antoine equation. The excess enthalpies were measured at 303.15 K, by means of an isothermal calorimeter (C80 SETARAM model). The molar excess Gibbs energies, calculated from the vapour–liquid equilibrium data and the molar excess enthalpies compared satisfactorily with group contribution method (DISQUAC).

Ref P-061

Synthesis and characterization of amphiphilic graft copolymers of poly (N-vinylpyrrolidone) macromonomers with α-methylstyrene and acid methacrylic.

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Graft copolymers have important application in the polymer industry [1-5] and have recently received a lot of attention [6,7] In fact; these grafted copolymers are widely utilized as surface modifiers for coatings, adhesives, dispersants and compatibilizing agents in polymer blends and also for biomedical use. In particular, the amphiphilic graft copolymers have been extensively investigated for their particular physico-chemical properties and self-assembly morphologies [8]. Especially, homo and copolymers of *N*-vinyl-2-pyrrolidone are of great interest in a number of industrial applications and have been utilized, for instance, in the preparation of membranes for ultrafiltration, as light sensitive coating material for lithographic printing plates and for the preparation of carbon fibers.

In this study, 2-Oxopropylmethacrylate-terminated poly(*N*-vinyl-2-pyrrolidone) is produced by cationic polymerization using $HClO_4$ as an initiator. Termination (end capping) step is accomplished using 2-hydroxypropylmethacrylate (2HPMA) and the polymer product has different chain lengths of molecular weight averages ranging from 672 to 3049 g/mol. The study also synthesised amphipathic graft copolymers having hydrophobic poly (α-methylstyrene) and acid methacrylic as a backbone chain and hydrophilic poly (*N*-vinyl-2-pyrrolidone) (PVP) as side chains of various lengths. The copolymer synthesis was accomplished by free radical copolymerisation of ω-Oxopropylmethacrylate PVP in the presence of α-methyl styrene or acid methacrylic. Measurements of the dynamic viscosity of the polymer solution (20% weight of macromonomers in ethanol) show that the viscosity is proportional to the average molecular weights $\overline{M}_n$. However, a reverse behaviour of the viscosity variation with regard to $\overline{\mathrm{M}}_\mathrm{n}$ is observed for graft copolymer samples. The viscosity variation with respect to the graft copolymer mass must be due to steric effets, which are strongly pronounced in grafted copolymer chains. Appearance of the number of side chains attached to poly (α-methylstyrene) backbone reveals that the grafting reaction has occurred with good efficiency.

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Keywords: Cationic polymerization, macromonomer, radical free copolymerization, amphiphilic graft copolymers, dynamic viscosity.

Ref P-062

A Transferable Force Field to Predict Phase Equilibria and Surface Tension of Ethers and Glycol Ethers.

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Due to their various applications as solvents in chemical industry and as promising additives for biofuels, there is considerable interest in the thermophysical properties of ethers and glycol ethers. Reliable and predictive models are thus required in this context. Hence, we propose in this work [1] a new transferable force field to simulate with the Monte Carlo method phase equilibrium and interfacial properties of systems involving such molecules. Based on the Anisotropic United Atoms force field, only one new group is introduced: the ether oxygen atom. The optimized Lennard-Jones parameters of this atom are identical whatever the molecule simulated (linear ether, branched ether, cyclic ether, aromatic ether, diether, glycol ether). Accurate predictions are achieved for pure compound saturated properties, critical properties and surface tensions of the liquid-vapor interface, as well as for pressure-composition binary mixture diagrams. Multifunctional molecules (1,2-dimethoxyethane, 2-methoxyethanol, diethylene glycol) have also been studied using a recently proposed methodology for the calculation of the intramolecular electrostatic energy avoiding the use of additional empirical parameters [2]. This new force field appears transferable for a wide variety of molecules and properties. It is furthermore worth noticing that binary mixtures have been simulated without introducing empirical binary parameters, highlighting also the transferability to mixtures. Hence, this new force field gives future opportunities to simulate complex systems of industrial interest involving molecules with ether functions.

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Keywords: Force field, AUA4, ether, glycol ether, phase equilibrium, surface tension.

Ref P-065

Measurement, Modeling and Molecular Simulation of Two- and Three-Phase Equilibria in Systems containing phenolic and furanic Derivatives with Carbon Dioxide at 328 ' 373 K and 0.1 ' 30 MPA or Methane at 443 K and 0.1 - 45 MPA.

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Environmental issues and the security of energy supply have stimulated interest to develop non fossil energy carriers and chemicals. Bioresources and coal have been identified as promising feedstocks to produce alternative fuels. For the refining industry, the derivative products like bio-oils or liquefied coal represent an important challenge due to their complex composition covering a large range of oxygenated compounds, mainly phenolic and furanic derivatives. The development of new refining processes requires the availability of adapted thermodynamic models that can be used in process and technico-economical calculations. Classic models such as cubic equations of state usually used with hydrocarbons are not appropriate in the case of oxygenated fluids due to the associative interactions that take place in these systems. New models have been developed to deal with these kinds of systems. Equations of state such as SAFT (Statistical Associating Fluid Theory) or CPA (Cubic Plus Associative) are known to reproduce in a satisfactory way the phase equilibria of oxygenated systems, not only the liquid – vapour behaviour but also the liquid split. In this work, we have evaluated two models, GC-PPC-SAFT (Group Contribution Polar Group Contribution Polar Perturbed-Chain Statistical Associating Fluid Theory) [1] and PSRK (Predictive Soave-Redlich-Kwong) [2] to predict two- and three-phase equilibria (VLE, LLE, LLVE) of binary, ternary and multi-components systems containing phenolic and/or furanic derivatives with carbon dioxide (328 - 373 K and 0.1 – 30 MPa) or with methane (443 K and 0.1 - 45 MPa). For that, we have performed new experimental measurements for these kinds of systems in our laboratory and made also some equilibrium calculations by molecular simulation using the Monte Carlo method with the AUA4 force field [3]. Our results show a good agreement between modeling, experimental data and molecular simulation calculations. Both models, GC-PPC-SAFT and PSRK appear to be predictive to describe phase equilibria of oxygenated systems gassed with carbon dioxide or methane in the studied Pressure-Temperature ranges.

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Keywords: phase equilibria, phenolic, furanic, methane, carbon dioxide.

Ref P-066

Evaluation of GC-PPC-SAFT Equation of state for VLE and LLE Predictions of biomass Fluids.

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The Group Contribution Polar Perturbed Chain Statistical Associating Fluid Theory (GC-PPC-SAFT) equation of state (EoS) was developed on the basis of combining a group contribution method [1] and the PPC-SAFT EoS [2]. This EoS has been introduced into process simulator and some process calculations will be described. The GC-PPC-SAFT has been extended recently for calculating water solubilities [3].

The predictive ability of this EoS is evaluated here on a database of 266 molecules which are representatives of both hydrocarbons and oxygenated hydrocarbons. Many properties are calculated and compared to the experimental data which were collected from DIPPR [4] and DETHERM [5].

The pure component vapour pressure and saturated liquid volume are well represented with absolute average deviations (AAD) of 14 and 2.8% respectively. The VLE calculations (Henry's law constant) of binary mixtures containing a molecule of interest and a gas (H_2, CH_4 or N_2) give encouraging results with the AADs of 25, 12 and 23 % for H_2, CH_4 and N_2 respectively. Evaluations on some binary mixtures with water [5] were also performed (infinite dilution activity coefficients in water with AAD of 32%, aqueous solubility with AAD of 30%, both on the logarithm scale). As shown on Fig. 1, the response of GC-PPC-SAFT equation regarding the logarithm of the octanol/water partition coefficient is also encouraging.

All results are obtained in a purely predictive way.

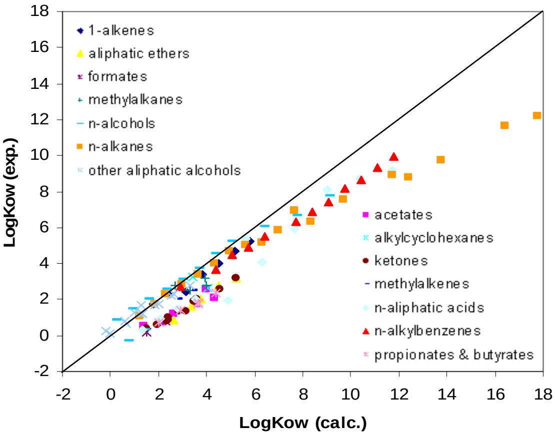

Fig 1: Comparison of experimental data vs. data calculated by GC-PPC-SAFT.

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Keywords: Group contribution, GC-PPC-SAFT, Biomass, VLE, LLE.

Ref P-067

Multiscale Modelling of the Surface Tension of planar and spherical Interfaces.

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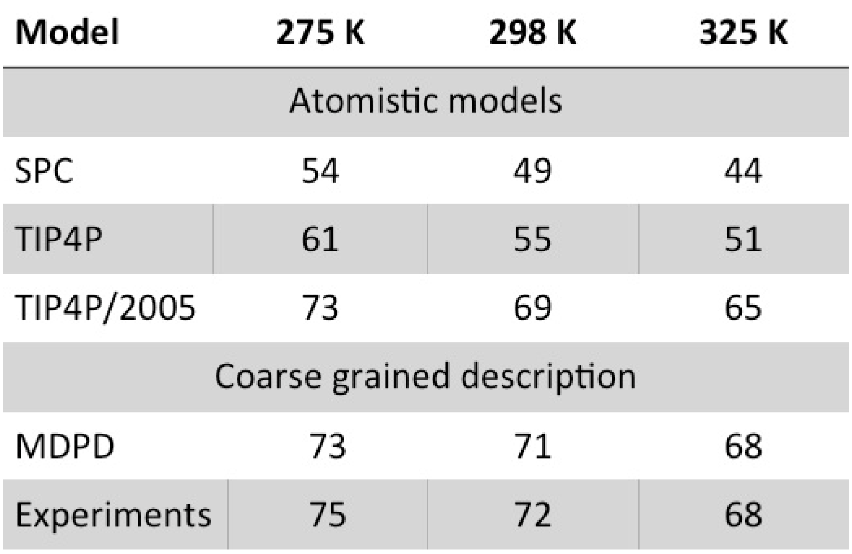
We report a mesoscale modelling of the liquid-vapour interface of water. A mesoscopic model of water has been established in many-body dissipative particle dynamics (DPD) to reproduce the interfacial properties of water (see Table1 for a comparison with atomistic models). Simple scaling relations have been established to link the atomistic and mesoscopic length and time scales. Our study demonstrates the capability of the DPD method to explore the interfacial properties of a water liquid-vapour interface and a water nanodroplet.

Table 1: Atomistic and coarse-grained models for the surface tension of water



Model	275 K	298 K	325 K
Atomistic models			
SPC	54	49	44
TIP4P	61	55	51
TIP4P/2005	73	69	65
Coarse grained description			
MDPD	73	71	68
Experiments	75	72	68

We also propose to show typical results about the calculation of surface tension of salt solutions.

Keywords: surface tension, mesoscale modelling, many-body dissipative particle dynamics.

Ref P-068

Gas solubilities for oxidation of cyclohexane in carbon dioxide expanded media by experiment and molecular simulation.

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The solubilities of carbon dioxide and oxygen in mixtures which are relevant for the oxidation of cyclohexane in carbon dioxide expanded solvents were determined both by experiment and molecular simulation. The studied solvents are cyclohexane, cyclohexanone, and cyclohexanol. The work covers not only solubilities of single gases in pure solvents but also mixed gases and mixed solvents.

A literature survey shows a lack of gas solubility data for carbon dioxide and especially oxygen in the systems which are of interest here. Experiments were carried with a synthetic method out to fill these gaps. The Henry's law constant of carbon dioxide in pure cyclohexane and in pure cyclohexanone as well as in mixtures of these components was measured between 298 and 393 K. Furthermore, the gas solubility of oxygen in pure cyclohexanol was measured in the same temperature range. Finally, the solubility of mixtures of the two gases in different solvents and the solubility of gases in different solvent mixtures was studied at 313 K.

Molecular simulations were performed with multi-center Lennard-Jones models with superimposed electrostatic sites. For some of the components of interest, molecular models are available in the literature [1]. For cyclohexane, cyclohexanol [2] and cyclohexanone new molecular models were developed in this work. Furthermore, a new, improved carbon dioxide model was developed [3]. Unlike interactions are modeled with the modified Lorentz-Berthelot combination rule. A single binary state-independent binary parameter was adjusted to experimental Henry's law constant data. The predictions from simulation are compared to the comprehensive new experimental data. Generally, a good agreement between the predictions and the experimental data is observed.

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Ref P-071

Modelling the Solubility of Carbon Dioxide in ionic Liquids with the PC-SAFT Equation of State.

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Ionic liquids are "green" promise solvents in various fields of chemistry and especially in problems related to environmental protection. These solvents are considered non-volatile, their use is far preferable to that of conventional volatile organic solvents [1]. This family of compounds has great potential for gas separation and recovery [2]. The aim of this study is to evaluate the capacity of the PC-SAFT [3] equation of state to represent the systems containing greenhouse gases and ionic liquid.

In this work, the equation has been first applied to the pure ILS in order to determine the pure-component molecular parameters. Then it has been applied to the binary system {CO_2 + ILS}. In this case, the interaction parameter k_{ij} was determined using liquid-vapor equilibria data. It is found that the solubility of CO_2 in ionic liquids is well predicted using this PC-SAFT equation of state.

List of symbols:

PC-SAFT	Perturbated-Chain-Statistical Associating Fluid Theory
ILS	Ionic liquids
k_{ij}	Binary interaction parameter

References:

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Keywords: Gas solubility, ionic liquid, PC-SAFT.

Ref P-076

Complementary 'Molecular Simulation-Eperiments' Approach for Obtaining Parameters of Equations of State Describing vapour-Liquid.

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In chemical engineering the equations of state (EoS) are routinely used to calculate thermodynamic properties. Molecular-based equations of state, such as those derived from the statistical associating fluid theory (SAFT), provide a framework in which the different microscopic effects such as nonsphericity and association interactions can be estimated and quantified in a systematic way. However the determination of parameters of the EoS describing vapor-liquid equilibria for fluid mixtures generally is obtained through constrained fitting of a large number of measurements that makes the process of its validation rather long and complex.

The prediction of vapour-liquid equilibrium (VLE) and phase behaviour based on accurate atomistic and molecular simulation approaches alone remains an enduring challenge for the computational chemist due to the large number of adjustable parameters describing the interaction between fluid molecules together with the excessively long calculations needed to represent these systems. This contribution will focus on the application of a methodology based on a combination of molecular simulation with experimental data in order to reduce the time and effort needed to generate parameters for SAFT-based EOS.

Prediction of VLE equilibrium for CO2-methanol mixtures in a wide temperature range is achieved using the equations of state SAFT and PC-SAFT. The generation of phase equilibria data for different mixture conditions has been carried out by molecular simulation-Gibbs Ensemble Monte Carlo (GEMC) using force fields optimized with respect to the physical properties of pure compounds. The data obtained by GEMC for mixtures at different temperatures have been used determine the binary interaction parameter and predict the phase equilibria at different temperatures. Comparison of predictions (SAFT and PC-SAFT) with experimental measurements will be presented.

Keywords: Gibbs Ensemble simulations, PC-SAFT, VLE, fluid mixtures.

Ref P-083

The Molecular Interaction Parameters in pure Gases based on the thermophysical Data.

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Real gases play a significant role in modern industries and the precise knowledge of their thermophysical properties is very important. These properties depend on the concentrations of predominant types of molecular clusters and on the molecular interaction parameters: effective bond energy, effective volume of the attraction zone and excluded volume. These parameters will be discussed basing on the Monomer fraction density theory [1].

The computer aided analysis of the experimental data from available databases, like [2], permits to find equilibrium constants for *n*-particle cluster fractions and to estimate corresponding interaction parameters, Figure 1.

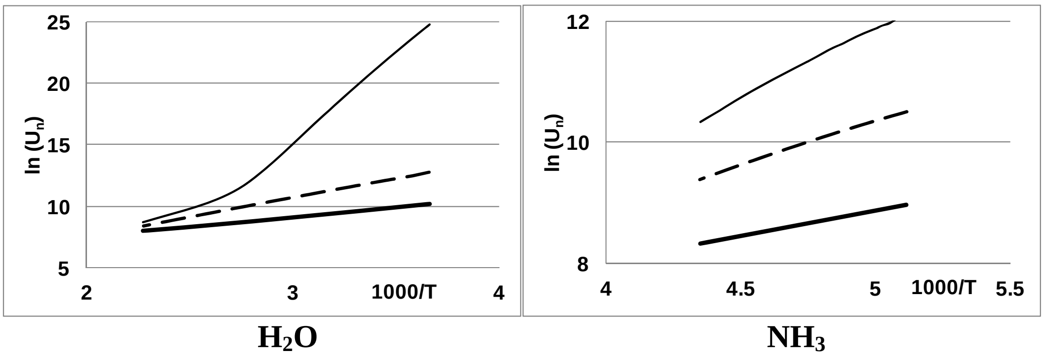

Figure 1. The contributions of *n*-particle clusters in the potential energy of the Water and Ammonia vapors in a logarithmic scale versus reverse temperature:
Thick lines – dimers; dashed lines – trimers; thin lines – tetramers.

The Figure shows that in the Ammonia vapor in all investigated temperature range (195.5 – 230 K) the activation energy $E_n = E_2 (n - 1)$, but in the Water vapor this dependence holds only for T > 380 K. At T < 360 K the activation energy for tetramers is 8 times larger than E_2. It can be considered as a soft structural transition between the predominant isomers of the Water tetramers: the solid-like type at T < 360 K and the liquid-like type at T > 380 K.

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http://webbook.nist.gov/chemistry/fluid.

Keywords: Real gas, thermophysical properties, molecular interactions, equilibrium constants.

Ref P-084

The supercritical Zone of extraordinary Properties.

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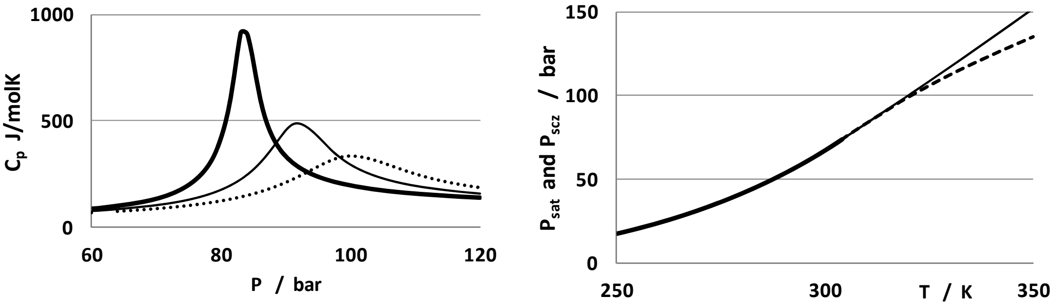
The utilization of supercritical fluids in modern industries grows very fast and it is important to know better their thermophysical properties. The zone with a remarkable change of the fluids' thermophysical properties at supercritical pressures and temperatures will be discussed. This zone may be marked by peak values of heat capacities C_v and C_p or other properties. It widens, when temperature and pressure shift from the critical point [1], Figure 1.



(a) (b)

Figure 1. The zone of extraordinary properties in supercritical CO_2, built with utilization of experimental data from [2]:

(a) Tracing of the zone by peak values of C_p: thick line - 310 K, thin line – 315 K, dashed line – 320 K;
(b) Prolongation of the saturation curve (thick line) in the extraordinary supercritical zone with its boundaries built by: peaks of the Joule-Thomson coefficient derivative by pressure (dashed line); peaks of the C_p (T, P) (thin line).

The zone of extraordinary properties is the result of the structural transition in supercritical fluids [1] and should be taken into account for the optimal parameters of technological processes selection.

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Keywords: Supercritical fluid, thermophysical properties, saturation curve, critical point.

Ref P-091

Isotherms of Fluids in Native and Defective Zeolite and Alumino-Phosphate Crystals: Monte-Carlo Simulations with 'On-the-Fly' Ab Initio Electrostatic Potential.

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Molecular mechanics methods have shown their efficiency at complementing and further validating experimental adsorption data of fluids in microporous solids [1]. However, the determination of the forcefield parameters that are used to compute the guest-host potential energy can be a difficult and time consuming process, especially for the parameters describing the electrostatic interactions. To overcome these difficulties, the electrostatic potential of the solid into which the fluid adsorbs can directly used from periodic *ab initio* calculation. This operation is done in a single step and only requires the solid crystal atomic positions. Another huge benefit of this approach is its versatility: there are virtually no limitations related to the solid crystal structure and the presence of defects in it (apart its size, which should be around several hundred atoms).

To illustrate the strength and elegance of this approach, we first confront the results obtained using the *ab initio* electrostatic potential and 'standard' charge parameters [2] in the calculations of the water isotherms in silicalite. Second, we consider the case of alumino-phosphate crystals and the inclusion of silica defects in them, compensated or not by Na^+. The water isotherms of the native and defective crystal structures are determined and compared. The case of the CO_2-N_2 mixtures isotherms is then investigated.

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Keywords: Adsorption, Solid, Isotherm, Monte-Carlo.

Ref P-093

The finite Size Effects in Computer Simulation of Phase Equilibria.

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The computer simulations of equilibrium behaviour of fluids represent a useful tool, which is commonly employed either to validate various theoretical approaches or to examine the quality of model force fields. Different simulation techniques were suggested to study the phase equilibria, the most popular being based on the thermodynamic integration, simulations in Gibbs ensemble and inhomogeneous simulations [1 – 3]. To mimic the properties of bulk phases the periodic boundary conditions (PBC) are used within the simulations in most cases. As a consequence the intermolecular interactions have to be truncated which then requires a special treatment. The influence of the long range interactions on the phase equilibria was discussed exhaustively by Trokhymchuck and Alejandre [3].

Except the effect of truncation of interactions, the equilibrium properties of simulated systems are affected by implicit finite size effects which follow from distortion of the fluid isotropy because of the boundary conditions. This phenomenon is responsible e.g. for the strong dependence of the interfacial tension values on the lateral system size if these values are determined using the inhomogeneous simulations [4] but similar influence is observed also in the case of vapour pressure and coexistence densities [5]. Oscillatory dependence of internal energy and pressure was also observed for compressed Lennard-Jones fluid [6]. Denton and Egelstaff then analyzed the impact of this effect on the fluid structure [7].

Within this contribution we make an attempt to link influence of the implicit finite size effects on the fluid structure with that on the thermodynamic properties and demonstrate a qualitative accordance between them.

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Keywords: Inhomogeneous simulations, Lennard-Jones fluid, Phase equilibria,
Finite size effects.

Ref P-095

The Influence of the Association Term on the Behaviour of vapour Phase of carboxylic Acids.

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The knowledge of the phase equilibria of systems containing associating components is of great importance in many industrial applications. Recently, mixtures related to biofuels have received great interest [1].

The association theory of Wertheim was adopted into various equations of state (EoS) leading to significant improvement of the description of the phase behaviour of systems containing associating components [2,3]. Only the first term in the free energy expansion is considered, which corresponds to formation of chainlike structures or trees due to the association. These assumptions are adequate for most compounds in liquid phases but certain classes of compounds show a rather different behaviour when the density is lowered, e.g. hydrogen fluoride forming cyclic oligomers or carboxylic acids forming dimers.

Sear and Jackson proposed a theory based on Wertheim's approach, which takes also the formation of ring structures (i.e. cyclic oligomers) into account [4]; the formation of double hydrogen bonds occurring for example for carboxylic acids represents a limiting case of their approach [5]. In both cases, they have shown that the fraction of rings (cyclic dimers) is dependent on density and that the equilibrium between tree-like structures and rings dramatically affects the phase behaviour of the systems.

We implemented the approach of Sear and Jackson into the PC SAFT EoS [6] and applied it to describe the phase equilibria of pure carboxylic acids and their mixtures with hydrocarbons. Different association models have been tested and the effect of the formation of double bonds on the predictions of thermodynamic properties is shown. This work was funded by the ANR (French National Research Agency, project ANR-09-CP2D-10-03).

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Keywords: associating fluid, SAFT, cyclic dimer.

Ref P-096

The critical temperature and properties of real gas from low order perturbed virial expansions.

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It is shown that a low-order expansion in powers of density about a suitable short-range reference system, called a perturbed virial expansion, is superior to the common virial expansion and provides a reasonably accurate estimate of both the critical temperature of simple fluids and thermodynamic properties of real gas over a wider range of densities/temperatures. The results are presented both for three common van der Waals hard-core models (square-well, Yukawa, and Sutherland) and the realistic Lennard-Jones fluid, and for real fluids.

Keywords: Perturbed virial expansion, critical point, real gas, saturation pressure.

Ref P-097

Fluid Phase Behaviour from molecular Simulation: Hydrazine, Monomethylhydrazine, Dimethylhydrazine.and binary Mixtures containing these Components.

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In the last years, molecular simulation has become a useful tool to accurately predict thermodynamic properties of fluids on the basis of molecular force field models. Especially in cases of industrially relevant hazardous and/or highly explosive substances, molecular simulation offers big advantages in the determination of pure substance and mixture properties. Hydrazine and its derivates, which are usually used as high-energy propellants in rocket thrusters, are good examples for these dangerous substances.

In the present work, new molecular models for Hydrazine, Monomethylhydrazine and Dimethylhydrazine are developed. The models are based on a rigid set of Lennard-Jones sites with superimposed point charges. The parameterization of the molecular interaction models is carried out using quantum chemical calculations and subsequent fitting to experimental vapor pressure and saturated liquid density data following a procedure that was proposed earlier [1]. To validate the molecular models, vapor-liquid equilibria for the pure substances and their binary mixtures were calculated and compared with all available experimental data and molecular models from the literature. In addition, the Henry's law constant for the physical solubility of Argon and Nitrogen in liquid Hydrazine, Monomethylhydrazine and Dimethylhydrazine are computed. The simulation results are in very good agreement with experimental data.

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Keywords: Molecular modeling and simulation, vapor-liquid equilibrium,
Henry's law constant, Hydrazine, Monomethylhydrazine, Dimethylhydrazine.

Ref P-099

CoMT-CAMD: A novel Method for simultaneous Process and solvent Design using PCP-SAFT Applied to CO2 Capture.

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CO_2 capture is an important potential measure to mitigate climate change. The energy-intensive industries require therefore appropriate capture technology on a reasonable cost. For high-pressure applications (pre-combustion), absorption is the most mature technology. A large optimization potential still lies in the selection of a suitable process solvent and the appropriate process conditions.

The fully integrated process and solvent design problem is prohibitively complex for a true deterministic solution procedure. Any practical approach requires the decomposition of the full problem. In previous studies, the decomposition was done by selecting the solvent using auxiliary, typically heuristic objective functions, such as the maximal selectivity of the solvent towards CO_2, or maximal solubility. The true process objective function, in contrast, should capture the full energetics of the absorption and desorption step.

In this work, a novel approach for integrated process and solvent design is proposed: Any molecule is represented by a set of molecular parameters of a physically-based model (the PCP-SAFT model [1],[2],[3],[4]). By treating these molecular parameters as continuous parameters, one can perform simple gradient-based process optimizations. The molecular parameters are thereby optimized alongside of process variables, such as desorber pressure etc.. This optimization ('Continuous Molecular Targeting' [5]) leads to both a hypothetical solvent and a set of process variables that minimize the process objective function. The objective function is here defined as process costs under various environmental, product and process constraints. In a subsequent step ('mapping step'), the best real solvent is efficiently identified by analysis a second order Taylor expansion of the optimization problem.

Thus, our approach also relies on a decomposition of the integrated process and solvent optimization problem into a 'continuous molecular targeting' step and a 'mapping' step. However, the newly proposed approach avoids any auxiliary objective function and does not *a priori* exclude any substances from the pool of solvent candidates. It allows for a direct access of molecular characteristics in the process optimization. Due to the strong molecular picture underlying PCP-SAFT, the high quality of the mapping of the target parameters is achieved. The suggested CoMT-CAMD approach thereby closely approximates the truly integrated process and solvent optimization problem.

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Keywords: Solvent design, CO_2 capture, PCP-SAFT, CoMT-CAMD.

Ref P-102

Rheological Behaviour of Magnetite / Ethylene Glycol Nanofluids.

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Nanofluids have emerged as suitable tailored working fluids in industrial, engineering, and medical applications, in fields ranging from transportation, microfluidics, heating, ventilating and air-conditioning systems, biomolecules trapping or enhanced drug delivery [1, 2]. The use of these new fluids in practical applications requires a previous accurate analysis of both heat transfer and rheological properties. Following our previous research on nanofluids [3-5], in this work a complete rheological characterization of Fe_3O_4/ethylene glycol magnetic ferrofluids is presented.

The analyzed nanofluids were prepared at particle mass concentrations 0–25% and the rheological behaviour was determined using a cone-and-plate geometry Physica MCR 101 rheometer. The flow curves for these nanofluids were obtained using the controlled shear stress technique at 283.15, 303.15 and 323.15K. A representation of viscosity versus shear rate for the studied nanofluids evidences non-Newtonian behaviour, with shear-thinning appearing for all nanofluid samples. Using strain sweep and frequency sweep tests, the storage modulus G´and loss modulus G” were also determined and analyzed.

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Keywords: nanofluid, rheology, magnetite, shear-thinnig, viscoelasticity.

Ref P-103

A new Route to the Kirkwood-Buff Integrals.

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Thermodynamic properties of mixtures can be obtained from Total Function Correlation Integrals, also referred to as Kirkwood-Buff (KB) integrals. Kirkwood and Buff related fluctuations in the grand-canonical ensemble to integrals of radial distribution functions over the volume. The convergence of the integral obtained from molecular simulations is often poor and it requires large simulation box sizes. Therefore, there is a considerable interest in developing more efficient methods to extract KB integrals from simulations.

The KB integral can alternatively be calculated directly from density fluctuations in the grand-canonical (GC) ensemble. The simulation of such ensemble for dense systems is however very challenging in molecular dynamics as well as in Monte Carlo simulations. To solve this problem we proposed a new approach based on the fact that a small system embedded in a large one is in the GC ensemble [1,2,3]. It means that the KB integrals can be obtained from simulations in the canonical or microcanonical ensemble.

The small size of the embedded system induces a dependence of the thermodynamic properties on size. This is taken into account through the formalism of the thermodynamics of small systems developed by Hill [4]. The new method was tested on atomic and more complex molecular systems like zeolite-adsorbents, acetone - methanol, acetone – CCl4 mixtures [1,2,3]. The calculated thermodynamic data, like the thermodynamic correction factor, Gamma, the concentration derivative of the chemical potential, were in very good agreement with experiments, see Fig. 1.

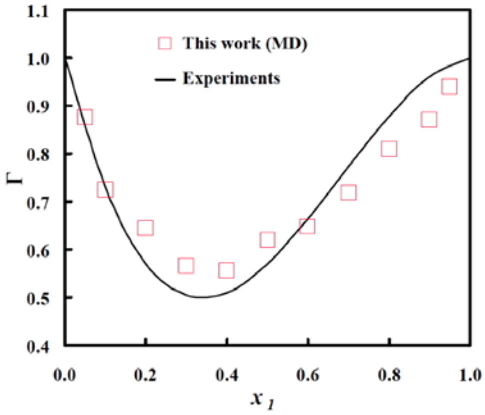

Figure 1 Thermodynamic factor in acetone (1) - CCl4 (2) mixtures at 298K and 1atm.

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Keywords: molecular dynamics, thermodynamics of small systems, Kirkwood-Buff integrals, local density fluctuations.

Ref P-104

Phase Equilibrium of 1:1 Salt aqueous Solutions with electrolattice Equation of State.

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The electrolattice equation of state (EOS) [1] is a new thermodynamic model that extends the Mattedi-Tavares-Castier (MTC) EOS [2] to systems with electrolytes. The MTC EOS is a lattice-hole model that considers local composition effects, derived in the context of the generalized van der Waals theory. The MTC EOS can be used as a conventional molecular model, as a group-contribution model, or as a region-contribution model. In the latter, molecules of polar compounds are split into three regions: dispersion, electron-donor, and electron-acceptor. In this way, it is possible to predict the phase behaviour of polar compounds and their mixtures accurately without the need to solve association equations as in the SAFT-family and CPA-family EOS.

In the electrolattice EOS, the Born term accounts for ion charging and discharging and the mean spherical approximation accounts for the long range ion-ion interactions in solution. The model has been successfully applied to correlate mean ionic activity coefficients [1]. In this paper, we report the first results of its application to vapor-liquid equilibrium, namely to aqueous solutions of 1:1 strong electrolytes. We also report results of saturated liquid densities and of the enthalpy of vaporization of water from such electrolyte solutions. These volumetric and calorimetric properties are relevant to the design and optimization of many chemical processes, including water desalination.

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Keywords: vapor-liquid equilibrium, salts, electrolytes, equations of state.

Ref P-106

Equation of State for complex Liquid near the Critical Point on the Basis of Van Deer Waals Model of Gas of fluctuations of Oder Parameter.

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The model of system near the critical point (CP) as gas of the fluctuations of the order parameter [1] has been proposed on the basis of the fluctuation theory of phase transitions [2] for the purpose to develop the extended equation of state of substance. It has the properties of Van der Waals gas of the fluctuations. The physical factors have been taken into account as follow:
1. Own volume of the fluctuations of the order parameter. The significant local density of substance inside the fluctuation $\rho_f \geq 3\rho_c$ ($r<R_c$) demands to take into account an own, "forbidden" volume. 2. Interaction forces between the fluctuations of order parameter at the distances, greater than a correlation length $r>R_c$ [1]. The qualitatively similar physical description of interaction of groups of molecules near the CP is given in the work [3] and in the method of collective variables [4]. 3. Presence of the complexes of the quasi-associations of fluctuations when going away from the CP. Presence of the complexes of quasi-associations of fluctuations for fluctuation region near the CP has been taken into account on the basis of the known coagulation phenomenon of fluctuations in the crossover region. 4. The entropy fluctuations have been taken into account in accordance with the ideas of the fluctuating values algebra [2] and considered in the works of M. Anisimov [5]. The extended equation of state of complex liquids (molecular solutions and metallic melts) has been developed. It has the asymmetric and symmetrical corrections of other known extended equations of state, used in the scientific literature for the analysis of experimental data in the wide vicinity of the CP. The parameters of equation of state are the linear functions of the compressibility factor of a substance.

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Keywords: Critical point, order parameter, complex liquids.

Ref P-110

Equation of State Employed on Models Development for Calculations of excess Molar Properties below to critical Conditions.

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Studies on excess molar properties data behavior of mixtures are motivation to the researchers due to importance of these data for the scientific and industrial applications, especially to understand the interactions occurring between the molecules as well as the design and optimization of chemical processes. Mathematical expressions to calculate the excess molar properties are presents in the literature, in attempt to describe the main interactional effects occurring between different molecules in mixtures. Normally, these expressions are based on equations of state (EOS) in which are represented by the sum of two terms: one related to attractive effects and other associated to the repulsive effects, both of molecular characteristic. In attempt to better the effects descriptions, besides to improve the correlation between experimental and calculated thermophysical properties, several modifications on EOS have been made, especially accounting pure compounds. Since the majority of the industrial compounds are found in mixtures format, it is necessary to adopt mixing rules, if the interest is to work with equations of state to describe and to understand the mixture effects. This work proposes to obtain expressions to calculate the excess molar volume and excess molar enthalpy using a non-cubic equation of state. The main structure of the EOS employed is that proposed by Peng-Robinson [1], in which its original repulsive term is substituted by the Carnahan-Starling [2] hard-sphere repulsive term; furthermore, generalized expression to calculate $\alpha(Tr,\omega)$ and $\beta(Tr,\omega)$ functions are used, whose aim is to improve the physical meaning of the calculated data. Experimental data of the excess molar volume and excess molar enthalpy are compared to the calculated excess molar properties data using the proposed expressions, showing satisfactory agreement.

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Keywords: Excess molar enthalpy, excess molar volume, modeling, equation of state, mixtures.

Ref P-111

Simulation of the Ress Process.

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RESS is a process to produce very small particles with a size down to the nanometer scale. First the valuable substance is dissolved under high pressure in a supercritical fluid. Then this solution is expanded in a nozzle. During this expansion both the solubility in the supercritical solvent as well as the temperature decrease. Both effects eventually lead to precipitation and the formation of particles of the solute.

The RESS-process is investigated numerically for a better understanding of the mechanisms of particle formation and growth. The aim is the identification of the optimal process conditions. There are various simulation methods for the simulation of technical processes. A widely employed approach is the macroscopic modeling of the complete process by the solution of the conservation equations. In case of RESS modeling, such method has been developed for naphthalene particle formation.

While it is possible to capture the whole process or at least the most important features of the process, such approach requires the input of several substance properties. In case of particle formation the nucleation rate is required and on the other hand the thermodynamic properties of the fluid need to be modeled by an accurate equation of state.

Molecular dynamics (MD) simulation is a complementary approach to the macroscopic approach. With molecular simulations it is not possible to simulate the complete technical process, however, one can mimic parts of the process and, in addition, obtain thermodynamic and kinetic properties. Here we discuss two different simulation methods of the particle formation process by rapid expansion from a supercritical solution for naproxen particles.

Keywords: particle formation, supercritical fluids, simulation.

Ref P-112

Description of the Adsorption Behaviour of the Main Components of natural Gas under Confinement using Monte Carlo Simulation and density Functional Theory.

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The objective of this work was to calculate the adsorption of the main components of the natural gas in slab geometry confinement using Monte Carlo molecular simulations and Density Functional Theory[1,2]. It is well-known that methane is the major component of Natural Gas reservoirs and represents the 90% of its composition, but water and CO_2 are also present to a certain extent in natural reservoirs. The knowledge of methane-water-CO2 high pressure adsorption is essential for the exploration, production and processing of petroleum fluids [3]. This fact is especially relevant when the case of tight gas reservoirs is considered, where the adsorption is very high and an external water based fluid is injected in the reservoir with the objective to modify the system interfacial properties improving extraction rates. Monte Carlo calculations were performed in slab geometry using the Grand-Canonical ensemble. In this case, the wall was described by a soft continuous potential, the so-called Steele 10-4-3 potential, which is representative for instance of the interaction with a solid planar carbon active substrate [4]. Methane was represented as a single Lennard Jones sphere [5]. Although very simple, it offers accurate results not only for phase equilibria but also for bulk properties in a wide pressure and temperature ranges. Concerning water, a rigid non polarizable model (TIP4P-2005 [6]) has been used, because it has been shown to provide accurate estimates of water bulk properties [7,8]. In the case of carbon dioxide, the EPM2 model, whose performance to describe CO2 phase equilibria and thermophysical properties has been stated [9], was considered. Finally, both methods provide very good estimations of the adsorption of this mixture whatever the thermodynamic conditions.

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Keywords: adsorption, Steele potential, confined fluids.

Ref P-113

Isothermal Vapor-Liquid Equilibria of compounds of blends (Biodiesel/Diesel) {(Ethyl hexanoate + n-Tetradecane) and (Ethyl decanoate + n-Tetradecane)}.

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The vapor pressures of three binary systems {Ethyl hexanoate (1) + n-Tetradecane (2)} and {Ethyl decanoate (1) + n-Tetradecane (2)}, were measured by means of static device [1] at temperatures between 373.15 K and 453.15 K. The data were correlated with the Antoine equation. From these data, excess Gibbs functions were calculated for several constant temperatures and fitted to a three-order Redlich-Kister equation using Barker's method.

Deviations were observed between experimental and predicted G^E, using group contribution UNIFAC (Gmehling version) model.

The major part of all energy consumed worldwide comes from fossil sources (petroleum, coal and natural gas). However, these sources are limited and will be exhausted. Vegetable oil for the production of biodiesel (Fatty acid methyl or ethyl estr, FAME or FAEE) is a promising substitute for petroleum-based fuels as biodiesel has many merits. However and until our days, the biodiesels are used in mixture with the diesel fossil. Biodiesels blends are most commonly B20 volume percent (vol.%) or less and are referred to here as Bxx, where xx is the vol.% biodiesel content in the fuel [2].

In this work, accurate phase equilibrium data (P, T, x) for a wide range of temperatures, pressures, and concentrations for binary mixture FAEE plus alkanes were determined.

The vapor pressure measurements were carried out using a static apparatus.

The molar volumes of the pure compounds were estimated with the Rackett method. The virial coefficients were evaluated from Pitzer correlation.

The vapor pressures of the pure compounds were measured at temperatures between 373.15 and 453.15 K, and the results fitted to the Antoine equation. The fig. 1 illustrates the experimental and predicted equimolar G^E by using group contribution UNIFAC (Gmehling version) model

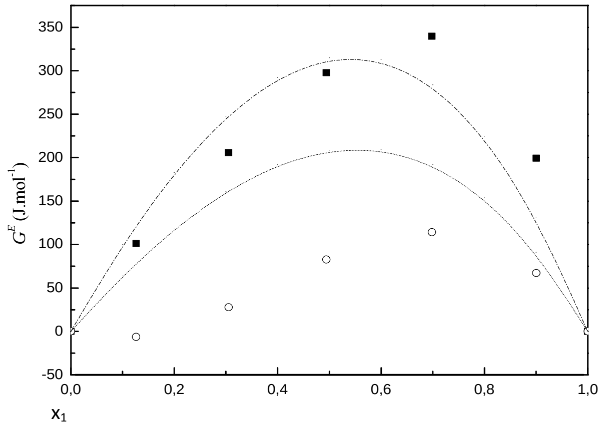

Fig. 1. G^E against x_1 for the Ethyl hexanoate (1) + Tetradecane (2) at: (■) 373.15;(○) 453.15 and ( ) modified UNIFAC (Gmehling) for G^E.

This work illustrated azétrope phenomena for Ethyl decanoate + Tetradecane mixtures. For all the systems, the equimolar G^E are positive for all the investigated temperatures, decrease with increasing temperature and the G^E curves are asymmetrical.

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Ref P-114

Experimental determination and prediction of (Solid+Liquid) phase equilibria for binary mixtures of compounds of Alkanes (compounds of diesel) and Fatty acids methyl esters FAMEs (compounds of biodiesel).

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Solid-liquid equilibria for two binary mixtures of n-Octacosane and n-Tetracosane + Methyl stearate were measured using differential scanning calorimeter (DSC).

The results obtained were compared with those predicted by the modified UNIFAC (Larsen and Gmehling).

The major part of all energy consumed worldwide comes from fossil sources (petroleum, coal and natural gas). However, these sources are limited and will be exhausted. Vegetable oil for the production of biodiesel (Fatty acid methyl or ethyl ester, FAME or FAEE) is a promising substitute for petroleum-based fuels. However and until our days, the biodiesels are used in mixture with the diesel fossil. Biodiesels blends are most commonly B20 volume percent (vol.%) or less and are referred to here as Bxx, where xx is the vol.% biodiesel content in the fuel [1].

In this study, the solid-liquid phase diagrams of binary mixtures formed by n-alkanes + saturated methyl ester fatty acid, n-Octacosane + Methyl stearate (2) and n-Tetracosane (1) + Methyl stearate (2) were determined by DSC. Results obtained with this technique are compared with those correlated with modified UNIFAC (Larsen and Gmehling) models [2-3].

For each binary system, the samples were prepared by heating very slowly in a Pyrex glass cell near the melting temperature of the major component. Small amounts of solid (4 to 5) 10^{-3} g were taken and sealed in an aluminium pan of the DSC NETZCH type 204F1 Phoenix analysis.

A typical DSC curve of liquefaction for binary systems of n-Octacosane + Methyl stearate is given in Fig. 1

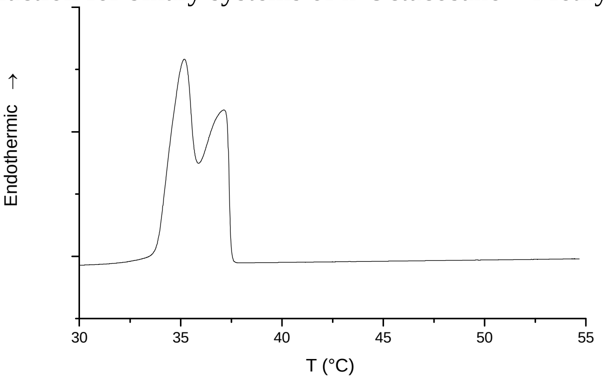

Fig. 1. *DSC thermogram for n-Tetracosane (1) + Methyl stearate (2) mixtures*.

Solid+liquid phase equilibria for two systems of binary mixtures of Alkanes and Fatty acids methyl esters have been studied. Obviously the DSC method is fairly satisfactory for the measurement of SLE. All the investigated binary systems are simple eutectic.

The modified UNIFAC (Larsen and gmehling versions) models are capable of correlating accurately the binary SLE data and predicting satisfactory the solid-liquid phase diagrams for the binary systems.

The data concerning the SLE, principally the eutectic points of the systems studied will be of great importance in the diesel/biodiesel mixtures.

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Ref P-115

Characterization of polymorphic transformation in Trimethoprim drug.

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Polymorphic transformation in Trimethoprim drug has been studied employing differential scanning calorimetry (DSC), microscopy, X-ray diffraction and FT-IR techniques. Trimethoprim (I) exhibited the sharp melting point at 201°C.

DSC of the Trimethoprim (I) indicated that the as received sample was crystalline. The molten Trimethoprim on cooling, however, produced a glassy amorphous mass. The amorphous product on heating to temperature >100°C transformed to Trimethoprim (II) which subsequently changed to Trimethoprim (I) prior to melting.

The present study demonstrates the utility of a diversified analytical approach for the characterization and quantitative analysis for two polymorphs of Trimethoprim.

Solid form diversity of pharmaceutical substances may influence the efficacy and safety of drug products. Physical chemical characterization of different solid phases that may occur during crystallization and pharmaceutical formulation processes because they have different crystal structures, polymorphs have different chemical and physical properties; they have different melting points, different chemical reactivity, different dissolution rates and different bioavailability.

Differential Scanning Calorimetry has been used for various applications in the pharmaceutical industry. These applications include, studying polymorphism of APIs, evaluating the stability/storage conditions of drug products, and for the purity determination of crystalline organic compounds.

Trimethoprim is an antibiotic drug a dihydropyrimidine antimicrobial and antiparasitic agent. It is the prototype of a group of nonsulfonamide drugs that inhibit dihydrofolate reductase in bacterial and protozoal cells. Although introduced as an antimalarial agent, it is now used primarily as an antibacterial agent, especially in combination with sulfamethoxazole (SMX).

The DSC curves recorded for Trimethoprim (I) during first heating, first cooling and second heating. This was followed by a prominent endothermic peak due to melting of the compound at T_f = 200.1 °C. The DSC curve recorded for the sample on second heating was totally different compared to that obtained in the first heating cycle. A small endothermic peak was found to precede a prominent exothermic peak at 88.5 °C and a twin endothermic peak at 169.4 °C. Careful analysis of the peak around 60 °C recorded at the increased sensitivity, revealed that this could be attributed to the glass transition temperature ‘Tg’, of the product obtained in the first cooling run. This temperature was found to be 60 °C from two independent experiments carried out employing 4.8 mg and 5.12 mg samples, respectively.

FT-IR patterns for as received Trimethoprim (I) sample and the sample obtained after heating amorphous mass at 100 °C for 1 h showed considerable difference.

This indicated that the original Trimethoprim (I) sample and the product obtained by reheating the cooled metastable amorphous mass were distinctly different as observed in X-ray diffraction studies.

FT-IR spectroscopy, X-ray diffraction on powder and DSC calorimetry enabled us to identify and characterise the different polymorphs of TMP; the results permit us to assert that TMP exists in at least two forms.

The observations made in this study showed that Trimethoprim (I) exhibited remarkable undercooling during cooling cycle. The melt of Trimethoprim (I) solidified to a glassy mass. This glassy substance on heating gave Trimethoprim (II) which transformed to form (I) prior to melting. The X-ray diffraction studies and FT-IR data have been found to be mutually consistent and lead to the conclusion that the melting of Trimethoprim (I) is irreversible leading to metastable solid which subsequently transformed to new stable polymorphic form i.e. Trimethoprim (II).

Keywords: Polymorphism, Trimethoprim, stability, thermal characterization.

Ref P-117

Properties of aqueous Solutions of ionic Liquids within the Bimsa Model.

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Considering their remarkable properties as solvents and electrolytes, ionic liquids represent nowadays a major field of research in chemistry. Even so, many questions remain regarding their ionic nature and the degree of association of these compounds, either as pure phases or diluted in a solvent.

We present here some results for the description of the thermodynamic properties of aqueous solutions of ionic liquids up to high concentration and for temperatures ranging from 298 to 333 K, using the BiMSA model.[1,2] This thermodynamic model is able to describe ions as charged spheres immersed in a solvent, considered as a continuum of permittivity $\square$. Ion *i* exhibit a specific diameter $\square_i$. The model takes into account the association between unlike ions to form a neutral pair.

Osmotic coefficients of solutions containing imidazolium-based ionic liquids were studied. Cations 1-methyl-ethylimidazolium, 1-methyl-ethylimidazolium, 1-methyl-ethylimidazolium were used in combination with chloride, bromide or methylsulfate. Previous works have already assigned specific diameters for the anions studied here.[1] Diameters for the cations were adjusted here, with plausible results, in terms of description accuracy of osmotic coefficients and parameter values obtained for the cation diameters and association constants.

The BiMSA model suggests that ionic liquids behave as slightly associated salts in water ($K < 10\ L.mol^{-1}$).

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Keywords: Thermodynamic modelling of electrolytes, Solutions of ionic liquids, osmotic coefficients.

Ref P-118

High Pressure Phase Equilibria in the Carbon Dioxide + 1-Dodecanol Binary System.

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Thermodynamic knowledge of the high-pressure phase behaviour of carbon dioxide + alcohol mixtures is essential for the design and implementation of many chemical and biotechnological processes. The binary system studied in the present work is a part of an extensive study on mixtures containing carbon dioxide + alcohols [1].

The carbon dioxide + 1-dodecanol system shows type III fluid phase behaviour, according to the classification of van Konynenburg and Scott [2]. In the literature, the upper critical endpoint was located at 7.635 MPa and 306.09 K, but the three-phase vapor-liquid-liquid equilibrium (VLLE) was not measured. Few vapour-liquid equilibria (VLE) studies were done on the carbon dioxide + 1-dodecanol binary system.

Phase behaviour measurements were made in a high-pressure visual cell with variable volume based on the static-analytical method. The three-phase equilibrium data and the upper critical endpoint were measured. The pressure, temperature and phase compositions of the two liquid phases are reported for this mixture. Vapour-liquid and vapour-liquid-liquid equilibria data for the carbon dioxide + 1-dodecanol system at 293.15, 303.15, 313.15, 333.15 and 353.15 K up to 9.36 MPa were determined.

The experimental data were modelled with the Soave-Redlich-Kwong (SRK) equation of state coupled with the MHV2-UNIFAC and Huron-Vidal at infinite dilution mixing rules. The predictions with the SRK/MHV2-UNIFAC are in qualitative agreement with the experimental data. The vapour-liquid equilibrium data were better modelled with the SRK Huron-Vidal at infinite dilution equation of state.

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Keywords: carbon dioxide; 1-dodecanol; high pressure; phase equilibria.

Ref P-119

Correlation and prediction of the phase behaviour and thermal properties of binary and ternary system of 2,2'oxybis[propane]+ benzene, toluene, m-xylene and cyclohexane.

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Ethers, such as 2,2'-oxybis[propane] (diisopropylether or DIPE) are used as gasoline additives because of their excellent anti-knock quality and environmental protection substance.

The complex behaviour of association and structure effect of ethers molecules with monoaromatic and cyclic hydrocarbons offers a serious test for the predictive potential of thermodynamic theories of mixtures. In this regard, the DISQUAC model, elaborated by H.V.Kehiaian [1,2] and based on the reticular model of Guggenheim-Barker [3,4] is appropriate to describe the phase behaviour vapour-liquid equilibria (VLE) and thermal properties (heat of mixing) of the mixtures, because of the inclusion of a quasi-chemical term that allows the model to be applied to associated mixtures.

The experimental isothermal P-x –y data at different temperatures of liquid binary mixtures DIPE + monoaromatics and cyclic hydrocarbons are measured using a static apparatus [3]. Data reduction by Barker's method provides correlation for excess molar Gibbs energy G^E [8]. The corresponding enthalpy of mixing H^E for these systems [5,6,7] have been measured at 303.15 K and constant pressure using a Calvet type microcalorimeter, C80 (Setaram, France). A Redlich-Kister type equation [9] was used to correlate experimental values of G^E and H^E.

The theoretical results obtained by the DISQUAC model are significantly closer to the experimental values. In addition the values of thermodynamic properties with both set of the interaction parameters obtained by the DISQUAC model have been compared with the predictions resulting from others models, such as the ERAS model [9,10,11] and the UNIQUAC model [12].

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Ref P-125

Improving the Modelling or Hydrogen Solubility in heavy Oil Cuts using an augmented Grayson Streed (AGS) approach.

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The Grayson Streed (G-S) method [1] is often used by the industry for calculating hydrogen solubility in petroleum fluids. However, its accuracy becomes very bad when very heavy fluids are considered. An improvement is proposed in this work based on a Flory-augmented activity coefficient model.

Hydrogen Solubilities in n-alkanes from n-C_7 up to n-C_{36} have been investigated, and a decreasing Henry constant with molecular weight is evidenced. The analysis of the Henry constant behaviour with molecular weight suggests a simple improvement to the model, using a Flory entropic contribution [2], thus keeping its predictive character. This improvement led to the necessity of refitting a number of fundamental hydrogen parameters. The resulting model behaves better for heavy components and for aromatics.

The petroleum fractions evaluated with the Augmented Grayson-Streed (AGS) model were taken from Cai et al. [3]. The importance of the petroleum fluid characterization is stressed. A sensitivity analysis has shown that the solubility parameter has a much larger than the other parameters: great care must be taken at calculating that property.

The predictions of the hydrogen solubility in petroleum fractions were improved compared with the Grayson Streed model, resulting an Absolute Average Deviation (AAD) of 21% for the AGS model vs. 46% for Grayson-Streed model, in the range of 80-380°C and 6.3-123 bar.

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Keywords: Hydrogen, solubility, heavy oil cuts, modelling.

Ref P-127

Implementation of PC-SAFT and SAFT + Cubic for Modeling Thermodynamic Properties of Haloalkanes. I. 11 Pure Halomethanes.

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In the current study the popular theoretically based model PC-SAFT and the recently proposed SAFT + Cubic have been implemented for correlating and predicting various thermodynamic properties of 11 pure halomethanes. It has been found that thanks to the correct estimation of the experimental critical temperatures and pressures, SAFT + Cubic exhibits a superior over-all robustness and reliability. In addition, SAFT + Cubic has a clear advantage in predicting sound velocities. However PC-SAFT is more accurate in modeling certain kinds of data, such as the isobaric heat capacities of saturated liquids.

Keywords: Equation of State, Statistical Association Fluid Theory, high pressure,
phase equilibria, sound velocity.

Ref P-128

Implementation of SAFT + Cubic and PC-SAFT for Comprehensive Description of Thermodynamic Properties of *n*-Octane and its Mixtures.

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The paucity of the available sound velocity and other auxiliary property data on supercritical mixtures restricts the comprehensive examination of the EoS models to just a few systems. In the current study pure *n*-octane(2) and its several mixtures such as methane(1) – *n*-octane(2) and nitrogen(1) – *n*-octane are considered. It is demonstrated that the recently proposed SAFT + Cubic Equation of State (EoS) has a doubtless advantage over the popular PC-SAFT model in predicting the elevated pressure densities. In addition, SAFT + Cubic appears as a robust estimator of sound velocities and compressibilities both at low and high pressures, which is not a case of PC-SAFT. Although SAFT + Cubic is capable of only rough estimation of heat capacities of pure *n*-octane, its results are closer to the experimental data than the predictions of PC-SAFT. Additional research should be performed for drawing grounded conclusions concerning the accuracy of both equations in modeling phase equilibira.

Keywords: equation of state, statistical association fluid theory, high pressure,
phase equilibria, sound velocity, compressibility.

Ref P-129

Some Observations Regarding the SAFT-VR-Mie Equation of State.

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This study demonstrates that the advanced theoretical basis and the consequential numerical complexity do not always guarantee the success of EOS models in predicting the experimental thermodynamic property data. Although one of the most accurate versions of SAFT, namely SAFT-VR-Mie might have doubtless advantages in predicting the data of non-spherical molecules, once again it is shown that there is a price to pay for the excessive model's complexity. In particular, the present study reveals a previously unnoticed kind of numerical pitfalls, yet generated by the chain term of the SAFT-VR-Mie EOS. A possible way of avoiding the numerical pitfall under consideration is proposed.

Keywords: Equation of State, Statistical Association Fluid Theory, high pressure,
phase equilibria, sound velocity.

Ref P-130

Molecular-Level Modelling of Air-Liquid Interface of Imidazolium-Based [Tf_2N^-] Ionic Liquids.

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We present molecular dynamics simulations of the air-liquid interface for three room temperature ionic liquids with a common anion: bis(trifluoromethylsulfonyl) imide ([Tf_2N]), and imidazolium-based cations that differ in the alkyl tail length: 1-butyl-3-methylimidazolium ([C_4mim]), 1-hexyl-3-methylimidazolium ([C_6mim]), and 1-octyl-3-methylimidazolium ([C_8mim]). The CHARMM type force field is used with the partial charges based on quantum calculations for isolated ion pairs. The total charge on cations and anions is around 0.9*e* and -0.9*e*, respectively, which somewhat mimics the anion to cation charge transfer. The surface tension at 300 K is computed by using the mechanical route and its value slightly overpredicts experimental values. The air-liquid interface is analyzed using the intrinsic method of Identification of the Truly Interfacial Molecules. Structural and dynamic properties of the interfacial, sub-interfacial and central layers are determined. To describe the structure of the interface, we compute the surface roughness, number density and charge density profiles, and orientation ordering of the ions. We further determine the survival probability, normal and lateral self-diffusion coefficients, and re-orientation correlation functions to characterize dynamics of the cations and anions in the layers. We found a significant enhancement of the cation density and preferential orientation ordering of both the cations and anions at the interface. Overall, the surface of the interfacial layer is smoother than the surface of the sub-interfacial layer and the roughness of both the interfacial and sub-interfacial layers increases with the increase in length of the cation alkyl tail. Finally, the ions stay considerably longer in the interfacial layer than in the sub-interfacial layer and dynamics of exchange of the ions between the consecutive layers is related to distinct diffusion and re-orientation dynamics behavior of the ions within the layers.

Ref P-139

A comprehensive structural analysis of the {methanol+inert} associating system *via* Monte Carlo simulations.

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The microscopic structure of hydrogen bonding mixtures has been systematically investigated by experimental and theoretical studies. Particularly, solutions of alcohols in nonpolar solvents represent a subclass of these associating systems of peculiar interest since the clustering topology in these mixtures is simple due to aggregate formation occurs only between molecules of the same kind. In this context, {methanol+inert} mixture is representative of a wide class of these systems since methanol is the simplest organic molecule able to exhibit a self-associative behaviour through hydrogen bonding. Some experimental works on this respect have been carried out by using Raman spectroscopy [1-4] and NMR [5, 6] techniques; on the other hand, a structural characterization for this associating mixture *via* molecular simulations [7-9] hardly exists. Thus, a proper description of the hydrogen-bonding networks of this fundamentally important system is still under debate. As a result, this work is aimed at providing new insights into the structure and topology of molecular clusters present in the solution of methanol with an inert solvent in the context of Monte Carlo simulations. To this end, *NpT* simulations of {OPLS methanol + Lennard-Jones spheres} have been performed at 298.15 K and atmospheric pressure encompassing the whole concentration range. The detailed structural information obtained from this study has greatly advanced our understanding of these systems and contribute to complete the physical scenario of this still active area of research.

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Keywords: hydrogen-bonding, structure, methanol.

EXHIBITION & SOFTWARE PRESENTATION

(by order of references)

*Ref E-xxx = Exhibition
*Ref S-xxx = Software

*Ref S-053**

Culgi: The Chemistry Unified Language Interface, a practical tool for general purpose chemical modeling.

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Computer modeling is a valuable tool for efficient formulation development of so-called soft materials in such diverse industries as chemicals, petroleum, pharmaceuticals, automotive, aerospace, and home & personal care. Integrating modeling activities into the R&D process increases the rate at which new products can be brought to market. A number of modeling techniques, ranging from atomistic to field based mesoscopic models, to statistical methods are used to solve various problems in the research process. Culgi (Chemistry Unified Language Interface) aims to integrate all relevant chemical modeling tools in one common platform. Modeling techniques include quantum, molecular, mesoscopic modeling and statistical methods such as Quantitative Structure Activity Relations. The library is designed from first principles up, in a C++ set of classes and functions, that can fully be controlled by common scripting languages such as tcl and python, but also by the powerful scripting editing tools from Culgi's Graphical Programming Environment. The novel design implies that the user, that is the industrial engineer or computational chemist, can develop proprietary applications easily. Thus, the library interfaces neatly between the expert software developer and application scientist. We discuss a few realistic business cases, including all aspects of successful industrial multiscale modeling, such as the importance of strong commitment to IT services and scientific consulting, as well as demonstration of dedicated workflows or script technology. Examples include drug delivery, commodity (polymer blends) and glues. An in-depth analysis of micro-emulsion design in the context of chemical oil recovery (in collaboration with Shell) is discussed in a separate presentation at this conference. Culgi is sponsored by several EU projects (Multimatdesign – Polymer Membranes, Selfmem – Polymer Membranes, Nanomodel – Nanocomposites, Biomimetic – Adhesives), Dutch government projects (Space Research, Biosolar Cells, and Microfluidics), and leading European, US and Japanese companies from a wide variety of industrial sectors. Culgi has development and support offices in Europe, China and USA, and representatives in Japan.

Keywords: computational chemistry, multiscale modeling, quantum; molecular, mesoscopic modeling.

*Ref E-054**

CULGI Demonstration.

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The Chemistry Unified Language (Culgi) aims to integrate relevant chemical modelling tools (quantum, molecular, mesoscopic and statistical) into one computational platform, with a focus on soft materials or formulations.

The computational technology, and a real-world application of multiscale modelling in the context of chemically enhanced oil recovery is presented elsewhere at this conference.

In this presentation at the stand of Culgi, we will present and discuss several practical aspects of multiscale modelling in an industrial setting. In particular, the writing of workflows in the CULGIs Graphical Programming Environment, that enables the rapid development of dedicated proprietary applications, and the relevance of Client-Server relations, that enable development in a heterogeneous computational infrastrucuture, from desktop or laptop, to production runs on a parallel cluster.

Attendees of the presentation will be offered hands-on tutorials, and trial licenses for testing of the software on laptops.

Demonstrated examples range from surfactants and polymers to colloids and actives, and techniques from molecular to mesoscopic, and combinations thereof, such as reactive systems (glues) and emulsion interfaces. Interested attendees are invited to present their own problems, and we could discuss how such system could be addressed by the Culgi modelling approach.

Keywords: Multiscale Modeling, Workflow, Client-Server relation, parallel computation.

*Ref S-089**

Simulis Thermodynamics: Software Presentation.

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Simulis® Thermodynamics, marketed by ProSim [1], is a thermophysical calculation server that generates highly accurate pure component and mixture properties (thermodynamic, transport, compressibility…) and fluid phase equilibria (liquid-vapor, liquid-liquid and liquid-liquid-vapor). Based on the AIChE's DIPPR database [2] and enriched by ProSim's thermodynamic experts it provides access to a property database of more than 2000 pure components, and to one of the richest thermodynamic models libraries available on the market: equations of state (SRK, PR, LKP, PPR78, PPC-SAFT…), G^E models (NRTL, UNIQUAC, UNIFACs…), EoS/G^E models (MHV2, PSRK, NRTL-PR…), electrolytes models (Edwards, UNIQUAC electrolytes, ULPDHS…) and specific models (Amines, Sour-Water, formaldehyde…). An "expert mode" feature is also available in Simulis® Thermodynamics, allowing the user to implement his own models. Simulis® Thermodynamics is available as a Microsoft Excel® add-in, a MATLAB® toolbox or as a software component which can be easily plugged in any other application requiring reliable and accurate thermo-physical properties. Simulis® Thermodynamics provides also a full set of services such as the generation of property tables, graphical display of properties, data regression of experimental properties, estimation of pure component properties, plot of phase envelope, calculation of petroleum fraction properties, unit conversion… All these services become automatically available in any software as long as it integrates Simulis® Thermodynamics. Another benefit of Simulis® Thermodynamics is its CAPE-OPEN [3] compliance through its implementation of the CAPE-OPEN standardized interfaces: "thermodynamic plug" and "thermodynamic socket".

References:

[1] www.prosim.net
[2] ROWLEY R. L., WILDING W. V., OSCARSON J. L., YANG Y., GILES N. F., DIPPR® Data Compilation of Pure Chemical Properties, Design Institute for Physical Properties, AIChE, New York, NY (2009)
[3] CAPE-OPEN Lab. Network, www.co-lan.org/Dissemination.html

Key words: Thermodynamic calculation server, component architecture, interoperability, integration, reusability.

*Ref E-137**

DECHEMA
Thermophysical databases and engineering software packages.

Ulrich Westhaus

DECHEMA e.V., Frankfurt am Main, Germany

The numerical database DETHERM provides thermophysical property data, which are indispensable for construction and design of chemical apparatus, plants and processes.

The DETHERM database provides thermophysical property data for about 31,600 pure compounds and 115,200 mixtures. DETHERM contains literature values, together with bibliographical information, descriptors and abstracts. At the time 7 million data sets are stored. The database is updated yearly and grows continually with around 8 % per anno. The follo-wing properties are stored:

- phase equilibrium data
- vapor pressures, critical data
- thermodynamic properties
- transport properties
- surface tensions
- electrolyte data

The DETHERM database is produced from the DECHEMA e.V. in cooperation with the DDBST GmbH, Oldenburg and the FIZ CHEMIE in Berlin.

A DETHERM Inhouse installation consists of a SQL database server in combination with the retrieval package DETHERM-ORS. The user friendly interface enables even unskilled users a rapid and easy access of desired data. The graphical display of data gives an overview on the distribution of the different data sets. For further processing the data can be exported in various formats (XML, CSV, IK-CAPE PPDX). Users of MS/Excel can cut & paste the data also directly. Seamless interfaces exist to a variety of process simulation and data like Aspen Properties or Simulis.

The user's own data can be readily handled with the data maintenance module. Running in Client-Server-Mode assures that all users of the system use identical data sets. Multiple data sets and the use of differing values from user to user can thus be avoided.

B) Data Preparation Package DPP

The DECHEMA Data Preparation Package (DPP) closes the gap between raw thermophysical data as stored in the DETHERM database and model based process simulation packages like Aspen Properties or Simulis. Besides selection und graphical display of data sets the package permits the regression of model parameters as well as the comparison of models with each other (e.g. comparison of the gamma models NRTL vs. Wilson vs. UNIQUAC or comparison of vapor pressure equations like Antoine vs. Wagner).

*Ref E-140**

InModelia : Design of experiments, Molecule properties.

Patrice Kiener

InModelia, Paris, France

InModelia is a software reseller and a consulting services company involved in:

- Neural networks for nonlinear regression.
- Design of experiments for explicit nonlinear algebraic functions and nonlinear ordinary differential equations. Knowing/computing the optimal points help reduce the number of experiments and return more accurate models, even in a nonlinear environment like thermodynamic models.
  Software Neuro Pex
- Graph machines, a special construction that uses neural networks, to compute in silico molecule properties, QSAR and QSPR. We get outstanding results, even with small datasets. This work is conducted with ESPCI-ParisTech.
  A. Goulon, T. Picot, A. Duprat, and G. Dreyfus
  Predicting activities without computing descriptors: graph machines for QSAR
  SAR and QSAR in Environmental Resesarch, vol. 18, pp. 141 - 153 (2007)

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Keywords: neural networks, design of experiments, graph machines, QSAR, QSPR.

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O-082	Tobaly P.	LSPM	Villetaneuse	France
O-043, P-048, P-049	Tomé L.I.N.	CICECO	Aveiro	Portugal
P-125	Torres R.	PDVSA Intevep	Los Teques	Venezuela
O-025	Toure O.	Université Blaise Pascal	Aubière	France
P-114	Trache D.	Ecole Militaire Polytechnique	Alger	Algeria
O-107	Travallonia L.	Federal University of Rio de Janeiro	Rio de Janeiro	Brazil
O-022	Trejos V.M.	University of Guanajuato	Guanajuato	México
O-058	Tsangaris D.	National Center for Scientific Research	Attikis	Greece
P-028	Tsivintzelis I.	Technical University of Denmark	Lyngby	Denmark
P-039	Turesson M.	Université de Bourgogne	Dijon	France
P-111	Türkb M.	Karlsruhe Institute of Technology (KIT)	Karlsruhe	Germany
P-027	Umer M.	RWTH-Aachen University	Aachen	Germany
P-091	Ungerer P.	Materials Design	Montrouge	France
S-089	Vacher A.	ProSim	Labège	France
O-074	Vesovic V.	Imperial College of London	London	United-Kingdom
P-116	Vinícius Domingues Silva M.	Universidade Federal de Uberlândia	MG	Brazil
P-103	Vlugt T.J.H.	Delft University of Technology	Delft	The Netherlands
O-082	Volle F.	LSPM	Villetaneuse	France
P-110	Volpe P.L.O.	Universidade Estadual de Campinas	SP	Brazil
P-029	von Solms N.	Technical University of Denmark	Lyngby	Denmark
P-068, O-070, P-097	Vrabec J.	University of Paderborn	Paderborn	Germany
O-059	Tavares F.W.	Universidade Federal do Rio de Janeiro	Rio de Janeiro	Brazil
O-041	Wender A.	IFP Energies Nouvelles	Rueil-Malmaison	France
E-137	Westhaus U.	DECHEMA e.V.	Frankfurt am Main	Germany
O-124	Williams T.H.	Process Systems Enterprise Ltd	London	United Kingdom
P-097	Windmann T.	Universität Paderborn	Paderborn	Germany
P-091	Yiannourakou M.	Materials Design	Montrouge	France
O-132	Panagiotopoulos A.Z.	Princeton University	Princeton	USA
P-026	Zaitseva A.	Aalto University	Espoo	Finland
P-002, P-003	Zermane S.	Université Mentouri de Constantine	Constantine	Algeria
P-061	Zohra Sebba F.	Université d'Oran	Oran	Algeria
P-104	Zuber A.	Texas A&M University of Qatar bState University of Maringá	Doha State of Paraná	Qatar Brazil

Objectives

The improved understanding of molecular-scale phenomena opens up an immense field of new possible applications for the chemical industry and beyond. The recent efforts in this field have resulted in models, simulation methods, and tools that allow not only solving academic problems but also contribute substantially to industrial research and development.
They open up routes to gain insight and improve processes which up until now could only be dealt with empirically.

The workshop is aimed at providing industrial experts with a clear vision of the opportunities that lie within this rapidly developing interdisciplinary field, where efforts from natural sciences and engineering are combined. It represents a unique opportunity to gain an overview of the state of research and its applications in the developing of engineering models.

There will be a number of review lectures will be provided, along with a large number of examples of success stories where these new technologies have been implemente.

The workshop is a joint initiative of the European EFCE « Thermodynamics and Transport Properties» and the German ProcessNet « Thermodynamics » working parties. It is organized by the French SFGP working party and the Ecole Normale Supérieure (ENS) Lyon. It will be held in Lyon, France, located on the Rhone River in the heart of the Rhône-Alpes region, from Monday morning March 19th to Tuesday afternoon, March 20th, 2012.

Organizing Committee

- Jean-Charles de Hemptinne (IFPEN)
- Raphael Huyghe (IFPEN)
- Jean-Noël Jaubert (LRGP Nancy Université)
- Patrice Méheux (SFGP)
- Pascal Rousseaux (Processium Lyon)
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- Eric Hendriks (Shell Global Solutions)
- Guenter Olf (Bayer)
- Gabriele Sadowski (Dortmund University)
- Philippe Sautet (ENS Lyon)
- Philippe Ungerer (Materials Design)

Workshop jointly organized by

EUROPEAN FEDERATION OF CHEMICAL ENGINEERING
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