

Thermodynamics 2003

April 9th – 11th, 2003

Cambridge UK

With thanks to Schlumberger Cambridge Research
for sponsoring the welcome reception at
Thermodynamics 2003.

Schlumberger

Foreword

Thermodynamics 2003 is the 18th meeting in a series of thermodynamics conferences which are held in the UK approximately every two years. The present meeting is organised jointly by Dr Ard Louis, of the University of Cambridge, and Professor Geoff Maitland and Dr Tony Goodwin, both of Schlumberger Cambridge Research. The meeting features the biannual Lennard-Jones Lecture which is presented this year by Professor Jean-Pierre Hansen FRS (University of Cambridge). The Lennard-Jones Lecture is organised by the Thermodynamics and Statistical Mechanics Group of the Royal Society of Chemistry with sponsorship from Unilever plc.

The conference also features the inaugural award of the C J Wormald Prize. This prize was established in recognition of the outstanding contribution made by Dr Christopher Wormald in the organisation and promotion of previous conferences in this series. The prize is for an outstanding piece of original research by a current or recent graduate student; it is awarded in 2003 to Ms Rosalind Allen of the University of Cambridge. The prize award and lecture will take place in session 9 on Friday afternoon.

A special session (Session 4b) in honour of Professor Keith Gubbins is scheduled for Thursday morning. Keith will be presented with a leather-bound copy of the special issue of *Molecular Physics* published recently to mark his 60th birthday. To further mark this event, the publishers, Taylor and Francis Ltd, are sponsoring pre-dinner drinks on Thursday evening.

I am immensely grateful to the local organisers, Ard Louis, Geoff Maitland and Tony Goodwin, for their hard work and dedication. I would also like to thank Schlumberger Cambridge Research for both sponsoring and hosting the reception on Wednesday evening.

The full Organising Committee for Thermodynamics 2003 is:

Dr Amparo Galindo (Treasurer)	<i>Imperial College London</i>
Dr Tony Goodwin (Local Organiser)	<i>Schlumberger Cambridge Research</i>
Professor George Jackson	<i>Imperial College London</i>
Dr Kathleen Johnson	<i>Liverpool University</i>
Dr Ard Louis (Local Organiser)	<i>University of Cambridge</i>
Professor Geoff Maitland (Local Organiser)	<i>Schlumberger Cambridge Research</i>
Professor Martin Trusler (Chairman)	<i>Imperial College London</i>

Finally, I am pleased to thank Cambridge Publications for providing conference administration and publication services for this meeting.

J P Martin Trusler
Chairman, organising Committee
April 2003.

Conference Information

Registration and Help Desk

The Registration and Helpdesk will be located in the first floor of the Department of Geology, (Earth Sciences, South Wing). It will be staffed on Wednesday from 10:00 till 14:00 and sporadically during major lunch and refreshment breaks.

Oral Presentations and Posters

The oral presentations will be given in the lecture theatres of the Department of Geology (Earth Sciences) and Physiology: these rooms are almost immediately adjacent to each other. The poster sessions and refreshments will be available in the large Physiology laboratory on the third floor.

Badges and Security

The conference will be located in two adjoining departments of the University of Cambridge. The Physiology department is quite sensitive about security issues. For that reason we kindly ask conference delegates to wear their badges at all times while in University buildings.

Emergencies

Fire, Police and Ambulance can be reached on internal phones by dialling 1999

PowerPoint Presentations

Delegates wishing to use PowerPoint in their presentations should bring their presentation on CD to the projectionists at the Registration and Helpdesk by 5pm on the day before their presentation. Those presenting their work on Wednesday afternoon are requested to deposit their CDs not later than 12:00 on Wednesday.

Messages

Messages for delegates can be sent by email or by fax. They will then be put on the message board.

Email to: Thermo2003@the-conference.com

Fax to: +44 (0)1223 333438

Internet access

Limited internet access will be available in the Registration room on the first floor of the Department of Geology.

Left Luggage

The colleges (Corpus Christi, Clare, and St. Catherine's) have left luggage facilities. There is a limited space for left luggage in the Physiology lab, but luggage here is left at the owner's risk.

Banks

The closest branches of major banks, along with several cash dispensers, can be found along Bene't Street, and on the Market Square, within a few minutes walk from the conference site, and right behind Corpus Christi College.

Car Parking

Car parking is extremely difficult to find anywhere near the centre of Cambridge, and there is no car parking on university grounds. The closest car-park to the conference is the Lion Yard. However this is very expensive (£25.00 for over 5 hours). The cheapest local car-park is Queen Anne's, off Gonville Place, across from Parker's Piece, and next to the Kelsey Kerridge Sports Centre and the Parkside Pool.

Conference Timetable

Wednesday April 9th, 2003

- 10:00-15:00. Registration
- 12:45-13:45. Lunch (Poster Session 1 begins)
- 14:00-15:30. Plenary Session I
- 15:30-16:00. Afternoon Break
- 16:00-18:00. Equation of State and Soft Matter Sessions
- 19:00. Buses depart colleges for Schlumberger Reception
- 22:00. Buses depart Schlumberger Reception for return journey to colleges

Thursday April 10th, 2003

- 09:00-10:30. Plenary Session II
- 10:30-11:00. Morning Break
- 11:00-12:30. Experimental Thermodynamics and Special Session in Honour of Keith Gubbins
- 12:45-13:45. Lunch (Poster Session 2 begins)
- 14:00-15:30. Plenary Session III
- 15:30-16:00. Afternoon Break
- 16:00-18:00. Simulation and Electrolytes Sessions
- 19:00. Drinks reception in Corpus Christi College
- 19:30. Conference Banquet in Corpus Christi College

Friday April 11th, 2003

- 09:00-10:30. Plenary Session IV
- 10:30-11:00. Morning Break
- 11:00-12:30. Non-equilibrium Thermodynamics and Confined Fluids Sessions
- 12:45-13:45. Lunch
- 14:00-15:30. C J Wormald Prize
- 15:30-16:00. Afternoon Break
- 16:00-18:00. Adsorption and Surfaces and General Sessions

Poster Sessions

Posters will be displayed in the Physiology teaching laboratory. Authors are expected to be available to discuss their poster presentations during breaks and at lunch times.

Catering

All refreshments will be served in the Physiology teaching laboratory. Drinks will be served during the breaks in the sessions and lunch will be a buffet available from 12.45pm.

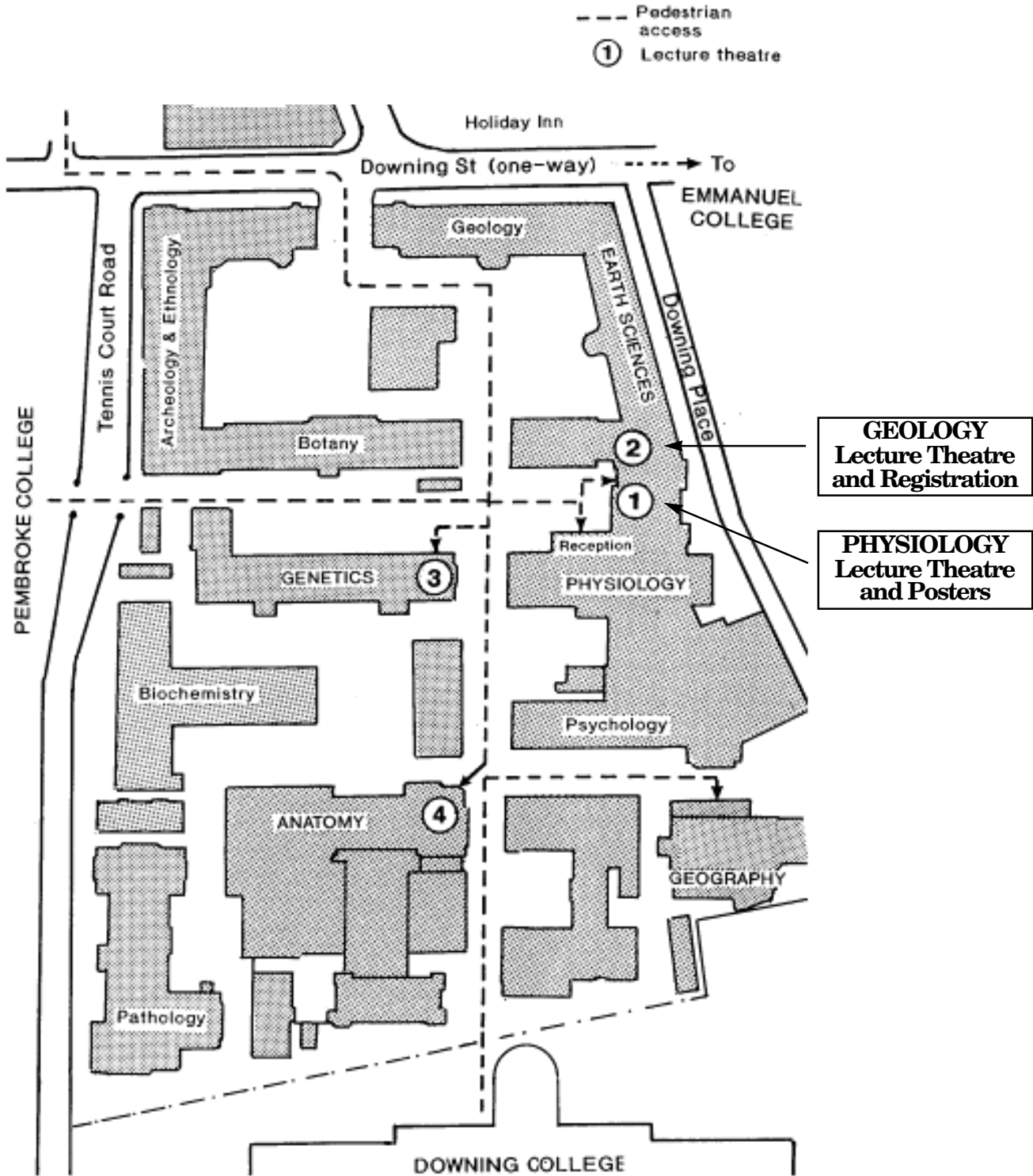
Schlumberger Reception

The reception will be held at Schlumberger Cambridge Research on Madingley Road. This unusual and innovative building has won many awards and houses the UK research facility for Schlumberger's Oilfield Services business. A drinks reception and buffet supper will be held in the main Winter Garden. There will be an opportunity to view some of the building with demonstrations of a number of current activities, including immersive 3D-visualisation and multiphase flow. Coaches will leave the accommodation areas at 19.00 and leave Schlumberger at 22.00 in time for participants to sample the Cambridge taverns before they shut.

Conference Banquet and Drinks Reception

The conference banquet will take place in Corpus Christi college. Before the banquet (at 19:00) there will be a drinks reception sponsored by Taylor and Francis Ltd. in honour of Keith Gubbins. This will take place in the Old Court at Corpus Christi.

**Map of the Downing Site
Lectures and Posters will be in the
Departments of Geology and Physiology**



Thermodynamics 2003

Conference Programme

Session 1
Plenary I

Physiology Lecture Theatre
Chaired by Prof Geoff Maitland

- 14:00** **The Lennard-Jones Lecture**
Hansen, JP:
Mixing Colloids and Polymers: from Coarse-Graining to Accurate Phase Diagrams
- 14:45** **Raviv U, Giasson S, Kampf N, Gohy J, Jerome R & Klein J:**
Water and Other Complex Fluids Confined to Molecularly Thin Films

Session 2a
Equations of State

Physiology Lecture Theatre
Chaired by Prof Ulrich Deiters

- 16:00** **Wilson S & Lee L:**
Chemical Potentials and Phase Equilibria of Lennard-Jones Mixtures: A Self-Consistent Integral Equation Approach
- 16:15** **Klamt A:**
COSMO-RS, a Novel a Priori Predictive Method for Fluid Phase Thermodynamics
- 16:30** **Colina C & Gubbins K:**
Molecular Modeling of Long Chain Hydrocarbons, Polymers and Surfactants in Supercritical Carbon Dioxide using SAFT
- 16:45** **Bourasseau E, Ungerer P & Fuchs A:**
New Optimisation Method for Lennard Jones Potentials - New AUA Potential for Prediction of Equilibrium Properties of Olefins
- 17:00** **Vega C, Jimenez-Blas F & Galindo A:**
Solid-fluid Phase Behaviour of Model Attractive Chain Molecules
- 17:15** **Canongia Lopes JN, Padua A, Rebelo LP & Bigeleisen J:**
Calculation of Vapor Pressure Isotope Effects in the Rare Gases and their Mixtures using an Integral Equation Theory
- 17:30** **Kalies G, Bräuer P & Messow U:**
Thermodynamic Prediction of Multicomponent Liquid Adsorption on Solids using Excess Quantities
- 17:45** **Estela JF, De Mendoza A & Trusler J:**
Helmholtz Energy, Extended Corresponding States and Local Composition Model for Fluid Mixtures

Session 2b
Soft Matter

Geology Lecture Theatre
Chaired by Prof Berend Smit

- 16:00** **Likos CN, Harreis HM & Goetze IO:**
Conformations and Interactions of Flexible Dendrimers
- 16:15** **Archer A & Evans R:**
Solvent Mediated Interactions and Solvation Close to Fluid-Fluid Phase Separation: A Density Functional Treatment
- 16:30** **Pàmies JC & Vega LF:**
Critical Behaviour of Homopolymers Studied by the Soft-SAFT EOS
- 16:45** **Lindvig T, Michelsen ML & Kontogeorgis GM:**
Binary and Ternary Liquid-Liquid Equilibria for Polymer Solutions
- 17:00** **Paricaud P, Varga S, Galindo A & Jackson G:**
Understanding the Thermodynamics and Fluid Phase Equilibria of Polymer-Colloid and Polymer-Solvent Systems
- 17:15** **van Roij R:**
Gravity Versus Entropy in Suspensions of Charged Colloids
- 17:30** **Costa D, Saija F & Giaquinta PV:**
Entropy and Correlations in a Fluid of Aligned Spherocylinders: The Onset of Smectic Order
- 17:45** **Harnau L:**
Interfacial Properties of Hard-platelet Fluids

Poster Session 1

- 01** **Aboudheir A, Tontiwachwuthikul P, Chakma A & Idem R:**
Applications of a Simplified Vapour-Liquid Equilibrium Model for CO₂ Absorption into MEA Solutions
- 02** **Adamenko I, Moroz K, Durov S, Prylutskyy Y, Scharff P & Braun T:**
Equation of State for C₆₀ Fullerene Aqueous Solution
- 03** **Aim K, Nezbeda I & Vıcek L:**
A Molecular-based Equation of State for Methanol
- 04** **Ajib S, Nilius A & Karno A:**
Thermodynamic Properties of a Tube Bundle Heat Exchanger
- 05** **Al-Zaza M, Mrevlishvili G, Mdzinarashvili T & Tediashvili M:**
Thermodynamics of the Temperature-induced Destruction of Phages
- 06** **Alcalde R, Aparicio S, Dávila MJ, García B & Leal JM:**
Thermophysical Properties of Lactam Containing Mixed Solvents at 298.15 K
- 07** **Alonso C, Montero EA, Chamorro CR, Segovia JJ, Martín MdC & Villamañán MA:**
VLE for the Ternary System Di-Butyl Ether + Cyclohexane + Heptane and its Corresponding Binary Systems at 313.15 K
- 08** **Alonso C, Montero EA, Martín F, Chamorro CR, Segovia JJ & Martín MdC:**
Excess Enthalpies of Binary and Ternary Mixtures Containing Tert-Amyl Methyl Ether(TAME), 1-Propanol and Hexane
- 09** **Anderson G:**
Thermodynamic Studies of Methane and Carbon Dioxide Hydrates using the Clapeyron Equation
- 10** **Aparicio S, Alcalde R, García B & Leal JM:**
Characterization of the n-Hexane + Hexan-1-ol + Methylbenzoate Ternary Solvent at 298.15 K According to the Kirkwood - Buff Fluctuation Theory
- 11** **Apostolakou A, Adjiman C, Galindo A & Jackson G:**
Phase Equilibrium of Pure Fluids with the SAFT-VR Equation of State Based on the Sutherland Potential
- 12** **Artigas H, Martín S, Rodríguez V, Lafuente C, Royo F & Cea P:**
Densities and Speeds of Sound of the Ternary Mixtures Cyclohexane + 1,3-Dioxolane + 2-Butanol and n-Hexane + 1,3-Dioxolane + 2-Butanol
- 13** **Avramenko N & Bogachov A:**
Thermodynamic Properties of Molecular Complexes of C₆₀, C₇₀ and their Simple Derivatives with the Aromatic Solvents
- 14** **Balankina E:**
Deviations of the Packing Factor Respect to the Ideal Packing and the Excess Acoustical Properties
- 15** **Ballenegger V & Hansen JP:**
Effective Dielectric Constant for a Polar Solvent Near an Interface
- 16** **Barros N & Feijóo S:**
The Calculation of the Thermodynamic Efficiency of the Soil Microbial Reactions: Application in Ecological Studies
- 17** **Barros N, Feijóo S, Fernández S & Gallego M:**
The Relationship of the Specific Substrate Degradation Rate and the Enthalpies of the Microbial Reactions in Soils
- 18** **Bauer W:**
Second Law Versus Variation Principles
- 19** **Belashchenko D & Ostrowski O:**
Computer Modeling of Liquid Ionic Systems Using Diffraction Data
- 20** **Belchior Torres R, Zaghini Francesconi A & Onófrío Volpe PL:**
Experimental Results and Comparison between PFP Theory and ERAS Model for Excess Molar Volume of Acetonitrile + Alcohol Mixtures
- 21** **Belousov V, Belousova I & Danilov O:**
Photoinduced Phase Transition in Fullerenes Solutions and Suspensions of Carbon Nanoclusters
- 22** **Belousova I, Belousov V & Danilov O:**
Thermophysical and Optical Processes at Interaction of Powerful Radiation with Molecular System Fullerene-Oxygen-Iodine
- 23** **Bogel-Lukasik E, Bogel-Lukasik R & Domanska-Zelazna U:**
Solution Thermodynamics of [C₄-, or C₁₀ mim][Cl] and an Alcohol
- 24** **Bolhuis P, Meijer E & Louis A:**
Colloid-Polymer Mixtures in the Protein Limit
- 25** **Boublik T:**
Equilibrium Behavior of Hard Non-spherical Body Fluids
- 26** **Bourasseau E, Jose J & Ungerer P:**
Measurement and Prediction of Saturation Pressures of Pristane. Experimental and Monte Carlo Simulation Results
- 27** **Brovchenko I, Geiger A & Oleinikova A:**
Computer Simulations of the Phase Behaviour of Water in Hydrophilic and Hydrophobic Nanopores
- 28** **Brovchenko I, Geiger A & Oleinikova A:**
Multiple Liquid-Liquid Transitions in Supercooled Water
- 29** **Bumba J & Kolafa J:**
The Global Phase Diagrams of the van der Waals-Dieterici and the BMCSL-Dieterici Equations of State
- 30** **Castillo-Borja F, Herrera Camilo G, Vázquez-Román R & García-Sánchez F:**
Predicting a Profile of Hydrate Formation Potential in Pipes
- 31** **Cebreiro S, Illobre M, Mato MM, Verdes P, Legido JL & Paz Andrade MI:**
Study on Excess Molar Enthalpies of MTBE + 1-Propanol + Hexane at 298.15 K
- 32** **Cendón J, Piñero M, Bessières D, Saint-Guirons H & Legido JL:**
High Pressure Density Measurements for the Mixture Methyl Nonfluorobutyl Ether + nHexane
- 33** **Cerdeirıña CA, Gonzalez-Salgado D, Romani L & Costas M:**
A Model for the Temperature Dependence of the Heat Capacity of Pure Liquids
- 34** **Cheluguet E:**
Effect of Polymer Polydispersity Characterization on Predicted Phase Behaviour of Polyethylene Solutions
- 35** **Cordeiro T & Filipe E:**
Surface Tension of Ionic Liquids
- 36** **Cuetos A, Martínez-Haya B, Lago S & Rull L:**
Liquid Crystal Transitions in Anisotropic Fluids. The Relative Influence of Entropy and Energy

37	Delmas G, Gouanvé F & Seguin M: Characterization of Ethylene-Propylene Elastomers by Turbidity at a Lower Critical Temperature using a Step by Step Temperature Increase	54	Heyden A, Düren T & Keil F.J: Study of Molecular Shape and Non-ideality Effects on Mixture Adsorption Isotherms of Small Molecules in Carbon Nanotubes: A Grand Canonical Monte Carlo Simulation Study
38	Denesyuk N & Hansen JP: Wetting Transitions in the Presence of Electrostatic Forces	55	Ishida M: Hierarchical Application of Thermodynamics to Process System Design
39	Deschamps J, Padua A & Costa Gomes M: Molecular Interactions of Oxygen, Carbon Dioxide and Water in Fluorinated Solvents	56	Job G: Fermi-Dirac and Bose-Einstein Distribution Functions Derived from Classic Thermodynamics
40	Dufreche J, Bernard O, Jardat M, Turq P & Bagchi B: Transport of Ions in Electrolyte Solutions: Are Ions Brownian Particles ?	57	Job G, Rüffler R & Lankau T: Teaching Thermodynamics - a New Concept
41	Fenz W & Folk R: MC Simulation of Phase Equilibria in Ising Fluids and their Mixtures	58	Johansson E & Ahlström P: Simulation of Water/Polymer Systems
42	Finken R & Hansen JP: Lattice Model of a Binary Mixture of Penetrable Particles	59	Jorge M & Seaton N: Molecular Simulation of Water/organic Co-adsorption on Activated Carbon
43	Franco-Melgar M, Haslam AJ & Jackson G: An Analytical Onsager-like Equation of State for Ordering Transitions in Systems of Attracting Rod-like Particles	60	Kakalis N, Kaku A & Pantelides C: Calculation of Thermophysical Properties in Process Modelling Tools with the SAFT Equation of State
44	Gascon I, Giner B, Haro M, Lopez MC & Cea P: Vapour-Liquid Equilibrium for the Binary Systems 2-Methyl-2-Propanol with Some Halohydrocarbons	61	Karimi Pour Haddadan F & Dietrich S: Liquid Crystal at Inhomogeneous Interfaces: Structural Forces
45	Gawel W, Sztuba Z & Mucha I: Some Regularities in the Quasi-binary Metal Chalcogenide Systems with Common Cation	62	Kermanpour F & Parsafar G: Investigation of the Temperature and Density Dependencies of the Effective Pair Potential Parameters using Variational Theory
46	Gelchinski B, Mirzoev A, Smolin N & Vyatkin G: The Computer Simulation of the Short-range-order Atomic Structure of Liquid Li-Si and Analyse of Atomic Structure by Voronoi Polyhedron Method	63	Khare R, McGrother S, Meunier M, Nath S, de Pablo J & Sum A: Simulation of Phase Equilibria of Alcohols, Sulfides and Thiols and their Mixtures with Alkanes
47	Ghotbi C, Taghikhani V & Hashemi S: Correlation of LLE Experimental Data of Ternary Systems Containing Water with Different Activity Coefficient Models Based on Quasi-Chemical Theory	64	Kock F & Herwig H: Local Entropy Production in Turbulent Shear Flows: A High Reynolds Number Model with Wall Functions
48	Giovanoglou A, Adjiman C, Galindo A & Jackson G: Mixture Design with the SAFT Equation of State	65	Koenig P & Roth R: Curvature Expansion of Density Profiles of Hard-Sphere Fluids
49	Gloor G, Blas FJ & Jackson G: Modelling the Surface Tension of Real Substances with a SAFT-VR Density Functional Theory	66	Kolafa J, Labik S & Malijevsky A: Accurate Equation of State of the Hard Sphere Fluid in Stable and Metastable Regions
50	Gloskowska M & Domanska-Zelazna U: Studies on Thermodynamic Properties of (Amine + Alcohol) Mixtures	67	Kolafa J, Labil S, Francova M & Malijevsky A: An Analytical Formula for the Bridge Function of Hard Sphere Fluid
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52	González-Salgado D, Troncoso J, Cerdeiría CA, Tovar CA, Carballo E & Romani L: A New Description of the Proximity Effect	69	Koshkin V: Supersolubility of and in Nanocrystals
53	Haddad Y: On the Stochastic Thermo-micromechanics of a Class of Material with a Time-history Dependent Response	70	Kostanovski V & Kostanovskaya E: The Analysis of a Curve 'Time-Temperature', Obtained at Heating of an Indefinitely Thin Plate by the Modulated Laser Beam
		71	Kovdriya Y, Rybalko A, Syvokon V & Sokolov S: Quasi-Equilibrium Processes in Two-Dimensional Electron System over Superfluid Helium
		72	Kozłowska MK, Domanska-Zelazna U & Rogalski M: (Solid + Liquid) Equilibria of [Poly(1-Butene) + n-Alkane] Binary Mixtures

Session 3
Physiology Lecture Theatre
Plenary II
Chaired by Prof Jean-Pierre Hansen

- 09:00** Wormald C:
Advances in Steam Mixture Research
- 09:45** Gubbins K:
Phase Transitions and Chemical Reactions at the Nano-Scale: Effects of Confinement
- Session 4a**
Experimental Thermodynamics
Physiology Lecture Theatre
Chaired by Prof Martin Trusler
- 11:00** García-Sánchez F, Eliosa-Jiménez G, Silva-Oliver G & Godínez-Silva A:
Phase Equilibria of the Nitrogen-n-Heptane System
- 11:15** Davis M, Gamboa A, Enriquez J, Douh ret J, Douh ret G & Joao - Carlos :
Evidence for Reverse Micelle Formation by Borderline Surfactants in Heptane
- 11:30** Goodwin A, Donzier E, Manrique M & Vancauwenberghe O:
Micro Electro Mechanical System (MEMS) for the Measurement of Density and Viscosity
- 11:45** D'Amore A, Di Nicola G, Giuliani G, Polonara F & Stryjek R:
PVTx in the CO₂ + Hydrofluoromethane Binary Systems
- 12:00** Audonnet F & P dua A:
Simultaneous Measurements of Density and Viscosity of {Methane + n-Decane} Mixtures from 303 to 393 K and up to 75 MPa using a Vibrating-Wire Instrument
- 12:15** Smirnova N:
Phase Boundaries and Aggregation in Mixed Micellar Solutions
- Session 4b**
Geology Lecture Theatre
Keith E Gubbins Session
Chaired by Prof Peter Cummings
- 11:00** Evans D & Searles D:
The Transient Fluctuation Theorem and NonEquilibrium Free Energy, Theorems
- 11:15** Nezheda J:
Thermophysical Properties of Fluids: from Simple Models to Applications
- 11:30** Deiters UK & Nasrabad AE:
Ab Initio Predictions of the Vapour—Liquid Equilibria of Noble Gases and their Mixtures
- 11:45** Herdes C, Figueroa-Gerstenmaier S, Medina F & Vega L:
Modeling and Characterization of Adsorbent Materials by GCMC Simulations and Experiments
- 12:00** Filipe E, Morgado P, Tom s R & El-Abed A:
Solution and Interfacial Behaviour of Semifluorinated Alkanes
- 12:15** Varga S & Jackson G:
Computer Simulation of the Macroscopic Pitch in Systems of Chiral Spherocylinders

Session 5
Physiology Lecture Theatre
Chaired by Prof Seth Fraden

- 14:00** Smit B:
 Simulating the Adsorption and Diffusion of Hydrocarbons in Zeolites
- 14:45** Seddon KR:
 Ionic Liquids: The Bear Necessities

Session 6a
Molecular Simulation
Physiology Lecture Theatre
Chaired by Prof George Jackson

- 16:00** MacDowell LG, Virnau P, Muller M & Binder K:
 Computer Simulation Study of a First Order Phase Transition: The Condensation of a Droplet
- 16:15** Scannu L, Hall C & Gubbins K:
 Phase Separation and Micellization in Supercritical CO₂/Surfactant Systems using Lattice Monte Carlo Simulations
- 16:30** Miller M & Frenkel D:
 Competition of Percolation and Phase Separation in a Fluid of Adhesive Hard Spheres
- 16:45** Predota M, Chialvo AA & Cummings PT:
 Structural Characterization of Aqueous Electrolytes in Contact with Rutile Surfaces by Molecular Dynamics
- 17:00** Pikunic J, Pellenq R & Gubbins K:
 Molecular Simulation of Adsorption and Diffusion of Simple Fluids Confined in Realistic Models of Nanoporous Carbons
- 17:15** Vrabec J & Hasse H:
 Grand Equilibrium: Vapour-Liquid Equilibria by a New Simulation Method
- 17:30** Giupponi G & Buzza M:
 A Monte Carlo Simulation Scheme for Non-ideal Dendrimers Satisfying Detailed Balance
- 17:45** Ungerer P, Wender A, Demoulin G & Bourasseau E:
 Molecular Simulation of H₂S-containing Mixtures

Session 6b
Electrolytes
Physiology Lecture Theatre
Chaired by Dr Amparo Galindo

- 16:00** Romero-Enrique JM, Rull LF & Panagiotopoulos AZ:
 The Role of Associated Pairs in the Gas-Liquid Transition of 1:1 Electrolyte Primitive Models
- 16:15** Vega C, Abascal JLF & Bresme F:
 The Phase Diagram of a Model of Charged Hard Spheres: The Restricted Primitive Model
- 16:30** von Ferber C & Löwen H:
 Polyelectrolyte-Surfactant Complexes
- 16:45** Clarke M & Bishnoi PR:
 Development of a New Equation of State for Mixed Salt and Mixed Solvent Systems and Application to VLE and SVLE Calculations
- 17:00** Briscoe WH, Horn RG & Attard P:
 Counterion-only Electrical Double Layer: A Constrained Total Entropy Approach
- 17:15** Jork C, Seiler M & Arlt W:
 Ionic Liquids - A New Class of Selective Entrainers for Extractive Distillation
- 17:30** Husson P, Jacquemin J, Majer V & Costa Gomes M:
 Solubility of Oxygen, Carbon Dioxide, Methane and Argon in Butyl Methyl Imidazolium Ionic Liquids
- 17:45** Woelki S & Kohler H:
 Modelling of Ion-specific Effects – A Local Balance Approach

Poster Session 2

- 01 Laforce C:**
Onsager Theory of Confined Hard-rod Liquid Crystal
- 02 Lagache M, Ungerer P & Boutin A:**
Prediction of Thermodynamic Derivative Properties for Mixtures by Monte Carlo Simulation
- 03 Lagache M, Ungerer P, Boutin A & Ridard J:**
Intermolecular Potential Development for Organic Mercury Compounds
- 04 Largo J & Solana JR:**
Monte Carlo Simulations of the Zero- and First- Order Perturbative Contributions to the Compressibility Factor of Square-well Fluids
- 05 Largo J & Solana JR:**
Liquid-Vapour Coexistence Curve for Square Well Fluids from a Generalized van der Waals Theory
- 06 Li L, Wang X, Zhang T, Liu Q & Zhou L:**
Microcalorimetric Study of Adsorption of C₂H₄ and O₂ on Ir/SiO₂ and IrCu/SiO₂ Catalysts
- 07 Lisal M & Nezbeda I:**
Simple Models of Single Repulsive, Attractive and Amphiphilic Chains in Normal and Associated Supercritical Solvents: Molecular Simulation Study
- 08 Macías-Salinas R, García-Sánchez F & Hernández-Galván MA:**
Modeling Liquid Mixture Viscosities via the use of an Equation of State-Based Model
- 09 Malijevská I:**
Solid-liquid Equilibrium Prediction in the Acetic Acid(1)- Cyclohexane(2) System
- 10 Marciniak A & Domanska-Zelazna U:**
Solubility of Ionic Liquid [emim][PF6] in Alcohols
- 11 Marcus Y:**
Standard Partial Molar Volumes of Ions in Solvents
- 12 Mato MM, de Ruiz Holgado MMEF, Salgado J, Arancibia EL, Legido JL & Paz Andrade MI:**
Experimental Excess Molar Enthalpies of Ethylnonafluorobutyl Ether + n-Alkane at 298.15 K
- 13 Mavlonov S, Rabimov S & Rabimov J:**
Relation between Entropy and Segregation Coefficient for System Al(or Pb)-Impurity
- 14 Mavlonov S, Makhmudov B, Rabimov S & Rabimov J:**
Research of Morphological Feature of Monocrystals Brought up in Conditions of the High Gravitation
- 15 Meier K & Kabelac S:**
Decay of Time-correlation Functions and Molecular Transport Mechanisms in the Lennard-Jones Model Fluid from Molecular Dynamics Simulations
- 16 Mendonça A, Dias F & Lampreia I:**
Isobaric Expansions of Aqueous Binary Mixtures of Ethylaminoethanol from 283 to 303 K
- 17 Mendiña C, MacDowell LG, Vega C & de Miguel E:**
Virial Coefficients and Critical Properties of Quadrupolar Lennard-Jones Diatomics
- 18 Morishige K & Tateishi N:**
Adsorption Hysteresis in Ink-bottle Pore
- 19 Mulia K & Yesavage VF:**
Modification of the Supercritical Temperature-dependent Attractive Parameter of a Simplified Perturbed Hard Sphere Equation of State
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The P-p-T Dependence of Methanol + Benzol and Methanol + Ethylbenzol Solutions
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11:15 **Wolf BA:**
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 Electrostatic Interactions in Computer Simulations of a System with One-dimensional Periodic Boundary Conditions

11:45 **Kolafa J:**
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12:00 **Yakovlev D, Boek E, Maitland G & Smirnova N:**
 MD Study of Viscoelastic Surfactant Bilayer Membranes

12:15 **Petravic J & Delhommele J:**
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11:15 **Bleha T & Cifra P:**
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11:30 **Wu J:**
 Unified Density Functional Theory of Complex Fluids

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12:00 **Sear R:**
 Statistical Mechanics of the Complex Mixture Inside *E. coli*

Thermodynamics 2003

Abstracts

The 2003 Lennard-Jones Lecture

Mixing Colloids and Polymers:
from coarse-graining to accurate phase diagrams

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Department of Chemistry, University of Cambridge

Abstract

Colloidal dispersions and polymer solutions are important “soft” materials which have been thoroughly investigated for many decades, not least because of their numerous applications in everyday life. Mixing colloids and polymers leads to rich rheological and phase behaviour, but challenges a Statistical Mechanics description, because of the large gap between the size of the colloidal particles (10^2 – 10^3 nm) and that of polymer segments (<1 nm). A coarse-graining procedure for the latter will be described, whereby non-ideal polymer coils are modelled as “ultra-soft” particles interacting via an *effective* pair potential between their centres of mass (CM). The latter is obtained by tracing out the monomer degrees of freedom for fixed CM configurations in Monte Carlo (MC) simulations of dilute or semi-dilute polymer solutions. The effective pair potentials are extracted from the CM pair distribution functions by an accurate inversion procedure. In good solvent, they turn out to be repulsive and very soft (of the order of a few $k_B T$ for fully overlapping polymers); they depend only moderately on polymer concentration. The effective (entropic) interaction between polymer coils and hard sphere colloids are determined in a similar fashion.

These effective interactions are used to determine a variety of thermodynamic and interfacial properties of polymer solutions, ranging from the osmotic equation of state to the surface tension. These properties in turn determine the depletion-induced attraction between colloidal particles. The calculated depletion potential due to the interacting polymers differs markedly from predictions based on ideal polymer models. This potential drives a demixing transition between dilute and concentrated colloid suspensions, and the resulting phase diagram is in quantitative agreement with recent experimental data.

The coarse-graining procedure can be generalized to polymers in poor solvent, and instructive parallels can be drawn between demixing of polymer solutions below the θ -point, and the “catastrophic” nature of the effective pair potential between polymer CM’s.

Applications of a Simplified Vapour-Liquid Equilibrium Model for CO₂ Absorption into MEA Solutions

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A simplified vapour-liquid equilibrium (VLE) model was developed to estimate the CO₂ partial pressure and the liquid bulk concentrations of all chemical species present in aqueous monoethanolamine (MEA) solution. The input data of the model were the initial concentration of MEA, the initial CO₂ loading, the equilibrium constants of the reactions, and the solubility of CO₂ into MEA solution. The VLE data predicted with the model for the CO₂-MEA system were found to be in accord with published VLE data of Austgen and Rochelle [1]. Two practical applications of the model have been given for the calculation of the bulk concentrations for all chemical species. First, the VLE model was integrated with an Absorption-Rate/Kinetic model and used for evaluation of the kinetics [2]. Second, the VLE model was integrated with a process-simulation program for CO₂ absorption into MEA solution in a packed column. Accurate kinetics data and accurate behavior of CO₂ absorption into MEA solution were obtained from these integrations.

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[1] Austgen and Rochelle, *Ind. Eng. Chem. Res.* 1991, 30, 543-555.

[2] Aboudheir et al., Paper number: 10224, 6th International Conference on Gas-Liquid and Gas-Liquid-Solid Reactor Engineering, Vancouver, BC, Canada, August 17-20, 2003.

Equation of State for C₆₀ Fullerene Aqueous Solution

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For biomedical testing water-soluble forms of fullerenes are undoubtedly of great interest. Hence, more detailed experimental and theoretical studies of the structure and thermodynamic properties of the C₆₀ fullerene aqueous solutions (C₆₀FAS) are important.

In the present work the PVT data of the C₆₀FAS were measured depending on the concentration of C₆₀ molecules (0.1 and 1.4 mg/ml) using the metallic bellows method with differential inductive sensor of linear shifts in the temperature range of 293 to 318 K and pressure range of 0.1 to 100 MPa. The sound speed (v_s) in the C₆₀FAS was determined by the direct pulse method of fixed distance. Note that on the liquid-vapor equilibrium line the density (ρ) of the C₆₀FAS was measured using the pycnometer method. As a result, we have found the numerical values for the isothermal modulus of elasticity (K_T), isobaric expansion (α_p), isothermal deviation of entropy factor ($T\Delta S$), enthalpy (ΔH), internal energy (ΔU) and isobaric-isothermal Gibbs potential (ΔG). Finally, the equation of state for the C₆₀FAS was obtained for the first time. Its parameters were analyzed in detail depending on the temperature and external pressure.

A molecular-based equation of state for methanol

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Following the rules set up by molecular theories of fluids, a perturbed form of an equation of state (EOS) in terms of the Helmholtz free energy for methanol has been developed. The reference term corresponds to short-range methanol and is approximated by the properties of a three-site extended primitive model of methanol (wherein repulsions are represented by hard body interactions and hydrogen bonds are mimicked by square-well attractions) developed and examined by Vlcek and Nezbeda (2003, this conference). The perturbation term of the equation is given by contributions of the dispersion forces and the dipole-dipole interaction. The parameters of the EOS have been determined in order to obtain the best representation of the vapour pressure and coexistence liquid densities over the vapour-liquid coexistence region of real methanol, while no attempt has been made to fit accurately the near-critical region. Despite the number of approximations employed, the accuracy of the equation of state has been found comparable to (or better than) that of the currently used semiempirical equations for methanol. As a result of its sound molecular footing, the equation seems to remain reliable also at conditions outside the coexistence region as well as for related thermodynamic properties. The potentialities and limitations of the present EOS theory will be discussed.

The support by the Grant Agency of the Academy of Sciences of the Czech Republic (Grant No. A4072301) is acknowledged.

Thermodynamic Properties of a tube bundle heat exchanger

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The heat exchangers are the general components both in the refrigeration machines and in the heating plants. The thermodynamic characteristics of the heat exchanger play an important role for the efficiency of the heat exchange between the two substances, which flows inside and outside the heat exchanger.

In this presentation we are going to illustrate the experimental results of investigations at a tube bundle heat exchanger with a capacity of 15 kW with different working fluids.

The heat exchanger contains 70 tubes with inner and outer diameter of 10 mm and 12 mm respectively and the longitude of 490 mm.

The arrangement is confined in a tube with the inner diameter of 150 mm and the outer one of 156 mm. It was used 6 flow directions sheets and 8 locations for the temperature sensors. The obtained results were taken into account as a bases for using the heat exchanger as a generator for the absorption refrigeration machine.

The investigations were initially carried out with water. The heat transfer coefficient was estimated for different flow regimes, i.e. the set of velocity and temperature combinations.

The next step is to determine the heat transfer coefficient under using another solutions as a working liquid for the absorption refrigeration machine under operating conditions. Our main objective is the optimisation of whole system to rise up its power output.

Thermodynamics of the temperature-induced destruction of phages

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It is known that the bacterial viruses (bacteriophages) represent very well-ordered nucleoproteic particles containing a protein shell (capsid) and phages genetic material-nucleic acid (DNA). This icosahedral geometry head has a tail, composed also from proteins, which has the function of injecting genetic material of viruses into the host cell. The problem of packing the genetic material in icosahedral phage capsids, closely associated with static physics of macromolecules. The DNA Creeping out of the phage head can be considered as a relatively simple physical process, conducted by the difference in medium conditions inside and outside the phage and not by some highly specific "device" and not accompanied by thermal effects associated with destruction of the capsid or other structure. Considering the process of DNA reptation of the phage particle, we assume that the whole phage that is in suspension which is "one phase", and the destructed phage is "the other phase". We obtained: the phage destruction under the temperature effect (a temperature range of 50–70 °C) is a similar phase transition of the 2nd type. The partial thermal capacity increment at DNA creeping out of the temperature-induced Un phage (a new phage, morphologically similar to T-even phage) head was calculated and was equal 1.3J/g.k. We drew the dependence of the Un phage thermal capacity on the temperature. We believe that the present investigation will allow to obtain a number of a new basic and principle (for physical and chemical biology) mechanisms associated with thermal, structural and functional properties of the phages.

Thermophysical Properties of Lactam Containing Mixed Solvents at 298.15 K

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Lactams such as 2-pyrrolidone (PYR) and N-methylpyrrolidone (NMP) are widely used in the chemical industry. In this work we report density, dynamic viscosity, speed of sound, refractive index and constant pressure heat capacity in the full composition range for the ternary system PYR + NMP + Water (W) at 298.15 K together with their constituent binary mixtures. From the experimental properties excess and mixing properties were calculated and correlated with composition.

Strong interactions by hydrogen bonding cause the high non-ideality of these systems although shape factors produced by the cyclic amides are important too, Figure 1.

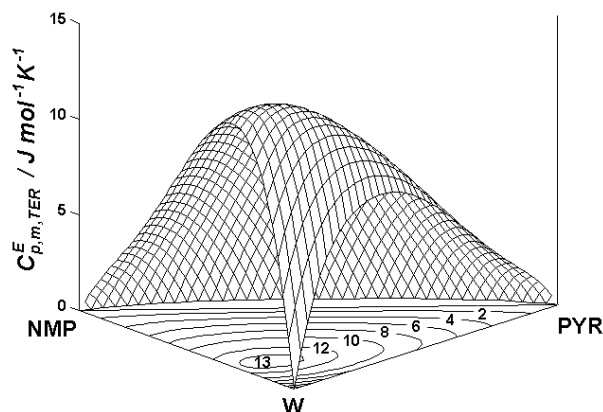


Figure 1. Excess molar constant pressure heat capacity, $C_{p,m,TER}^E$, for the ternary system PYR + NMP + W at 298.15 K.

[1] B. García, R.Alcalde, S. Aparicio, J.M. Leal. *Phys. Chem. Chem. Phys.*, 2002, **4**, 1170.

Intermittent permeation of cylindrical nanopores by water

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This presentation describes Molecular Dynamics simulations of water molecules in two reservoirs connected by a nanometre-sized cylindrical channel. The water molecules are found to enter and leave the channel spontaneously in a collective fashion [1]. For critical values of the channel radius, length and dielectric permittivity [2], channel filling is intermittent on a timescale of about 1ns. The free energy profile for the channel filling process is obtained using a biased sampling technique and the likely mechanism for the process is discussed.

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1 Allen, R, Melchionna, S, Hansen, J.-P., J. Phys. Cond. Matt. 2003, 15, S297

VLE for the ternary system di-butyl ether + cyclohexane+ heptane and its corresponding binary systems at 313.15 K

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Experimental isothermal P-x data at 313.15 K for the binary systems (di-butyl ether (DBE) + cyclohexane), (di-butyl ether (DBE) + n-heptane)] and the ternary system (di-butyl ether (DBE) + cyclohexane + n-heptane) are reported. Data for the system (cyclohexane + n-heptane) at 313.15 K have been published previously [1]. A static method using an isothermal total pressure cell (Van Ness' technique) has been used, having shown previously the high accuracy of the measured VLE parameters.

The experimental results of the corresponding binaries, will be presented and discussed using for data reduction by Barker's method using the equations of Margules, Wilson, NRTL and UNIQUAC.

The results of the ternary systems are presenting and discussing using for data reduction the equations of Wohl, Wilson NRTL and UNIQUAC. A prediction of the data for the ternary system has been carried out using Wilson, NRTL and UNIQUAC models.

[1] J.J. Segovia, M.C. Martín, C.R. Chamorro, M.A. Villamañán. J. Chem.Eng. Data 43,1021-1026 (1998)

Excess enthalpies of binary and ternary mixtures containing tert-amyl methyl ether(TAME), 1-propanol and hexane.

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A modified quasi-isothermal flow calorimeter from Hart-Scientific (model 4250) has been used for measuring the excess enthalpies of the ternary system TAME + 1-propanol + hexane and the corresponding binary systems at 313.15 K. Also the binary system TAME + 1-propanol has been measured at 298.15 K.

Data have been fitted using the equations of Redlich-Kister, NRTL and UNIQUAC. The values of the standard deviation indicate the agreement between the experimental results and the fitted ones. Positive experimental excess enthalpies were obtained for all mole fractions of the ternary mixture investigated, being larger than for the binary mixtures.

Vapor-liquid equilibrium data and excess gibbs energy for the binary and the ternary systems at 313.15 K have been measured and published previously [1,2]. All these data have been used for calculating the excess entropy of the same systems at 313.15 K.

[1] C Alonso, EA Montero, CR Chamorro, MC Martín, MA Villamañán. *Fluid Phase Equilib.* 182, 241-255 (2001)

[2] C Alonso, EA Montero, CR Chamorro, MC Martín, MA Villamañán. *Special Issue of Fluid Phase Equilib. for ECTP 2002* (in press).

Thermodynamic Studies of Methane and Carbon Dioxide Hydrates Using the Clapeyron Equation

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Over a century ago de Forcrand [1] studied gas hydrates using the Clapeyron equation. He used pressure-temperature data along the Ice-Hydrate-Vapor (IHV) and Liquid-Hydrate-Vapor (LHV) coexistence lines to determine the enthalpy changes of the two corresponding reactions, from which he determined the hydration number. Many others have followed in de Forcrand's footsteps as new hydrates have been discovered or as new experimental data has appeared. However, there is a widespread perception that the "de Forcrand" method produces only approximate results, due to lack of precise data, lack of rigor of the Clapeyron equation itself, or due to the approximations that must be used to analyze the data. Also, it is often stated that the method can only determine the hydration number at the quadruple point where the IHV and LHV curves intersect. Here it is argued that all of these perceptions are false; the Clapeyron equation is rigorous and there is a method of analysis that does not require any arbitrary assumptions. Furthermore, there is now accurate p-T data and physical property data for many gas hydrates that allows point-to-point determination of the dissociation enthalpies and hydration number. The new method of analysis is demonstrated for methane hydrate and carbon dioxide hydrate.

[1]. de Forcrand, R. *Comptes Rendus* **1902**,135, 959-61.

Characterization of the n-Hexane +
Hexan-1-ol + Methylbenzoate
Ternary Solvent at 298.15 K
According to the Kirkwood – Buff
Fluctuation Theory

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The microscopic structure of the ternary solvent n-hexane + hexan-1-ol + methylbenzoate (MB) and its constituent binary systems is analyzed according to the Kirkwood – Buff Theory using the measured excess molar volume and isothermal compressibility together with the activity coefficients calculated with the Dortmund UNIFAC model.

From the analysis of these binary and ternary systems we can conclude that the very different shapes and sizes of the molecules studied conduce to solvation spheres of like molecules. The size of these spheres decreases when a third component is added to the binary mixtures. Hexan-1-ol is only able of forming hydrogen bonds in the diluted regions when mixed with n-hexane whereas in the mixtures with MB or in the ternary mixtures these interactions are hardly weakened because the shapes of the molecules difficult the contact between alcohol molecules.

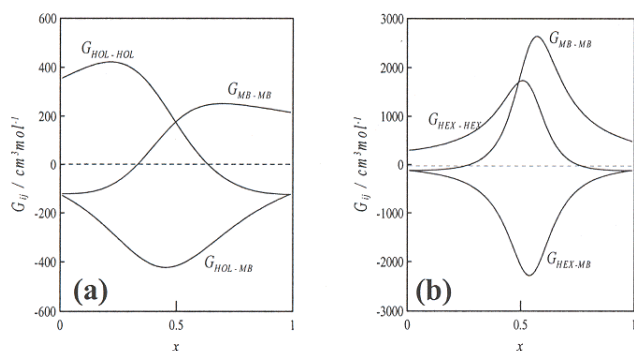


Figure 1. Kirkwood – Buff integrals, G_{ij} , for the (a) x hexan-1-ol + $(1-x)$ MB and (b) x n-hexane + $(1-x)$ MB binary mixtures at 298.15 K.

Phase equilibrium of pure fluids with
the SAFT-VR equation of state based
on the Sutherland potential

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Theoretical and experimental studies have shown that for large molecules, attractive forces are more short-ranged than those for small molecules. This has motivated the development of a molecular equation of state where the attractive part of intermolecular interactions could vary in range. The SAFT-VR approach [1] provides an analytic equation of state for fully flexible chains formed by tangent spherical segments, where the range of the attractive segment-segment interactions is controlled by a variable parameter λ . In this paper, we have chosen the Sutherland potential to describe the segment-segment interactions, where the repulsive part is a hard repulsion and the attractive part is given by an inverse power function of the reduced inter-segment distance. The exponent in the function is given by the parameter λ ; as λ rises, the range of interactions decreases. A constrained parameter estimation strategy is developed for determining the parameters for the SAFT-VR EOS solely from experimental phase-equilibrium data. The issue of parameter identifiability is addressed through sensitivity coefficients. The methodology is used to investigate the suitability of the Sutherland pair potential as well as the role of its range parameter in modelling the phase equilibrium behaviour of fluids such as n-alkanes, n-perfluoroalkanes and carbon dioxide.

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Solvent Mediated Interactions and Solvation Close to Fluid-Fluid Phase Separation: a Density Functional Treatment

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We apply a general density functional approach for calculating the force between two big particles immersed in a solvent of smaller ones to calculate the solvent mediated (SM) potential between two big Gaussian core particles in a binary mixture of smaller Gaussian particles, a simple model of polymers in solution. Within a mean field free energy functional, which generates the random phase approximation (RPA) for the bulk pair direct correlation functions, the binary solvent exhibits fluid-fluid phase separation and we show that the theory for calculating the SM potential captures effects of thick adsorbed films surrounding the big solute particles. For a single big particle there is a first order thin-thick adsorbed film transition and in the thick film regime, i.e. for solvent state points lying close to the binodal, on the side where the solvent is poor in the species which is favoured by the big particles, we find extremely attractive, long ranged SM potentials between the big particles whose range is determined by the film thickness. In the region of the solvent critical point we also find extremely attractive SM potentials whose range is now set by the bulk correlation length in the binary solvent and which increases and eventually diverges for state points approaching the critical point.

Densities and speeds of sound of the ternary mixtures cyclohexane + 1,3-dioxolane + 2-butanol and n-hexane + 1,3-dioxolane + 2-butanol

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We present here experimental measurements of densities and speeds of sound of the ternary mixtures cyclohexane + 1,3-dioxolane + 2-butanol and n-hexane + 1,3-dioxolane + 2-butanol at the temperatures of 298.15 and 313.15 K. Isentropic compressibilities and excess isentropic compressibilities have been calculated from experimental data and excess isentropic compressibilities were correlated with the Cibulka equation [1].

Results show positive values of excess isentropic compressibilities in almost the whole composition range for the ternary mixture containing cyclohexane, while excess isentropic compressibilities for the ternary system with n-hexane are negatives.

We also have compared experimental isentropic compressibilities with values calculated from the Free Length theory [2,3] and Collision Factor theory [4,5].

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Simultaneous measurements of density and viscosity of {methane + *n*-decane} mixtures from 303 to 393 K and up to 75 MPa using a vibrating-wire instrument.

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We present an experimental study of the density and viscosity of {methane + *n*-decane} mixtures from 303 to 393 K and up to 75 MPa using a vibrating-wire instrument. This system is representative of gas-condensate fluids (containing light and heavy hydrocarbons).

The technique used is a vibrating-wire sensor, which allows simultaneous measurements of density and viscosity, over wide ranges of temperature and pressure. The sensor is composed by a thin taut wire, from which a solid weight is suspended. An electromagnetic coupling is used to set the wire in motion and to detect the amplitude of the oscillations. The presence of the fluid surrounding the sensor changes the behavior of the oscillations. The application of a rigorous theoretical model to these variations allows the determination of the density and viscosity.

The present results were compared to literature data when possible. The precisions obtained are below $\pm 0.1\%$ in density and $\pm 1\%$ in viscosity. The accuracies are evaluated at $\pm 0.3\%$ and $\pm 3\%$, respectively. We have also tested viscosity prediction schemes whose results are discussed.

Thermodynamic properties of molecular complexes of C_{60} , C_{70} and their simple derivatives with the aromatic solvents

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Thermodynamic data on the interaction of C_{60} , C_{70} and also piperazine monoadduct of C_{60} fullerene $C_{60}N_2(C_2H_4)_2$ with the aromatic solvents in the liquid and in the solid phases are on demand. Special attention is necessary to investigation of the solute – solvent interaction for systems contained functionalized fullerenes whereas such data are very scarce.

The systems studied included mono-, di- and tri-methyl and mono-, di- and tri- halobenzenes as solvents. The regularities in thermodynamic stability of these molecular complexes of C_{60} , C_{70} and $C_{60}N_2C_4H_8$ with aromatic compounds on passing from solvent to solvent along a series of methyl- and halogen-substituted benzenes were discussed.

Solid solvates identified were characterized by their compositions, temperatures and enthalpies of incongruent melting transitions by means of DSC.

The recalculated “hypothetical” values of solubility (in respect to nonsolvated phase) where the changes tend to reflect the efficiency of molecular interaction in liquid solutions increase with increasing of numbers of methyl- and halogen- groups in the solvent molecules and also in the CH_3 , Cl, Br for the series of solvents with the same type of substitution. The analogous tendency was revealed on the thermodynamic stability of solid solvates for the solvent series above in terms of standard Gibbs free energy of the reaction formation. This work was supported by RFBR grant 03-03-32186.

Deviations of the packing factor respect to the ideal packing and the excess acoustical properties

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The earlier developed approach [1, 2] in the description of solutions and melts by the packing coefficient (γ) has been improved. In the earlier offered method only appearance of the excess molar volume was taken into consideration deducing the deviations of packing factor respect to the ideal packing. In the improved techniques the variation of the own molecular volume due to chemical process (association, dissociation) is also taken into consideration. The theoretical basis of the ideal packing on a molecular level has been obtained. The structural condition has been established, resulting in the absence of the excess isothermal compressibility coefficient (β_T) and isobaric expansibility coefficient in the case of nonideal solutions. The thermodynamic ratio established is necessary to add to the structural condition in order to the excess values of some acoustical parameters such as β_s , u^2 , $(B/A)_T$ became equal to zero for some nonideal solutions. The influence of shape, size and packing of particles on the value of the excess acoustical properties of solutions has been established.

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Effective dielectric constant for a polar solvent near an interface

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The conformation of proteins in a polar solvent (typically water) is strongly influenced by the dielectric screening effects of the solvent. These effects are well understood for charges immersed in a homogeneous liquid, but little is known on the electrostatic interactions between charges close to the interface formed between the protein (medium of low dielectric constant) and the water.

Various distance-dependent effective dielectric 'constants' are commonly used in this context [1,2]. Modeling the solvent as a confined dipolar fluid, we examine whether a local dielectric permittivity can be rigorously defined from a statistical mechanical calculation.

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The calculation of the
Thermodynamic efficiency of the soil
microbial reactions: application in
ecological studies

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Changes in the land use causes enhancement of the CO₂ released to the atmosphere and loss of soil fertility. It is important the search of bioindicators of soil microbiological quality to control those processes but that area of reserch is strongly limited by the methodologies employed due to the soil complexity.

Curiously, thermodynamics and microcalorimetry can provide the thermodynamic efficiency (η_H) of the soil microbial reactions, yielding an indirect calculation of the efficiency of the carbon assimilation by soil microbes.

In this work, an energy balance based on the irreversible thermodynamics is developed to compute the η_H of the microbial growth reaction when glucose is added to soil as carbon source. The study was made on six soil samples and results were compared to see if η_H is affected by several environmental factors. Results showed that η_H appears to be affected by the deforestation of the primary forests and the introduction of different arable lands.

Aknowlegments: This work has been supported by Xunta de Galicia (PGIDIT02PXIB2060)

The relationship of the specific
substrate degradation rate (Ac) and
the enthalpies of the microbial
reactions in soils.

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In this work it is proposed a mathematic development to compute the specific substrate degradation rate (Ac) of the soil microbial reactions by microcalorimetry. The equation obtained relates Ac to the enthalpies of the reactions taking place in the soil samples when an external carbon source is added, as follows:

$$Ac = \frac{\Delta_r H_x}{\Delta_r H_s} \mu \quad (1)$$

where $\Delta_r H_x$ represents the enthalpy of the microbial growth reaction, $\Delta_r H_s$ is the enthalpy of the substrate degradation reaction and μ the apparent microbial growth rate constant.

Ac values were calculated for six soil samples under different environmental conditions. The correlations found and the results of the Anova showed that Ac can be used as an emprial measure of stress in soil being sensitive to changing environmental conditions and strongly affected by the initial microflora and percent of nitrogen of the soil.

Aknowlegments: This work has been supported by Xunta de Galicia (PGIDIT02PXIB20601PR).

Second law versus variation principles

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The field-dependent equilibrium thermodynamics is derived with two methods: either by using the potential formalism or by the statistical method. Therefore, Pontrjagin's extremum principle of control theory is applied to an extended ensemble average. This approach allows to derive the grand partition function of thermodynamics as a result of a control problem with the Hamilton energy. Furthermore, thereby the maximum entropy principle follows and the second law in a modified form. This derivation can predict second law violations if cycles with irreversibilities in varying potential fields are taken into consideration. This conclusion is supported indirectly by experimental data from literature.

As an example the upper maximum gain efficiency of a cycle using the polymer solution polystyrene-cyclohexane as dielectrics is estimated to less than 1 promille per cycle.

Reference

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Computer modeling of liquid ionic systems using diffraction data

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Recently an iterational algorithm BELION was proposed [1-3] which allows to construct the models of ionic or partly ionic systems using the diffraction pair correlation functions (PCF's). Expressing interparticle potentials for pairs i-j as a sum of Coulomb and non-Coulomb terms and specifying the ion charges and initial non-Coulomb terms for each ion pair, one can simulate the molecular dynamics model of ionic liquid. Non-Coulomb potentials are repeatedly re-calculated using the difference between diffraction PCF's and model ones analogously to Schommers algorithm [4].

Using BELION algorithm and diffraction data we have constructed computer models of liquid NaCl, RbBr, AgBr, CuCl, CuBr, CuI containing 498 or 1968 ions. The ionic charges were varied. We obtain in all cases the good agreement between diffraction and model PCF's. Agreement with experimental data for atomization energy is obtained at ionic charges ± 1.00 for NaCl and RbBr, ± 1.15 for AgBr, ± 1.20 for CuCl, ± 1.48 for CuBr and ± 1.37 for CuI. Non-Coulomb terms are calculated. They have the deep minima for Cu-Cu pairs at the distances 1.90-2.35 Å.

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Experimental results and comparison
between PFP theory and ERAS model
for excess molar volume of
acetonitrile + alcohol mixtures

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Experimental data^[1] of excess molar volumes of $\{(1-x)\text{CH}_3(\text{CH}_2)_{n-1}\text{OH} + x\text{CH}_3\text{CN}\}$ for $n = 1, 2, 3$ or 4 at $288.15, 293.15, 298.15$ and 303.15 K and atmospheric pressure have been determined experimentally by using a vibrating-tube densimeter and used to test the applicability of the PFP Theory^[2-4]. According to model interactional contribution is the most important one to explain the V^E behavior. Good agreement is only achieved for the mixtures containing methanol or 1-butanol. For the mixtures containing ethanol and 1-propanol, which show a S-shaped V^E behavior, the correlation fails. Comparison with the ERAS-Model^[1] shows that both models are equivalent for acetonitrile + methanol and acetonitrile + 1-butanol mixtures, while the S-shaped V^E behavior of the remaining mixtures is reproduced only by the ERAS-Model.

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Photoinduced phase transition in
fullerene solutions and suspensions of
carbon nanoclusters.

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The paper presents the solution of the problem of creation of the fast-response optical limiters of laser radiation, using the photoinduced phase transitions in nonlinear-optical media—in fullerene solutions and in suspensions of the carbon nanostructures. It was shown that in the fullerene-containing solutions the main mechanisms are: nonlinear absorption from the excited levels of fullerene, photoinduced scattering on the small-scale inhomogeneities of refraction index during pulse propagation and the large-scale (after pulse end) density fluctuations, produced by phase transition liquid–vapor during energy dissipation from the triplet states. In the suspensions of the carbon nanoparticles the limiting mechanism is based mainly on the radiation scattering effects. Were studied the structural, spectral and thermodynamical properties of suspensions of amorphous carbon, of multilayer nanotubes and of atralen (the new version of carbon nanoclusters). The experiments and the theoretical analysis revealed the presence of two types of phase transformations in the studied suspensions, resulting in formation of light scattering centers, responsible for the optical limiting effects. These are, first, the production and development of vapor envelope around particles, heated by laser radiation due to the explosive boiling of water after its overheating over the critical temperatures, and second, phase transition solid-state–gas at the high intensities of laser radiation. It was established that the threshold intensity of radiation, leading to phase transitions and optical limiting, depends upon the structure of nanoparticles and on solvent nature.

Thermophysical and optical processes
at interaction of powerful radiation
with molecular system fullerene-
oxygen-iodine.

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The paper considers thermo-physical and optical processes, taking place during optical radiation interaction with molecular system fullerene-oxygen-iodine, serving the active medium for the gas laser (FOIL) on the iodine atom transition $\lambda=1.315$ mkm [1]. The generating iodine atoms are produced by collisions with the singlet oxygen molecules ($\Delta^1\text{O}_2$), produced during interaction with photosensitized fullerenes. The vaporization of solid-state fullerene and its excitation to the triplet state are provided by the wide spectral band radiation of pulsed flash-lamp ($T_{br}=10000\div 15000^\circ\text{K}$) action onto the surface layer of fullerene, deposited onto the cell walls by special technology. The variation of this layer temperature and of the saturated vapor pressure dependencies upon T were determined with the account for the experimentally measured light absorption cross-section and fullerene thermal capacity. It was shown that for the transient case (heating by the pulsed lamp) the concentration of gaseous phase fullerene in the fundamental and excited states is somewhat less than under the stationary heating, but yet is quite sufficient for singlet oxygen formation, The latter was registered by its intense luminescence at $\lambda= 0.76$ and 1.26 mkm. Proper choice of conditions of photoinduced phase transitions and molecular interaction provided realization for the first time of a novel type of lasing in the system fullerene-oxygen-iodine.

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Temperature dependence of the
liquid-liquid equilibrium in ternary
systems N,N-dimethylformamide +
methanol + methylcyclohexane (+ 2-
methylpentane)

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The present contribution addresses the study and the subsequent thermodynamic description of the temperature dependence of the liquid-liquid equilibrium in ternary systems N,N-dimethylformamide (abbr. N,N-DMF) + methanol + methylcyclo-hexane and N,N-DMF + methanol + 2-methylpentane. The equilibrium data were obtained at several temperatures by two experimental methods: the direct analytical method and the cloud-point method. Shapes of critical curves were obtained by the cloud-point method for both systems. The modified Wilson equation was employed to correlate the acquired results.

The results presented in this paper are part of a broader task concerning the study of thermodynamic properties in systems containing N,N-DMF, methanol and alkanes (C6). Their practical and theoretical relevance will be discussed in the contribution.

This work was supported by the Ministry of Education of the Czech Republic under Grant No. CB MSM 2234 00008.

Free energy and confinement force of nondilute polymer solutions in a slit

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Confinement of polymers into pores is of vital interest in chromatography, membrane separation, colloid stabilization, etc. A solution of flexible macromolecules in equilibrium with slit-like pores was examined by the lattice Monte Carlo simulations [1-3]. The real chain features were considered, such as excluded volume (solvent quality), solute concentration and slit wall attraction. It was found that partitioning of nonideal macromolecules into a slit with repulsive walls considerably deviates from the theoretical relations for ideal chains. The free energy of confinement ΔA and the confinement force f were computed as a function of slit width D in theta (of vanishing second osmotic virial coefficient) and athermal solvents. Force f exerted by polymer chains on the slit walls (of a repulsive nature) decreases with an increasing concentration. The concentration dependence of force f differs significantly among athermal and theta solutions. Related functions of polymer-induced depletion attraction should correspondingly be dissimilar. In case of attractive slit walls, the computed confinement force is given by a balance between steric repulsion and attractive bridging interaction due to polymer chains adsorbed onto the two walls. At the compensation point (exploited by critical chromatography) the simulations yield the zero confinement force and a flat concentration profile in a slit.

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Lattice Gas Theory for Adsorption of Surfactants from Aqueous Solution

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The temperature dependence of adsorption of surfactants from aqueous solution is unusual and not fully understood. As the temperature increases, the *critical surface aggregation concentration (csac)* decreases and the amount of adsorbed surfactant at concentrations above the csac increases. This is in sharp contrast to the adsorption behaviour that is usually observed for non-surfactants, which shows a decrease in adsorption with increase in temperature. This unusual temperature behaviour has not been reproduced with other theories or simulations of these systems.

We present a lattice gas mean-field theory for A(surfactant)/B(water) mixtures that describes micellization and surfactant adsorption, and includes hydrogen bonding. In our model, each particle (A and B) carries a scalar orientation variable. A hydrogen-bond is formed between two particles if they have the same orientation. Extending the work of Vause and Walker [1] to open systems, we map the current model to an identical model without directional interactions, but with a temperature dependent A/B attraction. The theory allows for the formation of micelles, and is used to calculate the bulk phase diagram and the cmc-line, and to investigate the adsorption behaviour of the surfactant solution in a small slit-like pore. The results are in qualitative agreement with experimental observations; the cmc and csac decrease, and adsorption increases, with increasing temperature up to temperatures somewhat above the LCST.

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Solution thermodynamics of [C₄-, or C₁₀mim][Cl] and an alcohol

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This work explores the solubility and the thermodynamic description by means of Wilson, UNIQUAC ASM and NRTL 1 equations of [alkylmim][Cl] in alcohols. We have focused on the imidazolium-based salts, such as [C₄mim][Cl] and [C₁₀mim][Cl], but also have results for other 1-alkyl's substituents. The DSC was used to determine the melting point, the enthalpy of fusion, the enthalpy of solid-solid phase transition and the temperature of the glass phase transition of our ILs. The alcohol solvents (C₂-C₁₂) investigated in this work are ethanol, 1-butanol, 1-hexanol, 1-octanol, 1-decanol, 1-dodecanol, 2-butanol, *tert*-butanol.

Our investigation permits to find eutectic mixtures with [alkylmim][Cl] and alcohols (1-decanol, 1-dodecanol, *tert*-butanol). The results of studies demonstrate positive and/or negative deviations from ideal solubility. The solubility of [alkylmim][Cl] in alcohols can be generalized in some mainly significant conclusions. The most important is to consider the effect of strong hydrogen bonds forming between the alcohol and solute during the packing in the solution process. It should be notice that the solid-liquid equilibria in systems [alkylmim][Cl] and alcohols depend on the ability of the solvent to be packed into the crystal structure of [alkylmim][Cl]. It confirm the best solubility of investigated ILs in ethanol, or 1-butanol, respectively, and it is the evidence of the highest interaction with the solvent.

Colloid-polymer mixtures in the protein limit

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We computed the phase-separation behavior and effective interactions of colloid-polymer mixtures in the "protein limit", where the polymer radius of gyration is much larger than the colloid radius. For ideal polymers, the critical colloidal packing fraction tends to zero, whereas for interacting polymers in a good solvent the behavior is governed by a universal binodal, implying a constant critical colloid packing fraction. In both systems the depletion interaction is not well described by effective pair potentials but requires the incorporation of many-body contributions.

Reference

Phys. Rev. Lett. 90, 068304 (2003)

Equilibrium behavior of hard non-spherical body fluids

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With the recent progress in description of processes in biochemistry, thermodynamics of aqueous ionic solutions and with a broad use of high pressure technologies an interest increases in improving our knowledge of the hard body equation of state (EOS), distribution functions and expression for the chemical potential. In this paper we study the second, third and fourth virial coefficients corresponding to the EOS for the hard chain [fuzed hard sphere (FHS)] model and to that for hard prolate spherocylinder (HPS) as functions of the number of segments (m) or the corresponding length-to-breadth ratio (γ). For FHS we determined the 2nd, 3rd and 4th virial coefficients for higher m (up to 10) and expressed these virials as functions of m . It is shown that the linear dependence of the FHS virial coefficients (found for low m) is deteriorating for higher m . A simple modification of the FHS model is proposed which improves prediction of the 2nd and 3rd virial coefficients; the 4th one - due to the fact that is given as a sum of three terms - is complex, similarly as in the case of HPS[1]. The variant of the EOS for FHS fluids is considered.

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New optimisation method for Lennard Jones potentials - New AUA potential for prediction of equilibrium properties of olefins

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This study proposes a new global procedure to perform optimisations of semi-empirical intermolecular potential parameters on the basis of a large reference database. To obtain transferable parameters, Ungerer [1] proposed an original method few years ago, based on the minimization of a dimensionless error criterion. In this work, we propose a new method to evaluate partial derivatives used in this procedure, in order to reduce the computing time and to obtain more consistent parameters. This method is based on the analysis of statistical fluctuations during a single simulation.

To test the efficiency of this new method, we have optimised the Lennard Jones potential parameters of the unsaturated hydrocarbon groups using the anisotropic united atoms description. The resulting parameters are consistent with those previously determined for linear and branched alkanes. Test simulations have been performed at temperatures ranging from 150 to 510 K for 11 different olefins. Equilibrium properties are well predicted, and critical properties can be evaluated with a good accuracy.

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Measurement and prediction of
saturation pressures of pristane.
Experimental and Monte Carlo
simulation results.

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This work presents the results obtained in the characterization of the 2,6,10,14 tetramethylpentadecane (pristane molecule), by establishing saturation pressures following two ways of investigation. First, an experimental study has been done in order to perform measurements of low vapour pressures (under 2300 Pa) using an original apparatus [1]. Then, Monte Carlo simulations have been performed to predict vapour pressures of pristane from 330 to 700 K. Gibbs Ensemble Monte Carlo has been used to predict vapour pressures at high temperatures, and thermodynamic integration to extend the prediction to lower temperatures. Simulations have been performed using the branch point sampling technique [2], and the Anisotropic United Atom potential optimised previously [3].

It is concluded that both types of results show good agreement.

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Counterion-only electrical double
layer: a constrained total entropy
approach

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In a counterion-only (CIO) double layer, the only ions in the liquid to be considered are the counterions that originate from the solid-liquid interface, and there isn't an ion reservoir in the bulk solution to establish a constant chemical potential for all ion species. What is the thermo-dynamic effect of the absence of the ion reservoir on the double layer interaction? This interaction has previously been treated in statistical-mechanical and density functional approaches. In these approaches, only the boundary condition of constant surface charge density is considered, and the distinction between the presence and absence of an ion reservoir manifests as different constructions of the Helmholtz free energy functional or different expressions for their effective Hamiltonian. These approaches however do not explicitly highlight the distinction between the different thermodynamic foundations upon which the CIO and the normal double layer theories are established. A constrained total entropy approach is undertaken in the current study based on an iso-thermal thermodynamic system. The double layer interaction free energy per unit area between two charged planar surfaces is obtained in a consistent manner for the boundary conditions of constant surface charge density and charge regulation. Once applied to the nonpolar medium, it reveals that the electrical double layer repulsion is weak and long-ranged. Asymptotically, the interaction decays as a power law, in contrast with that in the presence of an ion reservoir which decays exponentially at large surface separation. The applicability of the counterion-only model to describing colloidal stability in nonpolar media is discussed.

Electrostatic interactions in computer simulations of a system with one-dimensional periodic boundary conditions

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In computer simulation of particles in pores one-dimensional periodic boundary conditions are useful, and when the particles are charged one needs method for summing Coulomb interactions over simulation box replicas. Porto [1] worked out the Ewald type method. However, computational efficiency of the method is low because the reciprocal-space summation must be carried out over all charge pairs. Therefore, two other methods are presented. Modification of the term containing summation over non-zero reciprocal-space vectors [2] allows us to express the term as a sum of structure factors, containing charge positions, multiplied by coefficients depending on the reciprocal-space vector similarly as in the 3D Ewald method, however, an additional parameter must be introduced. In the modified Ewald type method one has single sum over charges. Another approach – the Lekner type method [3] is worked out for interactions characterised by any inverse power and using analytical continuation of the energy function one obtains the final expression in which the real space summation of the Coulomb interactions is transformed entirely into reciprocal space. The energy function contains double sum over charges, similarly as in the Ewald type method, but it has simple form that gives possibility to control easily and effectively the accuracy of the summation.

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Computer simulations of the phase behaviour of water in hydrophilic and hydrophobic nanopores

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Coexistence curves of water in nanopores with a smooth surface were simulated in the Gibbs ensemble. The evolution of the coexistence curves and density profiles of the coexisting phases with varying strength of the water-pore interaction was analysed.

In the hydrophobic pores the density of liquid water decreases towards the pore wall. The order parameter in the surface layer may be well described by a simple scaling law with an effective critical exponent of about 0.8, that is close to the value, obtained for the ordinary surface transition in semi-infinite Ising systems. Such behaviour of the surface layer causes an essential increase of the effective critical exponent of the coexistence curve compared to the 3D Ising value.

In the hydrophilic pores prewetting (or layering) transitions split from the main liquid-vapour transition, which takes place in a pore with a wall, which is already covered by two water layers. In such pores the density of the liquid water increases towards the pore wall. The formation of a wetting layer in the vapour phase with increasing temperature results in a “bottle-like” shape of the coexistence curve.

Multiple liquid-liquid transitions in supercooled water

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Three distinct liquid-liquid coexistence regions were observed for ST2 model water by restricted ensemble Monte Carlo simulations of the isotherms of homogenized systems [1] and by phase equilibria simulations in the Gibbs ensemble [2].

The lowest density liquid-liquid transition meets the liquid-vapor phase transition at a triple point and ends in a metastable critical point. Percolation analysis evidences, that this transition is caused by the separation of tetrahedrally coordinated water molecules with no additional neighbours in the first coordination shell. The highest density phase separation occurs when the tetrahedrally coordinated water molecules with any number of neighbours in the first coordination shell percolate. The densities of the obtained four phases of supercooled water correlate with experimentally observed densities of amorphous ice.

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The Global Phase Diagrams of the van der Waals-Dieterici and the BMCSL-Dieterici Equations of State

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A *global phase diagram* (GPD) is a mapping of classes of topologically equivalent phase diagrams to the space of material parameters. We look for all phase phenomena which are generated by a model of binary mixture of attractive hard spheres and which are described by the van der Waals-Dieterici or the BMCSL-Dieterici *equation of state* (EoS), and we calculate the GPD. The Dieterici approach multiplies the repulsive and attractive parts [1] while the traditional van der Waals approach sums them [2]. The comparison of the critical compressibility factor of these approaches indicates that Dieterici generalized formula [1] is more suitable for EoS development, especially for noble gases [3].

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Acknowledgements

Financial support by the Research Centre of Structure and Dynamics of Complex Molecular Systems and Biomolecules under the project No. LN00A032 is gratefully acknowledged.

Calculation of vapor pressure isotope effects in the rare gases and their mixtures using an integral equation theory

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Vapor pressure isotope effects (VPIE) in monatomic systems (neon to xenon, either between pure isotopes or in isotopic binary mixtures) were evaluated using an integral equation theory for a Lennard-Jones fluid with the Duh-Haymet-Handerson closure. The most relevant quantity obtained in this way is the average of the Laplacian of the potential energy of the system, $\langle \nabla^2 U \rangle$. The results correctly predict the different rare-gas VPIEs which span over several orders of magnitude.

Using a simple corresponding states principle, the method can predict VPIEs simply from the knowledge of isotopically independent Lennard-Jones parameters of each rare gas and the masses of its isotopes. The VPIEs map onto two reduced variable equations, either as a function of the reduced partition function ratio between pure isotopes, or of the reduced liquid activity coefficient at infinite dilution in isotopic binary mixtures.

Predicting a Profile of Hydrate Formation Potential in Pipes

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Hydrates are crystalline compounds of water and rather low molar mass gases that are formed at high pressure and low temperature. A predictive model to determine the incipient hydrate formation pressure based on the van der Waals-Platteeuw theory and using a generalised cubic equation of state is firstly established in this work. In addition, a mechanistic, homogeneous and one-dimensional flow model to calculate the pressure and temperature profiles of pipelines is developed. Both models are then combined to determine the incipient pressure of hydrate formation and, by comparing this value to the actual pressure along the pipe, to evaluate the hydrate formation potential in the pipe. The resulting model seems to produce sound results which should be used to prevent further hydrate development.

Study on Excess Molar Enthalpies of
MTBE + 1-propanol + hexane at
298.15 K.

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This paper reports experimental excess molar enthalpies, at 298.15 K and atmospheric pressure, of ternary mixture $\{x_1 \text{ MTBE} + x_2 \text{ 1-propanol} + x_3 \text{ hexane}\}$ and binary systems $\{x \text{ MTBE} + (1-x) \text{ hexane}\}$ and $\{x \text{ 1-propanol} + (1-x) \text{ hexane}\}$. The other binary mixture was published in previous work¹. Values of h_m^E were measured using a Calvet microcalorimeter. The excess molar enthalpy are positive for all the mixtures.

The group contribution model of UNIFAC, in the versions of Larsen and Gmehling, was used to estimate ternary excess enthalpy values. The results obtained with the Gmehling version are in better agreement with the experimental data.

The empirical expressions of Kohler, Knobloch-Schwartz, Colinet, Jacob-Fitner, Scatchard, Tsao-Smith, Mathieson-Thynne, Toop and Hillert were also applied to estimate ternary properties from binary results. The best results were obtained with Tsao-Smith equation, with the 1-propanol as asymmetric component.

Acknowledgements: This work was supported by Xunta de Galicia (XUGA PGIDT99PXI30103B)

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High pressure density measurements
for the mixture methyl
nonafluorobutyl ether + n hexane

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Hydrofluoroethers are finding many practical applications in industry, and they are being considered as potential candidates to replace other widely used halocarbons in other cases due to their friendly environmental profile. Nevertheless, thermophysical properties of these compounds are still scarce in literature.

In this work, the volumetric behaviour of the mixture methyl nonafluorobutyl ether + n-hexane has been studied by measuring its density in a pressure range from 0.1 to 25 MPa, and at temperatures varying from 283.15 to 313.15 K. The experimental device used was an Anton Paar vibrating tube densimeter equipped with a DMA 512 P high pressure cell.

Experimental data were correlated with a modified Tait equation. Excess molar volumes were computed, showing a very large deviation from ideality.

Finally, thermomechanical coefficients, i.e. isobaric thermal expansion and isothermal compressibility, and the internal pressure were calculated from these volumetric values.

A Model for the Temperature Dependence of the Heat Capacity of Pure Liquids

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Extensive data compilation have shown that the temperature dependence of the isobaric heat capacity of pure liquids C_p can take several forms [1] however, no attempt to understand these variety of $C_p(T)$ behaviours has been reported. In this work, a statistical mechanical two-state model for the associational part of the residual heat capacity $C_p^{\text{ass, res}}$ is presented. When $C_p^{\text{ass, res}}$ is added to the ideal gas heat capacity $C_p^{\text{id, gas}}$ all the experimental dependencies are qualitatively described. Furthermore, the existence of $C_p(T)$ curves with a maximum –not found in literature– is predicted. Measurement of highly sterically hindered alcohols corroborated this prediction.

Quantitative application of the model was successfully achieved for linear and branched alcohols and long-chain normal alkanes. The effect of pressure on C_p of linear alcohols was also explained. The model parameters took reasonable –and contrastable in some cases– values according to their physical meaning.

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Effect of Polymer Polydispersity Characterization on Predicted Phase Behaviour of Polyethylene Solutions

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Polymer solutions of organic solvents similar to normal hexane display complex phase behaviour, including regions of liquid-liquid-vapour co-existence. This behaviour can be accurately modelled using modern equations of state, which account for the polymeric nature of the polymer molecules. Typical industrial polymers are polydisperse in nature, with the shape of the molecular weight distribution curve varying from product to product. Accurate representation of polymer solution phase equilibria requires that, in addition to the use of an accurate equation of state and binary interaction parameters, the shape of the molecular weight distribution be properly represented. This study examines methods of mathematically characterizing polymer molecular weight distribution curves that are suitable for use in efficient phase equilibria calculations. Phase boundary and liquid-liquid fractionation calculations are performed for systems containing polyethylene dissolved in normal hexane, to determine the effects of polymer molecular weight distribution curve on the predicted phase behaviour.

Development of a New Equation of State for Mixed Salt and Mixed Solvent Systems and Application to VLE and SVLE Calculations

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An equation of state that can be used for phase equilibrium and other thermodynamic property calculations at high pressures is developed for systems that contain aqueous solutions of strong electrolytes and molecular species. The proposed equation of state is based upon contributions to the Helmholtz free energy from a non-electrolyte term and three electrolyte terms. The non-electrolyte term comes from the Trebble-Bishnoi equation of state and the electrolyte terms consist of a Born energy term, a Mean Spherical Approximation term and a newly developed hydration term. The parameters of the proposed equation of state are obtained from osmotic coefficient data because they are available for a large number of salts.

The application of the proposed equation of state to aqueous systems containing mixed salts and mixed solvents is illustrated by calculating the vapour liquid equilibrium (VLE) and solid vapour liquid equilibrium (SVLE) conditions for several systems. The solubility of CO₂ and CH₄ in salt water systems is examined at elevated pressures and temperatures. As well, the new equation of state is used in conjunction with the model of van der Waals and Platteeuw to predict the SVLE conditions for gas hydrate forming systems in the presence of single salts, mixed salts and a mixture of aqueous salts and methanol. It is found that the new equation of state is able to accurately represent the experimental data over a wide range of pressure, temperature and salt concentration.

Molecular Modeling of Long Chain Hydrocarbons, Polymers and Surfactants in Supercritical Carbon Dioxide using SAFT

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In this work, our aim is to adapt and extend, the Statistical Associating Fluid Theory (SAFT) equation of state, and to use it to understand the thermodynamics and phase equilibria of systems containing long chain hydrocarbons (HC), homopolymers, and copolymers in carbon dioxide (CO₂) in order to provide rapid predictions for a wide range of systems of interest to the scientific and industrial communities.

To accomplish this goal we apply the SAFT equation to the prediction of: (1) complete Joule-Thomson inversion curves (JTIC) of CO₂ and HC, (2) phase equilibria in CO₂/polymer systems, and (3) aggregation formation in CO₂/surfactant systems.

First, we studied the predictive capabilities of the SAFT equation of state for CO₂, through the JTIC. Very good agreement was obtained with both experimental data and molecular simulations. Additionally, we present JTIC for heavy n-alkanes, up to C₄₈H₉₈.

Second, we have predicted cloud curves of CO₂-polymer mixtures, including PDMS, PFOA, PTAN, PVAC, and PTAN-b-PVAC in CO₂. Good agreement with available experimental data was found.

Finally, we have carried out preliminary tests of the ability of the SAFT equation to predict aggregation of surfactants, for the PTAN-b-PVAC/ CO₂ system. Initial results are promising.

Surface Tension of Ionic Liquids

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Room temperature Ionic Liquids are emerging as novel replacements for volatile organic compounds, traditionally used as industrial solvents. Ionic Liquids are thermally stable, non-corrosive and non-flammable. They possess no significant vapor pressures and have the ability to dissolve a considerable variety of organic, inorganic and polymeric materials, at very high concentrations.

In this work, the surface tension, of two families of ionic liquids, $[C_n\text{mim}][X]$, where $[C_n\text{mim}]$ represents the 1-alkyl-3-methylimidazolium cation and $[X]$ the hydrophobic anions, $X = \text{PF}_6^-$ and $\text{N}(\text{SO}_2\text{CF}_3)_2^-$, have been measured, with the use of a pendant drop tensiometer, as a function of temperature, between 24°C and 65°C. The densities of the same ionic liquids were also measured as a function of temperature, using a vibrating tube Anton Paar densimeter.

The results allow a discussion on the influence of both the alkyl chain length of the cation and the nature of the anion on the surface tension of ionic liquids.

Acknowledgements

The authors wish to thank Prof. Kenneth Seddon, Henrique Guedes and Luís Paulo Rebelo for kindly supplying all the ionic liquids used in this work.

Entropy and correlations in a fluid of aligned spherocylinders: The onset of smectic order

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We investigate the nematic to smectic phase transition in a system of parallel hard spherocylinders, in the framework of the residual multi-particle entropy (RMPE) formalism. The model exhibits in particular a stable smectic phase based on purely repulsive, volume-excluded requirements. The RMPE includes - by definition - the re-summed contributions of all spatial correlations involving more than two particles. The vanishing of the RMPE signals the structural changes which take place in the fluid, for increasing densities. We have recently found that the ordering thresholds in an isotropic fluid of freely rotating spherocylinders, detected through the zero-RMPE condition, systematically correlate with the corresponding transition points, whatever the nature of the coexisting phase at higher densities. Monte Carlo simulations were carried out to determine the various contributions to the RMPE. We discuss the generalization of the RMPE formalism that is needed to study the nematic-smectic phase transition, with particular emphasis on a suitable choice of the pair distribution functions of the nematic fluid. We found that the zero-RMPE criterion accurately predicts the occurrence of the phase transition in the nematic phase, as estimated in previous investigations. Remarkably, although the transition appears as almost continuous, our approach sensitively identifies the underlying structural modifications which prelude to the smectic order in the parent nematic fluid. The RMPE approach emerges as a flexible tool to study the mesophase formation in model liquid-crystal systems, yielding accurate results, independently on the starting (be either isotropic or nematic) phase involved.

Liquid crystal transitions in anisotropic fluids. The relative influence of entropy and energy.

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We present a systematic Monte Carlo study in the NPT ensemble of the liquid crystal (LC) phases of fluids of elongated molecules. The study has focused on the effect upon the Liquid Crystal phase diagram of the type of pair interaction and of the presence of a second spherical component. Special attention has also been devoted to the behavior of the configurational entropy of the fluid and its relation to the stability of the LC phases. In particular, we have studied fluids of molecules with prolate spherocylindrical symmetry, interacting either via a hard or soft repulsive potential, or via a square-well or a Kihara attractive potential [1,2]. In addition, we have introduced a novel modification of the Kihara model which incorporates an orientation-dependent modulation of the depth of the attractive well. The molecular elongations and temperatures scoped in our study range $L^*=L/\sigma= 3-5$ and $T^*=kT/\epsilon = 1.5-5.0$, respectively. Typically, the fluid is expanded from a high density state to low density through Smectic B, Smectic A, Nematic and Isotropic phases. Some of these phases are occasionally absent depending on the interaction model or the temperature under study, and triple points for some of the models have been determined.

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PVTx in the CO₂ + hydrofluoromethane binary systems

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Abstract

A Burnett and an isochoric apparatus measured *PVTx* properties of the hydrofluorocarbon (CH₃F, CH₂F₂ and CHF₃) + CO₂ systems over a temperature range of 215-363 K and a pressure range of 100-5500 kPa covered both superheated vapour and two-phase regions [1-4]. The VLE parameters and virial coefficients were derived from the data. All studied systems exhibit a small deviation from the ideality. This could be presumably interpreted as a compensation of two opposing effects of repulsive forces of -CF groups in hydrofluorocarbons with CO₂ and attractive forces between the hydrogen (proton donor) in hydrofluorocarbons and quadrupoles in CO₂. A comparison of our results with few VLE data published in literature was showed a good their consistency. No other experimental *PVTx* data in vapor region were find in the literature for these systems.

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Evidence for Reverse Micelle Formation by borderline Surfactants in Heptane

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Enthalpies of mixing for 2-butoxyethanol + heptane and 2 – butoxy 2-ethoxyethanol + heptane were measured. Apparent molar enthalpies of the amphiphiles were determined up to an amphiphile mole fraction of 0.2. data were analyzed using the mass – action model of Roux and Desnoyers [1]. These analyses provided estimates of both the enthalpy and Gibbs energy of cluster formation. Both the enthalpy and entropy changes are significantly negative. This is consistent with the formation of metastable structured aggregates.

This result is in sharp contrast with cluster formation in water, where both the enthalpy and entropy increase [2] when micelle – like aggregates reduce the effects of aqueous solvent “hydrophobic structural enhancement”.

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Ab Initio Predictions of the Vapour--Liquid Equilibria of Noble Gases and Their Mixtures

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The prediction of thermodynamic properties of fluids without recurrence to experimental data (except for the values of the universal constants) is an old dream of physical chemistry. Its realization had been delayed by the fact that the simplest intermolecular forces, the dispersion forces, are caused by electronic correlation effects and cannot be calculated by many common quantum mechanical methods. It can be shown, however, that the *coupled cluster* method provides a sufficient, yet affordable way to obtain the pair potentials of neon, argon, and krypton. We used these pair potentials in Monte Carlo simulations (Gibbs ensemble method) to calculate vapour pressure curves and orthobaric densities. As long as only pair interactions are used, the results do not agree well with the experimental data; as soon as three-body potentials (Axilrod—Teller triple—dipole potentials) are included, the agreement becomes quantitative. We furthermore predicted the high-pressure vapour--liquid equilibria of some noble gas mixtures. Except for the critical region a reasonably good agreement between the predicted and the measured phase envelopes could be obtained.

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Characterization of ethylene-propylene elastomers by turbidity at a Lower Critical Solution Temperature using a step by step temperature increase

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Polymer solutions, made in volatile solvents, phase-separate at a Lower Critical Solution Temperature (LCST), T_i , due to the difference in solvent and polymer expansion coefficients. As T_i is molecular weight (MW)-dependant, the MW distribution of a sample can be obtained through a thermogram. This is a set of $h_i(T_i)$ where h_i is the turbidity for a fraction phase-separating at T_i , in a step by step T -increase. The range of T_i is 70 K lower for polyethylene (PE) than for polypropylene (PP). Random copolymers of ethylene (E) and propylene (P) such as synthetic rubbers are expected to phase-separate, as do homopolymers, on a continuous range of T_i such as $T_i(\text{PE}) < (T_i(\text{copolymer}) < T_i(\text{PP})$ as is indeed found. In the present work, sonication is used to achieve dissolution in pentane of rubber samples with a 52% E content in lieu of an elevation of T . In these conditions, two distributions are observed, separated by 30-40 K. The range of T_i (ζ s) suggests that micelles with E segments and inverse micelles with P segments at the molecular surface are stable in solution and probably reflect the morphology of the solid. In a second run, two of the three samples behave as expected without gap of turbidity. The thermograms of samples with the same average E/P content are found catalyst-dependent. They can be tracers of the length of E and P sequences in the sample. Strain microcrystals may be at the origin of the micelle stability .

Wetting transitions in the presence of electrostatic forces

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We present a theoretical study of the problem of wetting of a solid substrate by an ionic solution. The ionic solution is described as a mixture of positive and negative ions (point charges) placed in a solvent, which in turn is treated as a continuous medium of some dielectric constant ϵ . Within this basic description, the degrees of freedom of the ions and the solvent are not coupled. We first investigate how the molecular interactions between the solid and the solvent determine the thickness ζ of a liquid film created on the substrate. When ζ is defined, we examine the physical properties of the electrolyte confined in the film of a given thickness.

Our main question is how the presence of ions in the solution affects the first-order and critical wetting transitions, that are otherwise controlled by the substrate-solvent interactions. We show that, depending on the salt concentration, the electrostatic forces can produce two opposite effects - namely, change the second-order wetting transition into first-order and vice versa. These results are explained by the fact that changing the salt concentration leads, in turn, to a change in the range of electrostatic potential. Besides, we find that the strength of the substrate-solvent interactions required for the wetting transition to occur, is always less in the presence of salt.

Modeling of Phase Equilibria Containing Associating Fluids

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The CPA equation of state is a thermodynamic model, which combines the well-known cubic SRK equation of state and the first order perturbation theory based association term proposed by Werhheim, typically employed in models like the various variations of SAFT. The CPA model is applied for the first time to LLE for systems containing glycols and hydrocarbons. It is shown that excellent correlation is achieved with solely a single binary interaction parameter. The CPA model has been extended to mixtures containing cross-associating compounds such as alcohols, glycols, and water. The results are excellent provided that the correct combining rules are utilized for the association energy and volume parameters for the cross-associating compounds in the mixture. Moreover, the CPA model shows good results in predicting multi-component multi-phase equilibria for glycol-water-hydrocarbon systems.

Molecular interactions of oxygen, carbon dioxide and water in fluorinated solvents

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Fluorinated liquids exhibit peculiar properties as solvents that contribute to their recent applications in numerous fields: as substitutes for chlorinated solvents, as solubility enhancers in supercritical carbon dioxide, as environmental probes and in numerous biomedical applications (e.g. as gas carriers in vivo or as agents for drug delivery).

The present work concerns the study of the features of molecular structure and interactions that determine these particular solvation properties of fluorinated liquids.

Force fields based on quantum chemical calculations were formulated to describe families of fluorinated molecules, such as hydrocarbon-fluorocarbon diblocks and substituted fluorocarbons.

Standard Gibbs energies of solvation of different solutes (oxygen, carbon dioxide and water) in fluorinated solvents (perfluorohexylethane, perfluorooctylethane, perfluorohexylhexane and perfluorooctylbromide) were calculated by computer simulation using appropriate free energy routes. The results were compared, when possible, with experimental values in order to validate the force field models. Significant aspects of the solute-solvent interactions are interpreted using the results of simulation.

Transport of Ions in Electrolyte Solutions: Are Ions Brownian particles?

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We present recent developments about thermodynamics of electrolyte solutions. The equilibrium and non-equilibrium properties of ions have been studied to model concentrated electrolyte solutions. Originally based on semi-phenomenological equations, the dynamics of ions can now be understood in terms of Brownian motion. It allows more modern statistical theories to be incorporated. Thus, for the equilibrium properties, the Mean Spherical Approximation (MSA) can be applied up to high concentrations (12 mol L). The dependence of the ion transport coefficients with respect to the concentration has specially been obtained from three different approaches: A Smoluchowski/MSA theory gives the various transport coefficients for concentrated solutions. This analytical theory has been obtained after a careful analysis of the reference-frames and of the hydrodynamic interactions [1]. It is consistent with Brownian dynamics simulations. The latter allows the problem to be solved numerically [2]. The mode-coupling theory (MCT) given for self-diffusion explains the discrepancy between the short-time measurements (QENS) and the long-time ones (NMR, tracers) [3]. These results agree with the Onsager limiting laws. They generalize the latter in the case of concentrated solutions (1-2 mol L). They are self-consistent, i.e. the same diameters are used to describe all the physical properties of the system, so that there is no adjustable parameter.

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Helmholtz Energy, Extended Corresponding States and Local Composition Model for Fluid Mixtures

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We present the results of the prediction of densities, speeds of sound and vapour pressures of mixtures of primary natural gas components.

The mixture model is explicit in the residual Helmholtz energy, given as two contributions. One comes from an extended corresponding states model, described elsewhere [1], and the other is a correction term. The correction term involves local composition mixing rules and makes use of a coordination number model for square-well fluids from lattice gas theory [2]. The mixture model obeys the global and local balance of species and the restriction on second virial coefficients being quadratic in composition. Square-well depths were obtained from second virial coefficients. The mixture model uses only three adjustable parameters.

Densities with and absolute average deviation (AAD) of 0.16 per cent were obtained for eight systems formed from CH₄, C₂H₆, C₃H₈, N₂ and CO₂ for $90 < T/K < 675$ and $p/\text{MPa} < 510$ MPa. The AAD in speeds of sound was 0.18 per cent and that in vapour pressures was 2.3 per cent.

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The Transient Fluctuation Theorem and NonEquilibrium Free Energy, Theorems

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The Fluctuation Theorems give a generalization of the Second Law of Thermo-dynamics that applies to small systems observed for short times[1]. For thermostatted systems they give the probability ratio that entropy will be consumed rather than produced. In this paper we discuss the Transient[2] and Steady State Fluctuation Theorems[3]. We review recent experiments[4] that validate the Transient Fluctuation Theorems. We also discuss the relationship of the Transient Fluctuation Theorem to the Jarzynski-Crooks NonEquilibrium Free Energy Theorems[5]. These latter theorems show that differences in equilibrium thermodynamic state functions can be computed from sets of *nonequilibrium* thermodynamic path integrals. These theorems therefore generalize the concept of path independent state functions, outside the domain of purely equilibrium states.

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MC simulation of phase equilibria in Ising fluids and their mixtures

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The mean field theory for the pure Ising fluid [1] was recently extended to binary mixtures of an Ising and a van der Waals fluid [2]. Depending on the relative interaction strengths, their three dimensional phase diagrams show lines of tricritical consolute and plait points, lines of critical end points and magnetic consolute point lines. Our current efforts are to compare these mean field results with different Monte Carlo simulation techniques, investigating both first order (liquid-vapor and demixing) and second order (paramagnetic-ferromagnetic) phase transitions.

We show the resulting ρ, T phase diagrams of the pure Ising fluid for different magnetic interaction strengths R and constant pressure cross-sections of the x, T, p phase diagrams of Ising mixtures for different relative interaction strengths.

The methods we have used include Gibbs Ensemble MC, Multihistogram Reweighting, Hyper-parallel Tempering [3], the cumulant intersection method and the newly developed Density of States MC [4,5] technique. Grant: FWF 15247

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Solution and interfacial behaviour of semifluorinated alkanes

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Mixtures of alkanes and perfluoroalkanes (PFA's) are known to deviate strongly from ideal behaviour. Perfluoroalkylalkanes (PFAA's), with the general structure $F(CF_2)_n(CH_2)_mH$ (in short F_nH_m), join the two incompatible segments in the same molecule and display very interesting properties, including surface activity and micelle formation, both in alkane and perfluoroalkane solutions. In this work, partial molar volumes at infinite dilution of a number of PFA's (C_5F_{12} , C_6F_{14} , C_8F_{18} , C_9F_{20}) and PFAA's (F_6H_6 , F_6H_8 , $F_{10}H_8$, F_8H_{18}) in *n*-octane were measured. We have found that the experimental partial molar volumes at infinite dilution for the PFAA's in *n*-octane, are larger than those expected from the corresponding volumes of the parent hydrogenated and fluorinated segments.

The densities of two liquid PFAA's, F_6H_6 and F_6H_8 , have also been measured as a function of temperature. Again the molar volumes of these hybrid molecules are larger than expected. In the case of F_6H_6 , a hypothetical excess volume, due to simultaneous mixing and bonding, was calculated and found to be larger than the expected when comparing with the excess volumes of mixtures of hexane and perfluorohexane.

Lattice model of a binary mixture of penetrable particles

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Recently the phase behaviour of a continuous system consisting of a mixture of Gaussian particles has been investigated [1-3]. The demixing region found was much broader than a typical coexistence region for a mixture of hard particles. To gain more insight into the nature of the critical region, we have developed a lattice model of a binary mixture with multiple occupancies of the lattice sites. Using basic Statistical Mechanics techniques it is shown that the equation of state for this system is similar to the e.o.s. of the Gaussian particle mixture. The demixing region is investigated using Monte Carlo simulations and advanced theoretical techniques (SCOZA).

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B_2 or not B_2 ?

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X-ray diffraction of protein crystals is the primary way of deducing protein structure, which is of importance in elucidating protein function and to the development of drugs. Crystallization as practiced today is a trial and error method. About 4,000 of the 30,000 human proteins have been crystallized indicating the errors have the upper hand. With the completion of the human genome project, expression of the entire human protein corpus is a possibility. This is viewed as an important step in the new field of "proteomics". Recently it was noticed that all proteins that crystallized had second (osmotic) virial coefficients (B_2) that fell in a small range of values. Frenkel (Science, 97) proposed that this was due to the presence of a metastable critical point underlying the equilibrium phase diagram. We test this concept by employing non-absorbing polymers to create a potential of mean force between the proteins that would influence the position of the critical point. Our experiments reveal surprising results. First, light scattering results indicate that the polymer, poly(ethylene) glycol (PEG) is attracted to protein, in contrast to conventional wisdom that states PEG does not interact with proteins. Second, in contrast to several theoretical models, B_2 is not correlated with phase behavior. Our experiments and those of others reveal systematic and general trends that are indicative of an underlying physical explanation of crystallization in contrast to the "lock and key" mechanism favored by biochemists. Our experiments demonstrate that the "depletion" picture is over simplified and that explicitly including the polymer and protein on equal footing in free energy models is the correct approach.

An analytical Onsager-like equation of state for ordering transitions in systems of attracting rod-like particles

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A general methodology of Onsager [1] free energy functionals for the isotropic-nematic transition is presented to study ordering transitions in systems formed by cylindrically symmetrical molecules. A number of new analytical results are discussed. The adequacy of a scaled Onsager free energy in describing ordering transitions is exemplified by applying it to systems of hard spherocylinders (HSC). A closed analytical form derived from the Onsager description is also examined. The latter essentially constitutes an analytical equation of state (EoS) appropriate for use in engineering applications. The hard body model is extended in order to account for attractive interactions (treated at the van der Waals level) using an isotropic attractive interaction described by a square-well (SW) potential. The resulting EoS is used to determine the vapour-isotropic liquid, isotropic liquid-nematic, and vapour-nematic phase equilibria. For the attractive systems the effect of potential range and molecular aspect ratio on the vapour-liquid equilibria and ordering transitions is also examined in order to investigate the van der Waals limit in these kinds of systems.

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Viscosity and Surface Tension of Transparent Fluids from Surface Light Scattering (SLS)

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In the present work it is demonstrated that the SLS-technique can be used for a reliable determination of surface tension and liquid viscosity – without any calibration procedure – with an accuracy comparable or even better than for conventional methods. After an introduction into the technique, a newly developed approach is described, which allows in the case of transparent fluids, as it is of interest to this work, the analysis of scattered light in the forward direction at variable and relatively high wave numbers of capillary waves. This arrangement has been chosen due to signal and stability considerations and differs from the more commonly employed scattering geometry, where scattered light is observed close to the reflection direction.

In the second part of this work, the data evaluation procedure is introduced, which is based on an exact description of the dynamics of surface waves as given by the dispersion relation for a liquid-vapour interface resulting from the solution of the Navier-Stokes equation for an incompressible fluid. The investigation of the reference fluid toluene between 263 and 383 K under saturation conditions demonstrates for the SLS-technique an accuracy of better than 1 % for both properties of interest. Beside toluene, we applied the SLS-technique to alternative refrigerants, carbon dioxide, and a silicone oil. These data demonstrate the applicability of the technique to different fluids covering a wide range of viscosity, from about 10 μ Pas to 1 Pas.

Phase Equilibria of the Nitrogen-n- Heptane System

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Enhanced oil recovery by nitrogen injection is one of the methods of tertiary oil recovery that is used in certain Mexican fields. In order to describe and/or predict the process of nitrogen flooding by reservoir simulation, the phase behavior of the nitrogen-oil system has to be known. In this work, results are presented of experiments on the vapor-liquid equilibria of the nitrogen-n-heptane system. For this purpose, an apparatus has been designed and built (ARMINES, France) to study multiphase equilibria of multicomponent mixtures up to 60 MPa and 673 K. This apparatus is based on the static-analytic method involving a sampling-analyzing process for determining the compositions of the different coexisting phases. This capillary sampler injector makes the apparatus very practical and accurate for the measurements. The experimental data were represented using both cubic (PR) and non-cubic (PC-SAFT) equations of state.

Vapour-liquid equilibrium for the binary systems 2-methyl-2-propanol with some halohydrocarbons

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Isobaric vapour-liquid equilibrium measurements at 40.0 and 101.3 kPa are presented for the binary mixtures 2-methyl-2-propanol + chlorocyclo-hexane, + chlorobenzene, + bromocyclohexane, + bromobenzene. The measurements were carried out in an all-glass dynamic recirculating still (Fischer-Labodest).

The thermodynamic consistency of measurements was tested using the Van Ness method [1], described by Fredenslund et al. [2]. The vapour-liquid equilibrium data were satisfactorily correlated with Wilson equation [3]. Predictions with the UNIFAC method [4,5] were also obtained.

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Some regularities in the quasi-binary metal chalcogenide systems with common cation

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The title systems i.e. those of the type $M_aX_b - M_cX'_d$, where M is any metal, X and X' are chalcogens (S, Se, Te), are interesting because of theoretical and practical uses. Ternary compounds formed in these systems may be characterized by semiconductor properties.

As yet, the only certain method of searching for the compounds is a phase diagram determination. Nevertheless, there are some possibilities of predicting phase diagram shape, using regularities in phase equilibria of respective systems. The regularities appeared during our phase studies by thermal analysis on the systems: when the anions neighbour each other in the same group of Periodic Table, the system components form a continuous series of solid solutions (ss), e.g. $Tl_2Se - Tl_2Te$, $Ga_2S_3 - Ga_2Se_3$, $PbS - PbSe$, $Bi_2Se_3 - Bi_2Te_3$. This rule is also satisfied by systems built of double chalcogenides as $CdTl_2Te_4 - CdTl_2Se_4$.

When the distance between X and X' in the Periodic Table increases (up to another group) which is consistent with increasing difference in electronegativities of elements X and X', the tendency for compound formation also increases which results in regular successive changes in a phase diagram: continuous ss → wide-range terminal ss → narrow-range terminal ss → simple eutectic → one compound.

The computer simulation of the short-range-order atomic structure of liquid Li-Si and analyse of atomic structure by Voronoi polyhedron method.

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Among the alloys of alkali metals with elements of group III, IV, and V, Li-Si is interesting because the structure neither in the crystalline state nor in the liquid obeys simple Zintl rules. In order to discover the rules for the structure of liquid Li-Si it seems useful to find a small set of parameters describing the structure as a function of composition. Our approach is based on using the Reverse Monte Carlo (RMC) method for modelling three liquid Li-Si alloys ($\text{Li}_{80}\text{Si}_{20}$, $\text{Li}_{65}\text{Si}_{35}$ and $\text{Li}_{57}\text{Si}_{43}$). The equilibrium atomic structure obtained by RMC is analysed by the Voronoi polyhedron method in order to identify the most typical configuration of the nearest environment for atoms of each component. The input data used for this investigation are the results of modeling the structure of melts of the Li-Si systems using the Reverse Monte Carlo method (RMC) for three compositions ($\text{Li}_{80}\text{Si}_{20}$, $\text{Li}_{65}\text{Si}_{35}$ and $\text{Li}_{57}\text{Si}_{43}$). The structural factors of Li-Si melts were obtained experimentally by the method of a diffraction of neutrons. The tool of examination that we selected is a method of statistically-geometrical analysis using the Voronoi polyhedrons which permitted us to obtain detailed, unique information on the structure of the short-range order of topologically random systems. It is possible to assert that the Li-Si system as a whole follows the 'Zintl rule'. In fact, in the melt $\text{Li}_{57}\text{Si}_{43}$, where the ratio of components is almost one to one, the anion of silicon can receive only one extra electron from each cation of lithium and should demonstrate valence of about three. In the melt $\text{Li}_{65}\text{Si}_{35}$, where the ratio of components is close to 2:1, the anions of silicon gain 2 electrons and will derive chain structures.

Correlation of LLE experimental data of Ternary Systems Containing Water With Different Activity Coefficient models based on quasi-chemical theory

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Liquid liquid equilibrium (LLE) experimental data for ternary systems containing water is correlated with different activity coefficient models based on quasi-chemical theory. The optimization procedure is carried out in two steps. In first step the following function is minimised.

$$F_1 = \sum_{j=1}^m \sum_{i=1}^3 (x_{ij}^l \gamma_{ij}^l - x_{ij}^u \gamma_{ij}^u)^2 \quad (1)$$

where, x_{ij}^l and x_{ij}^u are the experimental mole fraction of component i of, respectively, lower & upper phase along a tie line j . γ_{ij} is the corresponding activity coefficient calculated from model and m is the total number of tielines. The regression results of binary interaction parameters obtained in first step are used as initial guess for the following optimization function. (2)

$$F_2 = \sum_{j=1}^m \sum_{i=1}^3 \left[(x_{ij}^{\text{exp}(l)} - x_{ij}^{\text{cal}(l)})^2 - (x_{ij}^{\text{exp}(u)} - x_{ij}^{\text{cal}(u)})^2 \right]$$

UNIQUAC binary interaction parameters of different ternary systems are produced according to the above mentioned procedure where the deviations between calculated and experimental mole fractions become considerably lower than those reported in literature. Experimental data of different ternary systems are also correlated with a generalized activity coefficient model based on quasi-chemical theory proposed by Wang et al [1]. Non-random factors are obtained according to the method proposed by Abusleme et al [2]. Accurate results have been also obtained using this generalized model.

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Mixture Design with the SAFT Equation of State

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The identification of suitable solvents for the series of n-alkanes and their polymers is an important issue in the oil and petrochemical industries. It may for instance be desirable to maximise the solubility of a polymer under given processing conditions, or to achieve the most effective separation between long chain n-alkanes and impurities. The choice of solvent can be narrowed down by noting that short-chain alkanes are readily available on-site and can usually offer good performance. The selection process is complicated by the fact that n-alkanes exhibit various types of phase behaviour when mixed together. In this work a general thermodynamic criterion, that is based on the concept of stability limits, is used to locate liquid-liquid immiscibility in binary mixtures. By taking advantage of the transferability in the SAFT-HS Equation of State [1] parameter space for a homologous series, a systematic methodology is developed to distinguish between different types of phase behaviour. This could prove to be an invaluable source of information during the solvent selection procedure, as it provides efficiently and robustly a set of promising solvents, in terms of their phase behaviour. The methodology has been applied to the case of n-alkanes. Its extension to other types of homologous series and to multicomponent systems is also discussed.

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A Monte Carlo Simulation Scheme for non-ideal Dendrimers Satisfying Detailed Balance

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We present a configurational-biased lattice Monte Carlo scheme that satisfies detailed balance for simulating non ideal dendrimers with explicit presence of solvent. Equilibrium properties such as radius of gyration, density profiles and structure factors of self-avoiding dendrimers are investigated under different solvent conditions for dendrimers up to generation 8.

In the athermal solvent case, our conclusions are the following: 1. The radius of gyration scales with the total number of monomers roughly as $R_g \sim N^{0.33}$. A more careful analysis however shows that there is a small (~30%) and nonmonotonic variation in the internal density of the dendrimer with N. 2. The intramolecular density profile is dense core like at low dendrimer generations ($g < 5$) and solid sphere like at high generations. 3. There is some ‘‘hollowness’’ in the core region of the dendrimer for higher generation dendrimers. 4. Terminal groups of the dendrimer are not localized at the periphery but delocalized throughout the dendrimer

Going from athermal to poor solvent condition, we find that there is a considerable collapse in R_g (factor of two) despite the high intramolecular density of dendrimers in athermal condition. We explore to what extent it is possible to define a θ -point for dendrimers and compare the properties of the dendrimer at the ‘ θ -point’ to simple random walk and non reversal random walk dendrimers.

Modelling the surface tension of real substances with a SAFT-VR density functional theory

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A principal goal of equation of state modelling is the use of models to predict the behaviour of a substance where little or no data exists, either by extending the description of obtainable data to a property where little data exists, or by using the physical property data from one substance to predict the behaviour of another substance. The SAFT approach [1] allows for the modelling of phase behaviour through an understanding of interactions at the molecular level. A density functional theory based on a mean-field implementation of this theory (SAFT-HS) can be used to qualitatively predict the surface tension of both non-associating and associating compounds [2]. The more sophisticated implementation (SAFT-VR) which includes an expression for the radial distribution function, $g(r)$, provides not only a better description of the vapour-liquid phase equilibrium, but is better able to reconcile the surface tension with this phase equilibrium. The density functional theory presented here makes use of the SAFT-VR parameterised $g(r)$ at contact, averaged in a way similar to that suggested by Toxvaerd [3]. The resulting theory accurately predicts the surface tension of alkanes directly from parameters optimised to the vapour-liquid equilibrium data. For associating compounds, the proportion of associative to attractive contribution to the free energy can be difficult to determine by optimising to VLE; in this case, surface tension data may be used in the optimising procedure itself to better determine these parameters.

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Studies on thermodynamic properties of (amine + alcohol) mixtures

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Excess functions of liquid mixtures containing amine and an alcohol show the strongest negative values found for the organic mixtures in the literature [1]. The extremely negative values are interpreted in terms of two opposite effects: 1) in pure state both the alcohol and the amine are self-associated by the formation of OH \cdots O and N-H \cdots N bonds, respectively; 2) strong intermolecular interactions between the hydroxyl and amine groups contribute negatively to H^E and V^E . Thus it means that O-H \cdots N bonds are stronger than the O-H \cdots O and N-H \cdots N bonds in the investigated systems [2].

In recent work the V^E have been determined for amine (hexylamine, octylamine, decylamine) + an alcohol (1-octanol, 1-nonanol, 1-decanol, 1-undecanol). The experimental results of V^E and H^E (literature results) have been predicted by the ERAS theory, Mod. UNIFAC [3] and DISQUAC [2].

The (solid-liquid) equilibria measurements have been discussed for the same mixtures on the grounds of the strong intermolecular interactions between amine and alcohol.

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McMillan-Mayer theory of solutions, effective interactions and thermodynamics

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The McMillan-Mayer (MM) theory of solutions [1], was formulated in the framework of the Grand Canonical Ensemble (GCE). Later, it has been applied heavily to study electrolyte solutions, colloids, polymer and biological molecules in solution [2,3]. More recently, within the context of “Soft Matter”, the concept of effective interactions has been developed in the Semigrand Canonical Ensemble (SGE) [4,5]. It is the purpose of this work to discuss the relationship between both approaches. The definitions for the effective interactions and the thermodynamic properties derivable from the partition functions are presented in both ensembles (GCE and SGE). Finally, the precise meaning of the excess thermodynamic functions as introduced by Friedman [3], is carefully analysed.

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A new microscopic description of the proximity effect

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Excess thermodynamic properties of liquid mixtures are magnitudes sensitive to the intramolecular interactions. The most important of these ones is the interaction that take place in a molecule that contain two or more polar groups (proximity effect). Kehiaian and coworkers described the proximity effect as the increasing perturbation of the polar groups when their proximity increases; in such interpretation the apolar groups keep invariant. This description allowed them to describe the thermodynamic behaviour of these systems using group contribution molecular models. In spite of this, up to our knowledge, studies based on the determination of molecular charge density were not developed in order to justified this description.

In this work, the molecular charge density of the polyfunctional molecules $\text{Cl}-(\text{CH}_2)_n-\text{Cl}$ ($n = 1-6$) were obtained using Gaussian 94 package at HF/6-31G**/6-31G*. Perturbation was quantified using the R_{AP} parameter defined with the help of the Theory of Atoms in Molecules of R. F. Bader. Analysis of the R_{AP} parameter showed that the polar groups perturb several neighbouring grouping atoms (apolar or polar groups). This fact makes the above-mentioned description inconsistent. In its place, the proximity effect should be defined as the perturbation that the polar groups induce in the neighbouring atom groupings.

Micro Electro Mechanical System (MEMS) for the measurement of density and viscosity

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In this work, a Micro Electrical Mechanical System (MEMS) has been developed to determine both density and viscosity of fluids. This device is based on a vibrating plate, with dimensions on the order of 1 mm and a mass of about 0.1 mg, clamped along one edge. The resonance frequency, under vacuum, of the first bending mode is about 12 kHz, at a temperature of 298 K, with a quality factor of about 2900. Measurements of the resonance frequency and quality factor of the vibrating plate were combined with mechanical properties of the plate to determine the density and viscosity of the fluid surrounding it at temperature and pressure. Densities, in the range (1 to 1800) kg·m⁻³, and viscosities, in the range (10 to 300000) μPa s, were determined with the vibrating plate for argon, methane, nitrogen, a natural gas, octane, toluene, a polydimethylsiloxane, a reservoir oil, and brine. These measurements, when compared with either accepted literature values or results obtained with experimental techniques that utilise different principles were found to lie within ±1 per cent for density and ±5 per cent for viscosity of the literature values.

Dissipative particle dynamics simulations of polymer brushes under compression in the Grand Canonical Ensemble

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We use the dissipative particle dynamics (DPD) method to study grafted polymer chains. This method was first introduced by Hoogerbrugge and Koelman and developed to polymers by Schlijper. The method uses a soft conservative force to represent the volume element of the polymer or solvent.

In a previous work, the DPD method has been established as a sensible tool to study equilibrium properties of polymer brushes. This work has been completed by a study of the polymer brushes under shear in solvents of different quality.

We report here DPD simulations of the polymer brushes under compression in the Grand Canonical Ensemble by fixing the chemical potential of the solvent. At each surface separation, we calculate the force between the plates using the components of the pressure tensor. We compare our results with some experiments which measure the interaction energy per unit area. We plan to study such polymer brushes under shear to give the normal and tangential pressures profiles as a function of the separation between the two plates.

Phase Transitions and Chemical
Reactions at the Nano-Scale: Effects
of Confinement

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The behavior of phases confined within nano-scale cavities can be strikingly different from that of the bulk material, due to finite size and confinement effects. The influence of such confinement will be discussed for freezing and melting phenomena, and for chemical reactions, in pores of simple geometry. For freezing and melting, both experimental and molecular simulation results will be presented; the results show qualitative agreement. Examples of the effects of confinement on reaction equilibria and reaction rates will be presented. Finally, some recent attempts to develop more realistic molecular models of disordered nano-porous materials will be described. Among the methods used to achieve this are mimetic simulation techniques, in which simulation protocols are developed to describe the synthesis of the material, and reconstruction methods which seek to construct models which match the experimental structural data.

On the stochastic thermo-
micromechanics of a class of material
with a time-history dependent
response

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The paper introduces first the basic concepts and postulates pertaining to the stochastic thermo-micromechanical theory of discrete material systems. Here, continuum mechanics concepts are replaced by considerations of microstructural response variables in the form of discrete statistical functions. Second, the deformation kinematics are presented in the light of the geometry of the underlying random microstructure. The latter is established within well-defined measuring scales according to the levels of observation into the material system. In this context, the establishment of the connection between the response behavior of the individual elements of the microstructure, their interactions, and the observable mechanical behavior would be an essential requirement. The fulfillment of such requirement seems possible by the introduction of the principles of set theory, together with the concepts of measure theory. The formulation of the thermo-micromechanical behavior of the discrete material system is then attempted, under a constant base temperature, via material operators within the scope of a deformation process of a Markov-type which leads to Chapman-Kolmogoroff functional presentation. The approach is applied numerically to the case of temperature-dependent creep of a fiber-composite system with a discrete microstructure.

Interfacial properties of hard-platelet fluids

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Suspensions of hard platelike colloidal particles have recently received experimental and theoretical attention, because of the rich phase behavior and the geophysical and technological implications. Whereas the theoretical studies have focused on the understanding of the interactions and the phase behavior of homogeneous bulk fluids, experimentally it turns out that boundaries such as the walls of the sample cells have a pronounced influence on the phase behavior. Liquid-liquid or wall-liquid interfaces are intrinsic inhomogeneities of the experimental samples which have been studied recently. Here we study interfacial properties of monodisperse and binary hard-platelet fluids using density-functional theory. Even for low densities, slight orientational packing effects are found for a monodisperse platelet fluid near a hard wall due larger intermolecular interactions between platelets as compared with those between rods. Complete wetting of the wall-isotropic liquid interface by a uniaxial nematic film for the binary platelet fluid is found within the Zwanzig model. For the fluid confined by two parallel hard walls we determine a first-order capillary nematization transition for large slit widths, which terminates in a capillary critical point upon decreasing the slit width. The nature of interfaces between coexisting fluid phases is discussed within Rosenfeld's "fundamental measure theory" adapted to the present model. We find interesting interfacial structures including non-monotonic behavior of the density and order parameter profiles as well as a maximum of the surface tension as a function of the pressure in the two-component system.

Wetting of Nanopatterned Substrates

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The statistical thermodynamics of fluids adsorbed on chemically patterned surfaces was first discussed by Cassie, over 50 years ago. Recent experimental advances in areas such as self-assembled monolayers and block copolymers have made it possible to chemically pattern on the nanoscale. Such patterns induce morphological structure in adsorbed fluid films. I describe a recent experimental and computer simulation study of patterned inhomogeneous fluid phenomena, with emphasis on some of the interesting statistical mechanics associated with these systems.

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Modeling and characterization of adsorbent materials by GCMC simulations and experiments

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A widely applied experimental method in the characterization of porous materials is the nitrogen adsorption isotherm. This experimental data needs to be interpreted through a model. In an attempt to use molecular modeling techniques for materials in a systematic way, we are working on developing a methodology for the characterization of adsorbent materials, including their Pore Size Distribution. For this purpose we use a combination of non-local Density Functional Theory and Grand Canonical Monte Carlo simulations. A regularization approach is used to guide the method to obtain the real PSD of the material. The methodology is applied to several materials, including novel adsorbents, such as SBA-15 and HMS, synthesized in our laboratory. Besides their technological importance for adsorption and catalysis, a great advantage of these materials is that the PSD is very narrow, and the geometry well defined, making them excellent candidates to test models for characterization of materials. The influence of the different molecular parameters and the experimental conditions on the final characterization and applications of the material will be discussed here.

Study of molecular shape and non-ideality effects on mixture adsorption isotherms of small molecules in carbon nanotubes: A grand canonical Monte Carlo simulation study

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The sorption isotherms for binary mixtures of methane, ethane, propane and tetrafluoromethane have been determined in carbon nanotubes using Configurational Bias Monte Carlo (CBMC) simulation techniques. At high loadings, a curious maximum for equimolar gas phase mixtures occurs with increasing pressure in the absolute adsorption isotherm of one or both adsorbing species. It was detected that there exist two fundamentally different reasons for this maximum. First, due to a higher packing efficiency, one component is able to displace the other component at high loadings. Here, it must be stressed that the displaced component is not necessarily the larger molecule. Second, non-ideality effects of the bulk gas phase can be made responsible for this maximum. The acceptance probability of a molecule insertion in a Grand Canonical Monte Carlo step is proportional to the component fugacity. If, owing to non-ideality effects of the gas phase, the fugacity of one component does not increase as steeply with pressure as the other component, a maximum can occur in the absolute adsorption isotherm of this component. These findings were demonstrated for various binary mixtures of CH₄, CF₄, C₂H₆ and C₃H₈.

Solubility of oxygen, carbon dioxide, methane and argon in butyl methyl imidazolium ionic liquids

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Measurements of the solubility of gases in commonly used room temperature ionic liquids based on butyl methyl imidazolium are reported as a function of temperature between 303 K and 343 K and at pressures close to atmospheric.

The experimental apparatus is based on a saturation method at constant volume, and involves the equilibration of known amounts of dry gas and degassed solvent. The quantity of dissolved gas is calculated from the measurement of the equilibrium pressure of the saturated solution. The solubility can be expressed in terms of molarities, mole fractions and Henry's law coefficients. From their variation with temperature, the partial molar thermodynamic functions of solvation such as the standard Gibbs energy, the enthalpy and the entropy are calculated. The precision of the experimental data, considered as the average absolute deviation of the Henry's law coefficients from appropriate smoothing equations is of 4% in the worse cases.

The choice of the gaseous solutes and of the butyl methyl imidazolium based ionic liquids, was motivated by the lack of reliable experimental data in spite of their potential use in industrial mixtures. Furthermore, solubility measurements can constitute an important source of information about the properties and structure of solutions, namely about the solute-solvent molecular interactions.

Hierarchical Application of Thermodynamics to Process System Design

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Process system design is a very creative. The object system is composed of many processes. There are two kinds of relationships between processes; successional relationships and mediative relationships. Based on this classification, the design is divided into three phases: (1) creation of concept generation, (2) creation of functionalities, and (3) effective utilization of utilities such as energy.. For each phase, appropriate diagrams such as process vector diagrams, material-utilization diagrams, and energy-utilization diagrams are proposed

Fermi-Dirac and Bose-Einstein Distribution Functions derived from Classic Thermodynamics

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The distribution functions named in the caption are commonly regarded as important results from quantum statistics. Actually, it is possible to obtain effortlessly these functions from classical thermodynamical reasoning.

Starting from protonation and redox reactions as role models going via single- and multilayer adsorption of thin gases or solved substances to surfaces it is possible to derive the functions for the occupation of quantum states by fermions (analogous to the Langmuir adsorption) or by bosons (analogous to the Brunauer-Emmett-Teller adsorption to indifferent surfaces).

It is possible to apply this concept to other subjects of statistical thermodynamics such as the partition function of translation and so the Sackur-Tetrode equation or the analysis of degenerate Fermi- or Bose gases.

Teaching Thermodynamics – A New Concept

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Thermodynamics is generally considered a difficult science by students. Its historical development has resulted in a unique structure which is generally incompatible with those of other physical sciences thereby making an intuitive understanding difficult. The starting point of the new concept developed by Georg Job [1] is the realization that the direct metrication of the common perception of heat led straightforward to the quantity which is called entropy today. On this basis, a consistent dynamical theory of heat and matter [1, 2] can be developed which includes both classical and statistical thermodynamics. One of the advantages of the new concept is a uniform description of mechanical, electrical, thermal and substantial systems, but also of microscopic and macroscopic, reversible and irreversible, static and kinetic systems. In addition a modified thermodynamical calculus results in short calculations which can be easily predicted by the students. This new representation of thermodynamics is compatible with the traditional one as well as with a newly developed unified concept of physics by G. Falk. The theoretical aspects are complemented by the proposal of more than forty simple but nevertheless impressive demonstration experiments. The concept is supported by the newly founded "Eduard-Job-Foundation for Thermo- and Matterdynamics" (www.job-stiftung.de) which promotes a variety of projects in education, research and business.

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Simulation of water/polymer systems

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The lifetime of high voltage cable insulators under outdoor conditions is severely reduced by polymer breakdown, e.g., by water treeing. Our goal is to understand the mechanism behind the breakdown using Monte Carlo simulations.

To get a deeper understanding of the behaviour of water in contact with the polymer, we are performing Gibbs ensemble^{1,2} calculations of the phase equilibria of water in the absence and presence of a uniform electric field. We are using two different water models, SPC/E³ and EP exp-6⁴. We will also combine water with alkanes, using the TraPPE⁵ and exp-6⁶ models, for binary phase equilibria simulations. The alkanes will subsequently be extended to longer, polymer chains.

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Molecular simulation of water/organic co-adsorption on activated carbon

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Activated carbons are widely used to adsorb organic components from air in environmental and personal protection applications. In this situation, water vapour is always present. However, the mechanism of adsorption of pure water and water/organic mixtures on activated carbon is not yet fully understood. We have used Monte Carlo simulation to investigate this phenomenon and attempt to develop a model for the adsorbent that is able to predict multicomponent adsorption equilibrium involving water and organic components. This model is applied to a prototype system consisting of water and ethane on commercial BPL carbon.

In order to model such a system, both the complex structure and the surface polarity of the activated carbon must be taken into account. This is due to the radically different behaviour exhibited by water (a strongly polar molecule) and ethane (an almost non-polar molecule). For this reason, such a system is also of significant fundamental interest both in terms of adsorption and of phase equilibrium in pores.

The carbon model consists of a distribution of slit-shaped pores (determined from pure-ethane adsorption) and a distribution of oxygenated sites (obtained from pure-water adsorption). It gives predictions that are in good agreement with experimental binary adsorption data and are far superior to the results of classical thermodynamic methods.

Ionic Liquids - A new Class of Selective Entrainers for Extractive Distillation

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Ionic liquids (IL) represent a new class of selective solvents. Due to their fascinating properties, they appear as promising substances for the optimization of a number of separation processes such as extractive distillation. [1]

IL are liquids that are comprised entirely of ions. By choosing task-specific anion-cation combinations, remarkable selectivities and capacities can be achieved with regard to the separation of many close boiling or azeotropic systems.

The presentation will cover the following aspects:

- Discussion of vapour-liquid (VLE) and liquid-liquid equilibria (LLE) of binary and ternary IL-solutions;
- Pre-selection process of suitable IL for their potential use as entrainers by determining the separation factor at infinite dilution;
- Experimental results demonstrating the influence of IL on the VLE for a variety of azeotropic systems;
- Evaluation of the IL-potential for the separation of azeotropic mixtures.

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Calculation of thermophysical properties in process modelling tools with the SAFT equation of state

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The SAFT equation of state has significant predictive advantages in comparison with conventional (e.g. cubic) EOS, especially in the case of complex systems such as polymers, refrigerants and surfactants. However, to date, its use in process modeling and simulation tools has been very limited. This is partly due to the complexity of the underlying equations that tend to make SAFT-based physical property evaluations much more expensive than those based on more well-established thermodynamic models.

This work is concerned with numerical methods for improved efficiency and robustness of physical property calculations based on the SAFT-VR equation of state, demonstrating that it is possible to achieve significant computational improvements over existing solution methods. We also consider some of the issues related to the incorporation of SAFT-based properties within process models in the context of general-purpose process modelling tools.

Thermodynamic Prediction of Multicomponent Liquid Adsorption on Solids using Excess Quantities

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Complete measurements of adsorption excesses for ternary or higher component liquid mixtures are time-consuming. Theory can contribute to reduce the often no realizable high experimental expenditure for determining adsorption equilibrium data.

Up to this day, the international standard of the thermodynamic prediction of multicomponent liquid adsorption bases to methods applying absolute quantities [1, 2]. Our calculations showed that these prediction methods give good qualitative results in the case of some adsorption systems, whereas the quantitative agreement between ternary predictions and measured ternary data often is only satisfactory [3].

In liquid phase adsorption, it is only possible to measure excess quantities. These quantities are elementary different from absolute quantities. The utilization of excess quantities as a basis of the thermodynamic formalism is a useful theoretical approach to predict multicomponent adsorption. New thermodynamic formulations are developed.

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Liquid crystal at inhomogeneous interfaces: Structural forces

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As soft anisotropic condensed materials, liquid crystals are characterized by large thermal fluctuations in their orientational order. Confining geometries such as thin films, which most applications of the liquid crystals are based on, change this fluctuation spectrum. This causes not only structural changes but leads also to fluctuation-induced forces on the confining walls which are also known as thermodynamic Casimir forces. These Casimir forces strongly depend on boundary conditions which can be tuned via geometrical or chemical modifications. We study the effect of laterally inhomogeneous anchoring strengths for the director as well as corrugated walls. Under such conditions also lateral and torsion forces may arise with interesting technological perspectives.

Investigation of the Temperature and Density Dependencies of the Effective Pair Potential Parameters Using Variational Theory

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Abstract

The variational theory (VT), in which the potential energy of a real system is evaluated relative to the hard sphere system, has been used to investigate the medium effects on the pair potential parameters. By adding the medium effects to the isolated pair potential, the concept of “effective pair potential”, (EPP) has been introduced. The advantage of such a potential (EPP) over the isolated pair potential is that the configurational energy can exactly be written as the sum of all EPP of all pairs available in the system. The parameters of such a pair potential will then show state dependency. We have obtained the EPP parameters for different dense fluids at various temperatures via the VT, and shown that they are density independent for densities greater than the Boyle density, $\rho_{B=1.8\rho_c}$, (where ρ_c is the critical density), while at lower densities the parameters depend on density as well as temperature. For any dense fluid, the depth of the EPP, ϵ , is found to be larger than its corresponding isolated pair. When the EPP parameters are used to reduce temperature and density, the cut-off parameter, $C=d/\sigma$ depends only on the reduced density and this parameter shows a strong principle of corresponding states for different fluid. The obtained expression for the cut-off parameter has then been used to predict the internal energy, accurately.

Simulation of phase equilibria of alcohols, sulfides and thiols and their mixtures with alkanes

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The Nath, Escobedo and de Pablo revised (NERD) [1] force field is highly accurate in predicting vapour-liquid phase equilibria of various hydrocarbons and their mixtures [2]. Coulombic potentials have been added to the NERD model to account for electrostatic interactions present in these molecules. Although NERD is a united atom force field, explicit hydrogen atoms were used when explicit charges are required, for the polar molecules [3].

We report here pure component phase diagrams for primary alcohols, thiols, sulfides, and hydrogen sulfide, calculated using the NERD force field [3,4]. We also present some mixture calculations containing these molecules and various alkanes. Simulations performed in this work were carried out using the Gibbs ensemble method, as implemented in Accelrys' Equilibria program. Our simulation results are in very good agreement with experimental data, where available.

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COSMO-RS, a novel *a priori*
predictive method for fluid phase
thermodynamics

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COSMO-RS is a novel predictive method for the thermodynamic properties of pure and mixed fluids. In contrast to group contribution methods, which depend on an extremely large number of experimental data, COSMO-RS calculates the thermodynamic data from molecular surface polarity distributions, which result from quantum chemical calculations of the individual compounds in the mixture. Winning the COSMOlogic First Industrial Fluid Properties Simulation Challenge organized by NIST and AIChE/COMSEF, COSMO-RS has just recently proven to be the most reliable and efficient tool for the prediction of vapour-liquid equilibria presently available.

Due to the almost general applicability of modern quantum chemical methods, COSMO-RS can be applied in many situations, where group contributions fail. New or complicated multifunctional chemical compounds, intra-molecular interactions, reactive intermediates, and even ions and zwitterions can be handled with no problems. Due to its accurate statistical thermodynamics, COSMO-RS is equally reliable at finite concentration and infinite dilution, even for strongly interacting and associating compounds. COSMO-RS appears to be a rather general predictive method for the thermodynamics of simple and complex fluid systems. In addition to some standard applications, a few successful applications to ionic liquids, electrolyte systems, polymers, and reactive systems will be shown.

Local Entropy Production in
Turbulent Shear Flows: A High
Reynolds Number Model with Wall
Functions

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An efficient use of energy is one of the major objectives in designing modern thermal systems like compact heat exchangers and power plants. This, however, can only be achieved if also the second law of thermodynamics is accounted for, since the amount of available work is linked to the amount of entropy production. Therefore, a thermal apparatus producing less entropy by irreversibilities destructs less available work. This increases the total efficiency of a thermal system. The amount of entropy produced can be used directly as an efficiency parameter of the system.

In our study, entropy production in incompressible turbulent shear flows of Newtonian fluids is analysed systematically and incorporated into a CFD code. There are four different mechanisms of entropy production: dissipation in a mean and a fluctuating velocity field and heat flux in a mean and a fluctuating temperature field. Based on asymptotic considerations wall functions for the four production terms are developed. These wall functions are mandatory when high-Reynolds number turbulent models are used since peak values of entropy production occur in the immediate vicinity of a wall. As an example pipe flow with heat transfer is analysed and compared to results from a direct numerical simulation with special emphasize on the entropy production in the near wall region.

Curvature Expansion of Density Profiles of Hard-Sphere Fluids

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We argue that the density profile of a hard-sphere fluid around an arbitrary shaped convex hard object can be written as a power series of both the mean and the Gaussian curvature of the underlying object. We determine the expansion coefficient functions numerically within density functional theory by studying density profiles in planar, spherical and cylindrical geometry. Using these coefficient functions we can construct the density profile of a hard-sphere fluid around any convex hard body and determine corresponding thermodynamic quantities like the surface tension and the excess adsorption. Our results confirm the prediction that thermodynamic quantities should only depend on curvature measures that are additive.

Time-reversible always stable predictor-corrector methods for molecular dynamics of polarizable molecules

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In polarizable models the induced dipoles depend on the electrostatic field which again feedbacks the dipoles. The self-consistent field (SCF) needed for calculation of forces in MD is therefore given implicitly by equation of the form $D=f(D)$.

One method [1] for efficient and accurate integration of the corresponding equations of motion makes use of an extended predictor and damping (relaxation, mixing) in the SCF equation. This method needs one evaluation of the right-hand side per integration step, is stable (errors do not cumulate), and the time reversibility error (drift in the total energy) is of the 5-th order with respect to the timestep.

In this paper a series of predictors is derived with the time reversibility errors of orders 7, 9, ... The integrators are tested on a polarizable model of water.

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This work was supported by the The Ministry of Education, Youth and Sports of the Czech Republic under the project LN00A032 (Structure and Dynamics of Complex Molecular Systems and Biomolecules).

Accurate equation of state of the hard sphere fluid in stable and metastable regions

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New accurate data on the compressibility factor of the hard sphere fluid are obtained by highly optimized molecular dynamics calculations in the range of reduced densities 0.25–1.03. Finite size effects are investigated in detail and corrected for. The relative inaccuracy at the 95% confidence level is better than 0.00004 but the last point. The data are fitted to a power series of $y/(1-y)$, where y is the packing fraction; the first four coefficients are determined so that virial coefficients B_2 – B_5 are reproduced. Two versions of the equation of state are given, one covering the full range of densities, and the other with the metastable points excluded.

This work was supported by the The Ministry of Education, Youth and Sports of the Czech Republic under the project LN00A032 (Structure and Dynamics of Complex Molecular Systems and Biomolecules).

An accurate analytical formula for the bridge function of the hard sphere fluid

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The values of the bridge function of the hard-sphere fluid as a function of the interparticle separation distance were calculated from our new accurate computer simulation data on the pair distribution function using the inverted Ornstein-Zernike equation at a number of densities in the fluid and metastable region. In addition, the elementary diagrams up to the fifth were calculated. These data have been combined in order to propose an analytical expression for the bridge function as a function of distance and density. The bridge function may serve as a severe test of theoretical closures to the OZ equation. It may also be used for more complex systems via the reference hypernetted approach.

Thermodynamics of solvation of the fullerenes

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In the present paper the thermodynamics of interaction of the fullerenes C_{60} and C_{70} with aromatic solvents is discussed. The thermodynamic and structural properties of solid solvates of C_{60} and C_{70} along with the thermodynamic data on solubility of the fullerenes obtained by these authors are reviewed.

The scaled particle theory (SPT) along with the polarizable continuum model (PCM) were used to describe the solvation of the fullerenes. SPT-PCM presents the general trends in solubility of the fullerenes in aromatic solvents as a competition of the favorable dispersion interaction energy and the unfavorable energy of the cavity formation. The estimations were further extended to higher fullerenes, where the model predicted monotonous favourable changes of the solvation properties with the increase of the fullerene cage. Lennard-Jones 6-12 atom-atom potentials were used to describe the crystal structures and crystal lattice energies of solid solvates of C_{60} and C_{70} .

Certain experimental evidence was found for the formation of the solid clathrate of extremely hydrophobic C_{60} with water. Differential Scanning Calorimetry showed the presence of finely divided water, trapped inside the fullerene matrix. Surprisingly, the molar ratio of trapped water to C_{60} was the same in different samples prepared. Similar type of non covalent interaction with the solvent is possible for carbon nanotubes.

Supersolubility *OF* and *IN* Nanocrystals

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The excess pressure P (or concentration C) OUTSIDE of small condensed particles in a medium being proportional to reciprocal size of a sphere or cube had been investigated by Laplas, Lord Kelvin, Ostvald, and Gibbs. The reason is a trend to minimize a surface, because surface (S) energy is disadvantageous for general two phases system free energy. The excess P (or C) determines evaporation (or dissolution) and so the S decreasing. So the solubility of lone particle's substance in a medium, exceeding equilibrium C above a flat S .

Not only decreasing of S but the formation of solution of a medium substance in small particles also can decrease a disadvantageous S energy in two phase system. These are changes INSIDE particles. The thermodynamics uses both ways for system free energy minimization. The accounting of the dependence of S energy on concentration of medium substance IN a small particle determines at definite conditions discussed an unexpectedly great (exponential) growth of a medium solubility in a particle with the increasing of S/V ratio. It is shown in particular pairs of substances being almost insoluble mutually in bulk state become the most soluble in nano-forms. (few tens of Angstroms). The experimental manifestations of effect and new approaches for nano-technologies are discussed, possibilities of intercalation technologies (see [1] will discussed especially.

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The Author thanks the Ukrainian Found for fundamental research for the support.

The analysis of a curve “time-temperature”, obtained at heating of an indefinitely thin plate by the modulated laser beam

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The results of analysis “time -temperature” curve for refractory metals (W, Mo, Ta) are represented. A sample in the form of indefinitely thin plate (ITP) was heated by a laser source of continuous operation- $q_{\Sigma} = q_{\text{const}} + q_{\omega}(\text{input signal})$.

The analysis of “time-temperature” curve, where temperature can be expressed in the form $T_{\Sigma} = T_{q_{\text{const}}} + t_{q_{\omega}}$, has shown that the frequency of an output signal T_{Σ} coincides with the frequency of an input signal $\omega_{\text{in}} = \omega_{\text{out}}$ during the solid phase heating. The amplitude of temperature’s harmonic part $t_{q_{\omega}}$ increases with the growth of T_{Σ} . The ITP method has properties of so-called “ideal system”: 1) equality of frequencies of entry and output signals and 2) linearity (the sum of input signals gives the sum of corresponding output signals on an exit).

The time of the horizontal part of the experimental curve “time - temperature” corresponds with the time that is calculated from a thermal balance on the basis of caloric properties. Therefore, the ITP method can be considered as a tool of measuring the temperature of melting in conditions close to a thermodynamic equilibrium. The degeneration of harmonic temperature $t_{q_{\omega}}$ in the process of malting is an interesting experimental outcome.

Quasi-equilibrium processes in two-dimensional electron system over superfluid helium

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Surface electrons (SE) localized over liquid helium form a two-dimensional system with equilibrium properties depending on the relation between mean kinetic energy of the charges and Coulomb interaction energy. The phase diagram of SE system in coordinates temperature - surface density has the separation line between itinerant (gas) and crystalline phases. The SE properties depend on their interaction with helium surface oscillations (ripples). The weakness of electron-ripple interaction in gas SE phase results, in the linear transport regime, to the thermal equilibrium between SEs and ripples with the temperature T and the main scattering mechanism is one-ripple processes. However the non-linear regime is easily achieved under increasing the driving electric field along the SE sheet and the effective electron temperature $T_e > T$. As a result the momentum relaxation is still described by one-ripple long wavelength processes whereas the energy relaxation is due to two-ripple processes where SE irradiates two short-wavelength ripples in near opposite directions. We study the non-equilibrium thermodynamic state of SEs and obtain the non-linear current-voltage characteristics. One concludes not only on the nature of SE transport but also on the ripple dispersion curve which follows, in the short wavelength range, the same dependence on wave number as that in long-wavelength limit.

(Solid + Liquid) Equilibria of [Poly(1-Butene) + *n*-Alkane] Binary Mixtures

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Recent industrial applications of poly(1-butene), PBu-1, increased a demand for physicochemical and thermodynamic data concerning this polymer. The solubility of the polymer in three long-chain *n*-alkanes (tridecane, octadecane, tricosane) was studied using a dynamic method and a differential scanning calorimetry (DSC) [1]. It was found that in the first and the second heating runs of the mixture the multiple endotherms for PBu-1 were detected as for pure polymer. This was attributed to the solid-liquid phase transition and the solid-solid phase transition into the tetragonal modification (Form II) of PBu-1 during successive heating runs [2, 3]. On the contrary, in the next few heating runs of the mixture one new endotherm for the same sample was detected. It was assumed that the new higher temperature endotherm was the evidence of the different crystal form of PBu-1 over the systematic thermal conditioning and ageing at room temperature. Performing DSC heating experiments over a large concentration range allowed the construction of the phase diagrams of polymer-solvent system. From this diagrams it was found that the solubility of PBu-1 is the highest in tridecane and the lowest in tricosane. Similar conclusion was made from a dynamic method.

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Onsager theory of confined hard-rod liquid crystal

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We propose a new level of discretization for the study of long hard-rod liquid crystal under the confinement of two parallel walls. Our approach is based on the Onsager integral equation for the one particle orientation distribution function. We slide the system into a set of layers wherein the orientational distribution functions are set homogeneous and assume that the influence of the top and bottom layers can be assimilated to an interaction with another type of hard-rod molecules. This technique can be easily generalized to investigate various geometrically constraint systems. In this first presentation, we have considered the capillarity effect due to the presence of two walls inducing nematic order and we have computed some properties of the surface extrapolation length in a twisted cell.

Intermolecular potential development for organic mercury compounds

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Organic mercury compounds can be found in petroleum and natural gas products in various concentrations. The knowledge of the thermodynamic properties of these compounds is important for the petroleum industry : in addition to their poisoning of industrial catalysts, these compounds damage aluminium alloy heat exchangers and pipelines by corrosion and present a health risk for engineers upon inspection and maintenance of mercury contaminated equipment. Among thermodynamic properties useful for industry, the solubilities of organic mercury compounds such as dimethylmercury ($\text{Hg}(\text{CH}_3)_2$) and diethylmercury ($\text{Hg}(\text{C}_2\text{H}_5)_2$) in organic or aqueous solvents are important to determine. Since experiments are difficult to perform due to the very high toxicity of these molecules, it is very interesting to be able to predict these properties by molecular simulation. We have thus used Monte Carlo techniques to simulate these systems. The first step in this study is to develop the intermolecular and intramolecular potential of such compounds (nothing has been done on this subject in the literature).

Prediction of thermodynamic derivative properties for mixtures by Monte Carlo simulation

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Thermodynamic derivative properties comprise mainly isothermal compressibility, isobaric thermal expansivity and heat capacities. By extension, they comprise also the Joule-Thomson coefficient, which can be obtained by combining heat capacity, isobaric thermal expansivity, molar volume and temperature. These properties are generally difficult to evaluate with equations of state. In a previous work, we showed how statistical fluctuations in the NPT ensemble could be used to evaluate these properties with a good accuracy in the case of pure components and simple gas mixtures [1].

Here, we present two types of applications of this technique to more complex studies of industrial interest : prediction of inversion conditions of natural gas and fluids behaviour near their critical point.

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Monte Carlo simulations of the zero- and first- order perturbative contributions to the compressibility factor of square-well fluids

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Following the procedure developed by Smith et al. [1] (see also ref. [2]), we have determined by MC-NVT simulations the zero- and first-order terms in the expansion of the compressibility factor of square-well fluids in power series of the inverse of the reduced temperature for different densities and well widths. The values of the compressibility factor obtained from this expansion truncated beyond the first order term, are compared with those obtained directly by MC simulations we have performed on the SW system. The aim is to test the rate of convergency of the perturbation expansion and whether this procedure, without any theoretical approximation, is accurate enough. Potential widths λ ranging from 1.1 to 2.0 have been considered. We have found that this approximation is very accurate for any value of the potential width, density and temperature, except perhaps for small potential widths at very low temperatures.

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Liquid-Vapour coexistence curve for square well fluids from a generalized van der Waals theory

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Several theories [1-4] proposed for the coordination number of square-well fluids are used in combination with a generalized van der Waals theory (GvdW) to obtain the liquid-vapour coexistence curve of these fluids. Among them, the coordination number model recently proposed by the authors [4] provides the best agreement with simulation data, although in the neighbourhood of the critical point needs to be improved for low values of the potential width. In spite of this, the predicted values for the critical densities and temperatures as a function of the well width λ are in fairly good agreement with available simulation data [5].

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The activity coefficients at infinite dilution for organic solutes in an ionic liquid

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Very few studies have been done on the activity coefficients at infinite dilution for alkanes, alkenes and aromatic compounds in an ionic liquid [1,2].

In this work the activity coefficients at infinite dilution, γ_{13}^{∞} have been determined for the solutes: alkanes, cycloalkanes, alkenes, alkynes, benzene, and methanol at the temperatures 283.15 K or 298.15 K or 313.15 K or 323.15 K in the ionic liquid: [HMIM][BF₄⁻]. The γ_{13}^{∞} values are discussed in terms of intermolecular interactions.

The partial molar excess enthalpies at infinite dilution, ΔH_1^E have also been determined at 298.15 K from the Gibbs- Helmholtz equation.

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Microcalorimetric study of adsorption of C₂H₄ and O₂ on Ir/SiO₂ and IrCu/SiO₂ catalysts

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The properties of surface on silica supported Ir and Ir-Cu was investigated using microcalorimetry. The addition of Cu causes the dramatic decrease of the adsorption of H₂. Also, the ethylidyne(CH₃C≡) produced upon the adsorption of C₂H₄ was suppressed greatly. It has also been found that the oxidation of C₂H₄ decreased by the addition of Cu when C₂H₄ was adsorbed on the Oxygen pre-adsorbed Ir and IrCu/SiO₂ catalyst.

Conformations and interactions of flexible dendrimers

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Dendrimers represent a new class of polymeric materials with a highly branched architecture and possessing a vast flexibility in their design and molecular architecture. Recent advances in synthetic chemistry have led to the possibility of manipulation of these macromolecular compounds at the nano-scale, opening the way to a vast range of potential applications. In this contribution, we are going to present recent simulational and theoretical approaches to the understanding of the shapes, sizes and conformations of dendrimers and to the effective interactions of the same. It will be demonstrated that dendrimers evolve from "fractal" to "compact" objects with a dense core and a fluffy corona upon increase of their terminal generation number and that the end-monomers are distributed throughout the macromolecules. The effective interaction between the dendrimers is soft and tunable with generation number, displaying a Gaussian form with a prefactor that depends on solvent quality and generation.

Binary and ternary liquid-liquid equilibria for polymer solutions

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Liquid-liquid equilibrium (LLE) is more to model than vapor-liquid equilibrium, because two highly non-ideal phases with different compositions must be described simultaneously by the same model. At this point it has only been studied to a limited extent in the literature for polymer solutions, and it has thus not been clarified which polymer thermodynamic models, if any, should be used for the calculation of LLE. The major reason for this is probably that it is a difficult numerical challenge to construct a robust algorithm for LLE, since the governing equations require very accurate initial estimates if solved by multi-variable second-order methods. If e.g. an ordinary PT-flash algorithm is used for the calculation, it is a time-consuming task to construct the entire liquid-liquid coexistence curve. The limited amount of systematic literature studies of LLE for binary- and ternary systems follow this semi-manual approach. It should be emphasized that such an approach does not allow for a production of phase diagrams on a routine basis. In this work, two algorithms have been developed that generate the liquid-liquid coexistence curve automatically once the system has been specified. One algorithm applies for binary LLE, the other for ternary LLE. A tracing method for the construction of the LLE coexistence curve for low-molecular-weight systems has previously been proposed by Fredenslund et al. (1980), but a refined mathematical formulation is required for systems containing polymers. Using the developed LLE algorithms, PC-SAFT has been used for the calculation of liquid-liquid coexisting curves. The investigation shows, that PC-SAFT holds a very good potential for the representation of these complex systems

Simple Models of Single Repulsive, Attractive and Amphiphilic Chains in Normal and Associated Supercritical Solvents: Molecular Simulation Study

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Solvent driven changes in chain conformations that occur in normal and associated supercritical solvents have been investigated systematically using simple molecular models. Repulsive and attractive chains are modeled as 10 connected hard-sphere and square-well segments, respectively, and the amphiphilic chain is represented by diblock chain consisting of five square-well and five hard-sphere segments. The normal solvent is modeled as a square-well fluid and the associated solvent is represented by the extended primitive model of water. Using the configurational-bias Monte Carlo combined with the parallel tempering technique, we calculate the mean square end-to-end distance and radius of gyration for the single repulsive, attractive and amphiphilic chains over a broad range of densities and temperatures. Subsequently, the coil-to-globule transition temperature at which the chain adopts a quasi-ideal conformation is determined.

Computer Simulation Study of a First Order Phase Transition: The Condensation of a Droplet.

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The condensation of a super-saturated vapour enclosed in a finite system is considered. A theoretical analysis reveals that the vapor is found to be stable at densities well above coexistence, while the system size required for the phase transition to occur is found to be governed by a typical length scale which depends on the coexistence densities, temperature and surface tension. This phase transition is signaled by a typical length scale which depends on the coexistence densities, temperature and surface tension. When fluctuations are neglected, the chemical potential is seen to show a discontinuous drop at the spinodal point.

In order to test the theoretical predictions we perform a simulation study of condensation and obtain van der Waals loops in the chemical potential/density and pressure/density plane. The results confirm that the effective spinodal point where the system becomes unstable may be identified with a phase transition in which large density fluctuations lead to the formation of a liquid droplet. A study of the fluctuations in the system allow us to measure the free energy of formation of liquid droplets and slabs, as well as to test the nucleation theorem.

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Modeling Liquid Mixture Viscosities Via the Use of an Equation of State- Based Model

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A viscosity model based on the Eyring's theory and a cubic equation of state (Soave-Redlich-Kwong and Peng-Robinson) has been applied to the correlation and prediction of experimental liquid viscosities of aqueous and non-aqueous binary mixtures within a wide range of temperature, pressure and composition (encompassing low-pressure and compressed liquid conditions). The different degrees of asymmetry of the viscosity-composition behavior exhibited by the binary mixtures considered in this study were conveniently handled via the application of the Wong-Sandler approach for the mixing rules used in the aforementioned equations of state. The results obtained were highly satisfactory for various non-aqueous (non-polar/non-polar, polar/non-polar and polar/polar) and aqueous (water/non-polar, water/polar) binary mixtures over the whole composition range at a low pressure. The predictive capabilities of the present approach were also verified in the representation of liquid viscosities at elevated pressures preserving the same model parameters previously obtained at low pressure.

Solid-liquid equilibrium prediction in the acetic acid(1) – cyclohexane(2) system

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Solid – liquid¹ and vapor-liquid² equilibrium was measured in our laboratory on the acetic acid – cyclohexane system. Excess enthalpies for the system were found in literature³. Using these data and enthalpies of melting of the both pure components calculations of the simple eutectic solid-liquid equilibrium were performed.

First approximation of the ideal mixture yielded eutectic point with $\Delta T \cong 50^\circ$ and mole fraction of acid 0.25 instead of 0.08.

The two-parameter Redlich-Kister equation fitted in this case activity coefficient unsatisfactorily as systems with organic acids embodied uncommonly steep limiting part. Also a flat part of acetic acid solubility was not reproduced properly – S-shape was obtained instead.

The six-parameter Redlich-Kister equation yielded very good results.

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Solubility of Ionic Liquid [emim][PF₆] in Alcohols

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Ionic Liquids (ILs) are new generation of solvents for catalysis and synthesis which have been demonstrated as potential successful replacements for conventional media in chemical processes. To design any process involving ionic liquids on an industrial scale it is necessary to know a range of physical properties including viscosity, density, interfacial tension and heat capacity, as well as liquid-liquid equilibrium (LLE) and solid-liquid equilibrium (SLE) data.

In our previous work the solubility of 1-ethyl-3-methyl-imidazolium hexafluorophosphate, [emim][PF₆] in aromatic hydrocarbons (benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene) and of 1-butyl-3-methyl-imidazolium hexafluorophosphate, [bmim][PF₆] in the same aromatic hydrocarbons, and in *n*-alkanes (pentane, hexane, heptane, octane) and in cyclohydrocarbons (cyclopentane, cyclohexane) has been measured [1].

Recent work presents solid-liquid equilibrium and liquid-liquid equilibrium phase diagrams determined for [emim][PF₆] + alcohols by a dynamic method. In every cases, with the exception of methanol, there are miscibility gaps. The shape of the equilibrium curve is similar for [emim][PF₆] in every alcohol. The observations of upper critical solution temperatures were limited by the boiling temperature of the solvent. The solubility of [emim][PF₆] decreases with an increase in the chain length of the alcohol.

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Standard partial molar volumes of ions in solvents

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The standard partial molar volumes of many electrolytes, mainly uni-univalent, in various solvents are known [1]. These can be separated into the ionic values by accepted assumptions. These values consist of the sum of the intrinsic volume, the (negative) electrostriction, and any solvent structural effects. Intrinsic volumes of ions were recently published [2]. The electrostriction can be calculated from the pressure dependence of the relative permittivity, according to either the Benson & Copeland [3] expression or the more elaborate shell-by-shell calculation according to Marcus and Hefter [4]. For hydrogen bonding solvents: water, MeOH, EtOH, EG, FA, NMF, and NMA, and for dipolar aprotic solvents, such as acetone, PC, MeNO₂, MeCN, DMF, and DMSO, the calculated values agree well with the experimental ones without requiring a structural term. The shell-by-shell calculation appears to be the more accurate one for cations but the simpler one is better for the anions if the electrostriction is appreciable. For very large (hydrophobic) ions a structural term is required, fitted with group contributions, but cannot as yet be independently estimated.

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Experimental Excess Molar
Enthalpies of ethylnonafluorobuthyl
ether + n-alkane at 298.15 K.

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The purpose of this work is to report experimental H_m^E {x ethylnonafluorobuthyl ether + (1-x) alkane (hexane, or octane, or decane, or dodecane)} at the temperature of 298.15 K and atmospheric pressure. These systems have been chosen because the mixtures containing hydrofluoroethers and alkanes have been proposed recently as alternative environmentally friendly refrigerants, fire-extinguishers, foam blowing agents[1], solvents and vapour desiccants in the cleaning process of semiconductors [2]. Values of excess molar enthalpies were measured using a Calvet microcalorimeter. The binary experimental data were fitted using a Redlich-Kister variable-degree polynomial[3]. The excess molar enthalpy are positive for all the mixtures.

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Relation between entropy and
segregation coefficient for system
Al(or Pb)-impurity

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In our previous works influences of the high gravitation on coefficient of segregation in Al and Pb experimentally were investigated. The micro diagrams of a state Al(or Pb) - impurity were constructed in view of the arisen hydro dynamical pressure in a liquid at centrifugation of a liquid, that has affected temperatures of the melting Al(Pb)-impurity. At these constructions were assumed, that the concentration influences coefficient of segregation of impurity insignificantly. However, in the literature of thermodynamics of regular solutions is shown, that coefficient of segregation depends not only on concentration of impurity, but also on thermodynamic parameters of a melt - heat of melting of enthalpy and including, entropy. The purpose of the present message - to establish ratio between coefficient of segregation and entropy for some systems Al(Pb) - impurity. Proceeding from general thermodynamic situations is present where K-coefficient of segregation of an impurity; s, C_M concentration of impurity in solid and liquid solvents, ΔH_m and ΔS_m enthalpy and entropy of the melting; ΔH_L , ΔH_s , and ΔS_L , ΔS_s - accordingly enthalpy and entropy of displacement of components in a liquid and solid condition. Sizes ΔH_m and ΔS_m concern besides component, the relation of which concentration in solid and liquid phases is accepted for coefficient of segregation K_0 . If a liquid solution - ideal, and the firm solution - diluted regular, it's possible to use more simplified ratio.

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Research of morphological feature of monocrystals brought up in conditions of the high gravitation

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The study of influence of strong gravitation on the process of growth crystals is a little investigated area. In terrestrial conditions the strong gravitation can be simulated placing growing material in a field of centrifugal forces. The description of morphological features of monocrystals of aluminum of high clearness (99,9999%) is given here, crystallized in a field of centrifugal forces on installation allowing to create in an alloy acceleration up to 10^3g (g-acceleration of a terrestrial gravitation) the results of research, one of, features – formation of a deepening on open an end face of a monocrystal are given. The sample was located in graphite test tube, which previously was exposed digestion at 1273K. The sample with graphite test tube was located in quartz ampoule. After pumping out and soldering up the ampoule was placed horizontal in the furnace, placed on shoulders a centrifuge. Crystallization was made with speed of 1–3mm/min. Frequency of rotation of a centrifuge was equal to 1500 of revolutions/min. Were observed the next features on a surface of monocrystals. The cross section of monocrystals has some rejections from the form of a circle, that corresponds to research of S.Barua. On a surface of a crystal there are strips of growth, which frame halt of surface, that is the strips are divided into two equal halfcircles with unit which is taking place in the point of a surface perpendicularly which leaves tangential speed.

Decay of time-correlation functions and molecular transport mechanisms in the Lennard-Jones fluid from MD simulations

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In time-correlation function theory, transport coefficients are either expressed as integrals of time-correlation functions of their corresponding thermodynamic fluxes (Green-Kubo integrals) or, equivalently, they are related to the long-time limit of the slope of generalized mean-squared displacement functions (Einstein relations). These expressions are employed in molecular dynamics (MD) simulations to determine the viscosity, bulk viscosity, thermal conductivity and the diffusion coefficient. Moreover, time-correlation functions themselves are interesting subjects to study as their decay behaviour provides insights into the transport mechanisms on the molecular scale. Recently, the viscosity, bulk viscosity and the self-diffusion coefficient of the Lennard-Jones fluid were determined by MD simulations over a wide range of fluid states with high accuracy employing the Einstein relation method. With these results, the temperature and density dependence of the transport coefficients could be characterized. Furthermore, the corresponding time-correlation functions were calculated at every simulated state point. In this presentation, the decay behaviour of the shear stress, pressure fluctuation and velocity autocorrelation functions will be analyzed and interpreted in terms of the underlying molecular transport mechanisms. Particular attention will be given to the influence of cluster formation on the transport coefficients in the gas region and the decay of the time-correlation functions in the vicinity of the critical point and at high densities. Finally, the influence of the molecular transport mechanisms on the density and temperature will be discussed.

Isobaric Expansions of Aqueous Binary Mixtures of Ethylaminoethanol from 283 to 303 K

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Accurate density data has been obtained in aqueous binary mixtures of ethylaminoethanol, over the whole composition range at intervals of 5 K in the temperature between 283 and 303 K. Thermal expansibility effects on this amphiphile/water mixture are analysed in terms of excess molar isobaric expansions, $E_{p,m}^E$, for the mixture, and of excess apparent molar isobaric expansions, $E_{p,\phi,i}^E$, for both chemical substances in the mixture.

Limiting excess partial molar isobaric expansions have been calculated as well, from the temperature dependence of limiting excess partial molar volumes. An analytical method based on Redlich-Kister fitting equations of V_m^E as a function of the mole fractions has been used to obtain $V_m^{E,\infty}$.

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Virial Coefficients and Critical Properties of Quadrupolar Lennard-Jones Diatomics

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Recently, we have been involved in the calculation of second virial coefficients of quadrupolar [1] and dipolar [2] Lennard-Jones dimers and shown that this models allow for an accurate description of experimental results for the crossed virial coefficient of mixtures such as Xenon and Carbon Dioxide [3].

In this communication we present results for the third virial coefficient of quadrupolar Lennard-Jones dimers [4]. The coefficients are employed to predict the critical properties from two virial series. The first one employs the exact second and third virial coefficients. The second one approximates the fourth order contribution by using estimates obtained for hard dimers [5]. It is found that both methods yield fairly good predictions, with a somewhat better performance of the approximate fourth order expansion. The two methods are complementary, however, because they consistently bracket the exact value as determined from computer simulations [6].

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Competition of Percolation and Phase Separation in a Fluid of Adhesive Hard Spheres

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Many systems composed of mesoscopic particles interact through attractive forces whose range is very short in comparison with the particle diameter. Examples include colloidal silica suspensions, copolymer micelles and solutions of globular proteins.

Such systems present considerable difficulties to computer simulation, since physically important configurations constitute a tiny fraction of the whole configuration space. Furthermore, the formation of large, long-lived clusters impairs ergodic sampling.

Using a combination of special Monte Carlo techniques, we study the interplay of percolation and phase separation in the archetypal model for systems with short-range attraction: Baxter's adhesive hard spheres. We obtain the first numerical estimate for the fluid-fluid critical point, finding that it lies deep within the percolated regime, in contrast to the existing analytic predictions of the Percus-Yevick compressibility equation.

Adsorption hysteresis in ink-bottle pore

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To examine the mechanism of the adsorption hysteresis in ink-bottle pores, we measured the temperature dependence of the adsorption-desorption isotherms of argon, oxygen, nitrogen, and carbon dioxide onto SBA-16 ordered mesoporous material with cagelike pores. The hysteresis loop always shrank with increasing temperature and eventually disappeared at a hysteresis temperature (T_h), well below the bulk critical temperature (T_c). When the relative pressures p/p_0 of the capillary condensation and evaporation are plotted as a function of reduced temperature T/T_c , all the data are represented by a common curve. We also calculated the temperature dependence of the capillary condensation and evaporation pressures under the assumption that adsorption and desorption in an ink-bottle pore may be regarded as the process of disappearance and formation of a gas bubble in a liquid droplet confined to the pore. A fit between the observed and calculated transition pressures in a wide temperature range was reasonable in the light of several assumption and approximations used. This clearly indicates that the energy barrier for the formation and disappearance of vapor bubbles in the liquid confined to the pores is responsible for the appearance of the adsorption hysteresis and the hysteresis temperature is not concerned with the so-called capillary criticality. At temperatures higher than T_h , the reversible capillary condensation takes place, because the energy barrier between a full liquid pore and the vapor coexisting with the liquid film becomes surmountable.

Modification of the Supercritical Temperature-dependent Attractive Parameter of a Simplified Perturbed Hard Sphere Equation of State

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Abstract

A simplified perturbed hard-sphere equation of state (SPHS EOS) has been developed and the temperature dependence of the parameter $a(T)$ has been improved by separating it for the subcritical and the supercritical temperatures. By equating the first and the second derivatives of $a(T)$ with respect to temperature, the supercritical function retains one of the three constants obtained from the vapor pressure fit. This approach improved prediction of location of 56 c_p maxima (T_r^M) data points of selected pure fluids compiled by Kim^[1], but not its magnitude (c_p^M).

For mixtures, the total absolute deviations in T_r^M of methanol-acetone and n-pentane-acetone binary mixtures c_p at supercritical temperatures^[2] calculated using the SPHS EOS is about one-half of those calculated using the Peng-Robinson EOS. This study showed that proposed modification could be translated into improvement in heat capacity calculations only if the crossover problem is solved.

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The P-ρ-T dependence of Methanol + Benzol and Methanol + Ethylbenzol solutions

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Density is one of the main physico-chemical characteristics of substances. Therefore its study is very important for technological processes, calculations and for modernization of solutions theories. There is a lack of information in the literature about the density of liquid solutions. To counter this, the present work contains the measurement of methyl alcohol solutions density and aromatic hydrocarbons (benzol, ethylbenzol). The investigation has been held by the method of hydrostatic weighing in the temperature interval 290-500 K and pressure 0.1 – 60 MPa at mass concentration. The results of the experiments show that solutions density properties digress from the rule of additive to the negative sides; and the size of digressing depends on temperature and pressure. The concentrations dependence of methanol-benzol and methanol ethylbenzol systems density. For each of the solutions the state view equation may be used.

$$\rho^4 = A + BP^{0.5} + CP$$

Where P is pressure in MPa; A,B,C – coefficients depending on temperature.

For each solutions by the method of the minimum square the coefficients of A,B,C have been calculated and described by the following

$$A = \sum_{i=1}^5 a_i T^i; B = \sum_{i=1}^6 b_i T^i; C = \sum_{i=1}^6 c_i T^i;$$

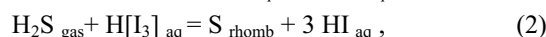
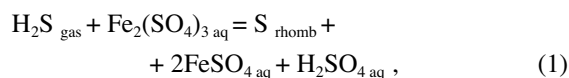
The state equation describes the whole massif of the experimental properties with the error 0.05 – 0.1%.

Thermodynamics Of The Reactions Of The Liquid-Phase Redox- Processes Of Processing Of Hydrogen Sulphide-Containing Gases

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Thermodynamics of the reactions of the liquid-phase deposition of the elementary sulphur from hydrogen sulphide and hydrogen sulphide containing gases presents interest for development of the technological processes of hydrogen sulphide-containing gases from hydrogen sulphide purification with simultaneous elementary sulphur obtaining. The ferro-ferrisulphate and iodide-thriiodide redox-processes, based on using following reactions:



were investigated in this research by two methods – calorimeter and electrochemical. Studying of the hydrogen sulphide oxidation by Fe (III) sulphate and complex iod $\text{H}[\text{I}_3]$ solutions was carried in solute isoperibolic calorimeter at standard conditions. Values of enthalpies of the reaction (1) and (2) were obtained by the special selective thermochemical cycles. On their base along with using reference data on entropy of products of the reactions and original substances temperature relations of Gibbs Energy and the equilibrium constants of the hydrogen sulphide oxidation processes were obtained. It is found that temperature greatly influences on values of equilibrium constants. However, these reactions are practically irreversible even at 373 K.

Thermophysical properties of fluids: From simple models to applications

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Recent systematic and extensive computer simulations on realistic models have shown that the long-range interactions have only marginal effect on the properties of fluids. This finding justifies the use of short-range models upon which a perturbation theory may be developed. Moreover, such models are usually also amenable to a theoretical treatment. Extended primitive models for water, methanol, ethanol, and carbon dioxide have been developed and two types of their applications to fluids are exemplified: (i) expressions for the thermodynamic properties of real fluids in a perturbed form are derived, and (ii) the primitive models are used directly in simulation studies to investigate the origin of specific phenomena, as e.g. preferential solvation in the mixed water-methanol solvent.

Influence of the concentration of associating fluids in the local tetrahedral structure of water

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The non-ideal behavior of the structural properties of aqueous solutions of associating fluids has been studied through molecular dynamic simulations. Mixtures of water plus methanol, acetone and dimethyl sulfoxide has been analyzed in order to study the influence of the solute concentration in the local structure of the water molecules in the mixture. The orientational order parameter q [1], which measures the tendency of the water molecules to adopt tetrahedral structures, have been computed for water molecules with these three solutes. We have found a different tendency, being the dimethyl sulfoxide who most perturb the local order of water, followed by the acetone and methanol. This parameter indicates a reduction in the local tetrahedral order of water when the solute concentration is increased, followed by a clear minimum at different concentrations according to the solute, probably due to the formation of different water-solute complexes. The degree of perturbation caused by the solute in the local structure is reflected dynamically in the variation of the hydrogen bond lifetimes[2] between water-water and water-solute molecules.

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Calculations of chemical potential of hard discs using Monte Carlo simulations

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The aim of this work is to verify the applicability of Scaled-particle Monte Carlo (SP-MC) simulations in case of two dimensional system. We calculate chemical potentials of simple and binary systems of hard discs in a large interval of densities [1]. The comparison was accomplished with data obtained from correlation of received simulation data with results from another method using computer simulations [1] and with results obtained from a number of equations of state [2,3]. It is possible to say that the SP-MC method approved itself also for calculations in case of the two dimensional hard bodies. The results are very accurate and these algorithm can be ranked among the most accurate methods using computer simulations.

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Acknowledgements:

This work has been supported by Centre of Complex Molecular Systems and Biomolecules under grant No.LN00A032.

2D phase separation in fluorinated / hydrogenated systems by MC simulations

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It is well known that hydrocarbons and fluorocarbons tend to demix. In a recent work we obtained experimental evidence of phase separation in mixed films of fluorinated and non-fluorinated alcohols at the air-water interface. Moreover, the coexisting phases display peculiar geometric shapes that could be observed by AFM microscopy.

In this work we have been able to model the experimental results by MC simulation, using a very simple model. Basically, only a section of the monolayer was simulated using an united atom Lennard-Jones potential [1] and a two-dimensional simulation box. The effects of temperature, density and deviations from the Lorentz – Berthelot combining rules were systematically investigated. The simulation results show that high densities and positive deviations to the Lorentz rule are the key factors to the formation of the geometric patterns observed experimentally.

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Acknowledgements:

This work has been supported by Centre of Complex Molecular Systems and Biomolecules under grant No.LN00A032.

Surface scaling function for critical adsorption and the Casimir torque in a wedge

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Geometrical structures of confining surfaces modify the critical adsorption of a binary liquid mixture. We calculate, within the framework of mean-field theory, the temperature dependence of the order parameter profile in a wedge (with opening angle γ), and close to a ridge ($\gamma > \pi$), both above and below the critical temperature T_c of demixing. In order to characterize the effect of the wedge on critical adsorption we introduce a suitably defined *reduced excess adsorption*

$(\Gamma_{\pm}(\gamma, \tau))$. The amplitude of this quantity diverges as $\Gamma_{\pm}(\gamma) \sim 1/\gamma$ for small opening angles, is linear close to $\gamma = \pi$ for $\gamma < \pi$ and diverges exponential-ly for $\gamma > \pi$. There is evidence that, within mean-field theory, the ratio $\Gamma_+(\gamma)/\Gamma_-(\gamma)$ is independent of γ . We calculate the Casimir torque acting on the sides of the wedge as a function of the opening angle using the *renormalized* stress tensor. The torque is a linear function of $1/\gamma^2$.

Critical behaviour of homopolymers studied by the soft-SAFT EOS

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SAFT is becoming a standard equation for engineering purposes, as well as an approach to test molecular theories in predicting the properties of complex fluids. Both features are considered in this work, in which we use the soft-SAFT equation of state to predict the critical constants versus chain length for pure polymers. We study the dependence of the critical properties of chains up to 10^6 monomer units. The equation is able to accurately predict the critical properties for short chain lengths and the infinite chain length scaling regime, within the same assumptions. Soft-SAFT gives quantitative agreement with experimental and Monte Carlo simulation data, available only for short *n*-alkanes. For very long chains, the equation predicts mean-field scaling behaviour, as expected. Moreover, it is found that the critical compressibility factor of an infinitely long *n*-alkane chain equals 1/5. This is not contradictory to Wertheim's theory, as demonstrated.

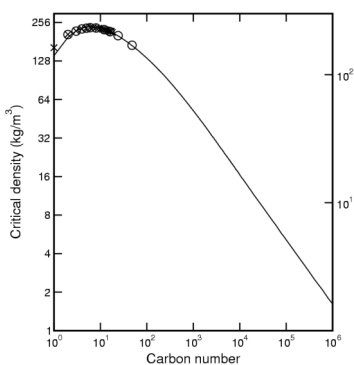


Figure. Mass critical density as a function of the number of monomer units. Crosses: experimental. Circles: molecular simulations. Line: soft-SAFT.

Equation of State and Volumetric Properties of some Practically Important of Fluids

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An analytical cubic equation of state (EoS), derived by Ihm et al. was applied to N₂, O₂, and SF₆ systems, which are important from standpoint of industry. The best available effective isotropic pair-interaction potential energy functions have been taken to evaluate second virial coefficients for each system required by the EoS. The rest of the corresponding parameters of the EoS are insensitive to the details shape of the potential and are calculated through LJ(12-6) model potential. The calculated second virial coefficients were applied to predict the density of all systems in both sub-critical and supercritical regions. Seemingly, good consistency could be obtained with experiment for all systems. A comparison has been made between this EoS and other well-known EoSs.

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Equation of State and PVT Properties of Refrigerants Based on Speed of Sound Data

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This work describes a method for predicting constants in the equation of state for saturated and compressed refrigerant fluid from analysis of speed of sound results and using two scaling constants. The theoretical EOS is that of Song and Mason [1], which is based on statistical-mechanical perturbation theory, and the two constants are enthalpy of vaporization and molar density, both at the normal boiling temperature. The second virial coefficients required by the EOS are calculated from a two-parameter corresponding states correlation, which is obtained from a speed of sound data analysis with the two constants enthalpy of vaporization and molar density, both at the normal boiling temperature as scaling parameters. This EOS is applied to six refrigerants: 1) 1,1-dichloro-2,2,2-trifluoro-ethane (R123), 1,1,1,2-Tetrafluoroethane (R134a), 1,1-dichloro-1-fluoroethane (R141b), 1,1-difluoroethane (R152a), chlorodifluoromethane (R22), and difluoromethane (R32). The results show that the liquidlike densities of these refrigerants at the temperature range $0.8 T_{nb} < T < 1.1 T_c$ can be predicted to within 3%.

In contrast to other EOSs proposed for this class of fluids which are specific for a narrow range of temperature of fluids, the main advantage of the present work is that, given second virial coefficient for the gas and some high density information, the entire PVT surface of refrigerants fluids in a nearly wide range of temperature and pressure with a good accuracy will be predicted.

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Understanding the thermodynamics and fluid phase equilibria of polymer-colloid and polymer-solvent systems

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The features governing the phase equilibria in purely repulsive systems of hard spheres and hard sphere chains are first examined, using a simple description based on the Wertheim TPT1 theory. For hard spheres of the same size as the segments of the chain, the system is fully miscible. In the case of colloid-polymer systems where the hard spheres representing the colloidal particles are made much larger than the chain segments, the system demixes into two phases. The like- (colloid-colloid, polymer-polymer) and the unlike (polymer-colloid) interactions are treated on the same microscopic level, i.e. the well-known Asakura-Oosawa (AO) approximations are not used. Both the effect of varying the chain length and the diameter of segments in the polymer are determined from the spinodal instability. The maximum value of the segment diameter, which may produce phase separation, is determined from a simple approximate analysis. The mechanism of the phase separation is found to be enthalpic. The nature of fluid phase equilibria in polymer-solvent systems is completely different. For simple systems in which the size and energy parameters of the spherical molecules and the chain segments are all equivalent, a region of liquid-liquid coexistence is found when the chain length is increased, and the system exhibits a lower critical solution temperature (LCST). The nature of LCST behaviour is studied using a mean-field treatment of the attractions. In both cases, the effect of polydispersity is also examined using continuous thermodynamics, and the results are compared with those for a discrete ternary mixture.

Development of a transferable guest-host potential model for molecular simulation of hydrocarbons adsorption in zeolites. Selectivity of alkane/alkene mixture in silicalite

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A meticulous optimisation process [1] has been used to determine a transferable guest-host force field. Using the Anisotropic United Atom (AUA4) potential model previously developed for hydrocarbons properties and mixing rules, we are now able to predict single component and binary mixture adsorption in zeolites. The transferability of the proposed force field is demonstrated for alkane and alkene molecules.

Grand Canonical Monte Carlo simulations have been performed to study the behaviour of linear and branched alkanes, and alkenes in silicalite zeolite. Pure component adsorption isotherms show good agreement with the various experiments. Isothermic heats of adsorption Q_{st}^0 and adsorption entropies have also been calculated and compared to experiments [2,3].

Alkane/alkene selectivity study in silicalite has been carried out. Entropic effects are responsible for a reversal in selectivity at high loading for ethane/ethylene mixture. The reversal of adsorption selectivity disappears for longer alkane/alkene mixtures since the effect of the double bond strongly decreases with chain length.

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Phase behaviour of mixed-solvent electrolyte systems

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The effect adding charged species to binary liquid solutions is a complex phenomenon due to the variety of interactions involved, and to the fact that the magnitude of the interactions is strongly influenced by the nature of the charged species added and their concentration. In this work we investigate the phase behaviour of water + alcohol binary mixtures in the presence of salt using an extension of the statistical associating fluid theory [1,2]. Pure component intermolecular parameters for the non-ionic species are determined by comparison with experimental vapour-pressures and saturated liquid densities, and two water + alcohol unlike adjustable parameters are used to optimise the agreement with experiment. The salt is incorporated in the model as fully dissociated, where anion and cation are modelled as two hard-spheres of different size with long-range Coulombic interactions treated in the mean spherical approximation at the level of the restricted primitive model. The experimental Pauling radii are used for each of the ions. Water-ion and alcohol-ion attractive interactions are obtained by studying the VLE at different temperatures. We observe that the choice of dielectric constant incorporated in the approach crucially determines the ability of the calculations to reproduce the experimental data; a number of approximations to incorporate the dielectrics of the solvents are discussed. The phase behaviour of the water+alcohol+salt mixtures is then studied without modification of the binary intermolecular parameters.

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Excess volumes and excess isentropic compressibilities of some esters + glycols system at T = (298.15 and 308.15) K

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Excess molar volumes V_m^E , and excess isentropic compressibilities, K_s^E for the binary mixtures of esters (Methyl acetate, Ethyl acetate, Butyl acetate and Isoamyl acetate) + glycol (Ethyleneglycol, Propyleneglycol, diethyleneglycol and triethyleneglycol) have been calculated from the experimentally measured densities and speed of sound at T = (298.15 and 308.15) K. The V_m^E values for all the systems except for ethyl acetate, butyl acetate, isoamyl acetate + propylene glycol were found negative over the entire mole fraction range. A rise in temperature has been found to result into more negative V_m^E values. A perusal at the K_s^E values reveals large and negative values over the whole composition range. The speed of sound of all the mixtures were predicted by free length theory (FLT) and collision factor theories (CFT). CFT calculations were found to predict the speed of sound reasonably better than FLT formulations, which showed large deviations from the experimental values

A Grand Canonical Monte-Carlo study of selenium in silicalite-1 zeolite: Adsorption mechanism, atomic and electronic structure

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We present a tight binding grand canonical Monte Carlo (TB-GCMC) simulation of the adsorption of Selenium in silicalite-1 zeolite. The calculated adsorption / desorption isotherms exhibit a large hysteresis loop, unexpected for adsorption in a microporous system with pore size of the order of 0.5 nanometers. This behavior results from the favored two-fold co-ordinated chain structure of Selenium that grows inside the complex 3-dimensional microchannel network of silicalite. The atomic and electronic structure of the confined phase are discussed as a function of the filling rate: *ab initio* calculations indicate that a semi conductor to metal transition, resulting from a change of the chain configurations at large filling rates can be expected.

Non-equilibrium molecular dynamics simulations of molten sodium chloride

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The main problems arising in all non-equilibrium simulations come from temperature control. When local flows become important, it is not a simple matter to differentiate between the flow velocity and thermal motion. A way to bypass this problem is to control the temperature given by the "configurational expression", which does not depend on velocity. We compare the responses of molten NaCl to strong shear and strong constant and oscillating electric fields using kinetic and configurational thermostats. The differences in response increase with the increase in the external perturbation, and in very strong fields one can observe striking structural differences. In the case of shear flow, the differences are of general nature seen in all liquids (string phase vs. shear thickening and turbulence), while in an electric field they are peculiar to ionic fluids and are related to the degree of dissociation. We also show how structural properties can be deduced by evaluating the configurational temperature expression.

Soret Effect in Complex Fluids

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The presence of a thermal gradient in a fluid mixture or particle dispersion induces a relative matter flow of the components known as thermal diffusion or Soret effect, which plays a crucial role in many naturally occurring processes, and set the scene for giant fluctuations in non-isothermal mixtures. Although clearly framed by non-equilibrium thermodynamics, the Soret effect still lacks a general microscopic picture. It is particularly puzzling the occurrence of 'negative' Soret effects, relatively rare situations where particles tend to concentrate at the hot side. By measuring the Soret coefficient S_T of charged micelles, we have recently investigated¹ charge contributions to thermal diffusion, showing that electrostatic interactions play a crucial role on the Soret effect. In the single-particle regime, S_T grows as the square of the Debye-Hückel length. Yet, collective effects yield a fully reversed situation even at very low c . Single particle behaviour and collective contributions can be understood in terms of a 'microscopic thermocapillary effect'. Yet, a general relation between thermal diffusion and microscopic particle-solvent and interparticle interactions is still lacking. We present results relative to a number of systems ranging from proteins near crystallisation to mixed ionic-nonionic micelles, showing that the Soret coefficient can be carefully tuned in amplitude and even is sign by controlling solvent-particle interactions.

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Description of the behaviour of strongly non-ideal mixtures with GEQUAC

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To describe phase equilibria in a physically consistent manner, the correct consideration of the different intermolecular interactions has to be accounted for.

In the GEQUAC-model (Group Surface Explicit QUAsi-Chemical theory) interactions are characterized by their strength as well as by the degree of mutual orientation [1, 2]. In deriving GEQUAC all the necessary symmetry conditions are considered resulting in an equation not showing the inconsistencies regarding the local compositions as other renowned models do.

In previous work GEQUAC was developed as a group-contribution method for alcohols+alkanes and for ketones+alkanes. The simultaneous prediction of VLE data and enthalpies of mixing with high accuracy shows the principal physical correctness of the model equation. Present work concentrates on finding the model parameters for ketones+alkanes. With these binary parameters we will be able to predict ternary mixtures of alkanes + alcohols + ketones.

Parallel to this parameter-finding procedure the further development of the model is based on Monte-Carlo simulations. Special focus is put on the correct accounting for the mutual orientation of poles on the molecules' surfaces to reliably describe isomeric behaviour.

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Molecular Simulation of Adsorption and Diffusion of Simple Fluids Confined in Realistic Models of Nanoporous Carbons

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We present a reconstruction method to build models that quantitatively match the experimental diffraction data of real nanoporous carbons. Our approach is based on reverse Monte Carlo (MC) with carefully selected constraints that describe the three-body correlations. Through successive MC moves, using a simulated annealing scheme, the model structure is matched to the experimental diffraction data, subject to the imposed three-body constraints.

We modeled a series of saccharose-based carbons and tested the resulting models against high resolution transmission electron microscopy (TEM) data. Simulated TEM images of the resulting structural models are in very good agreement with experimental ones.

For the carbons studied, the pore structure is highly convoluted, and the commonly used slit pore model is not appropriate. We simulated adsorption and diffusion of Lennard-Jones nitrogen using grand canonical MC and canonical molecular dynamics, respectively. The adsorption isotherms and self-diffusion rates in these models do not resemble those for fluids in slit pores having the same pore size distribution. The isosteric heats of adsorption and self-diffusivities in these models show the behaviour observed experimentally. This behaviour is qualitatively different than that in the slit pore model.

Solubility of imidazoles,
benzimidazoles and
phenyloimidazoles in different
organic solvents

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The use of imidazoles and their derivatives in chemical processes is becoming increasingly important. Their possibility of metal-complex formation may be widely used in pharmacy. This work presents solubilities of seven imidazoles (1-*H*-imidazole, 2-methylimidazole, 2-methylbenzimidazole, benzimidazole, 2-phenylimidazole, 4,5-diphenylimidazole, 2,4,5-triphenylimidazole in organic solvents (dichloromethane, 1,2-dichloroethane, chloro-1-butane, bromobenze ne, toluene, 2-nitrotoluene) by using liquid chromatography and sythetic method. The solubility of these imidazoles in chloroalkanes is extremely low. In all these solvents studied, the solubility of phenylomidazoles is significantly lower than the solubility of 1-*H*-imidazoles, or benzimidazoles.

Experimental solubility results were compared with values calculated by means of the Wilson, UNIQUAC and NRTL equations utilizing parameters derived from SLE results.

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Thermogravimetric researches of
fullerene like nanoparticles doped
polymers

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Introducing highly dispersive fragments of metal in a polymer matrix influences the nature of its thermal degradation. Thus, the kinetic researches of a thermogravimetry demonstrate the dependence of activation energy of the termodestruction and the temperature of the beginning of disintegration on stability of metal to oxidation with the increase of these values from gallium up to gold [1]. In the present work the thermostability of the systems of polymer - fullerene like nanoparticles were investigated by means of the methods of thermogravimetry. Epoxy and epoxy – acrylic resins were taken as a matrix, into which multilayer carbonic nanotubes and “Astralens” were entered before solidification [2]. The stabilizing influence of such doping is revealed at a minor level of concentration of the introduced components (less than 1 %). The connection between the thermostabilizing effect and the increase of the physical-mechanical characteristics of metal - polymer aggregates were discussed.

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Structural characterization of aqueous electrolytes in contact with rutile surfaces by molecular dynamics

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Molecular dynamics simulations were conducted to characterize the microstructure of the (110) rutile-aqueous electrolyte interface at ambient and high temperatures, for three types of rutile surfaces; neutral non-hydroxylated and hydroxylated, and negatively charged partially hydroxylated. The fully atomistic description of the rutile surface and its interactions with the fluid phase was based on *ab initio* calculations, while the aqueous phase was described by the SPC/E model and the corresponding parameterization for the chloride, rubidium and strontium ions. State conditions, electrolyte composition, and mineral surface density charge were chosen to mimic titration as well as x-ray standing waves experiments. Simulation results for the species axial distributions were compared with the corresponding x-ray data to determine the ion heights and relative locations with respect to rutile surface sites, prior to their use in complexation modeling.

On independence of the solvation of interaction sites of a water molecule

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To support simplifying assumptions used in analytic theories of aqueous systems, we have used computer simulations to examine correlations in the bonding of the individual sites

of a water molecule using two qualitatively different extended primitive models, EPM4 and EPM5. We have studied these correlations not only for the fully interacting water molecule (considered as a solute) but also for a series of other solutes made from the water molecule by turning off some of its interaction sites. We have found that for the EPM5 solvent the local density of water molecules bound to a specific site is independent of the state of the other sites being turned on or off; for the EPM4 solvent such an independence does not hold exactly but the correlations have been found to be very small. These facts fully justify previously used speculative approximations for the calculation of the solvation Helmholtz free energy of a water molecule, and lend also support to the first order thermodynamic perturbation theory of Wertheim.

Water Adsorption on Ordered and Disordered Silica Substrates

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The adsorption properties of water on various silica substrates are investigated by way of Grand Canonical Monte Carlo simulations (GCMC). Using the SPC and PN-TrAZ potential, we have been able to reproduce the experimental adsorption isotherm of water on mesoporous silica surfaces at 300 K. The numerical sample of mesoporous silica glass (pore size: 3.6 nm) was obtained by off-lattice reconstruction, known to reproduce in a realistic way the geometrical complexity of high specific surface Vycor, (chord distribution, and small angle neutron scattering correlation peak). The chemistry of the surface is made realistic by hydroxylation.

The simulated adsorption isotherm and isosteric differential enthalpy of adsorption compare well to experimental data for Vycor, showing the ability of the PN-TrAZ potential to describe the hydrophilic properties of silica surfaces. This study was extended to several crystallographic faces of cristobalite. Their adsorption properties are rather different from each other. The influence of local hydroxyl density is then discussed. It is shown that the hydrophilic properties are not simply related to surface hydroxyl density but are also related to local structure of the silica surface. In spite of the very large hydrophilic differences of the ordered faces, it is possible to reproduce the adsorption isotherm in the mesoporous disordered sample by applying a natural average procedure. The distribution of energy of sites can help to understand these results.

Volume and Compressibility Studies of Amino Carboxylic Acids in Water and Aqueous Sodium Sulphate.

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Various biological processes involve volume changes and hydration of molecules, and their understanding needs a proper idea of the state and the behaviour of the molecules in the medium [1]. To understand these phenomena, model compounds including amino acids [2-4] have been studied. Partial molal volumes and partial molal adiabatic compressibilities of amino acids were obtained in water and aqueous solutions of sodium sulphate at 288.15, 298.15 and 308.15 K. These values were fitted to molal concentration and values at infinite dilution were obtained. Their variations with temperature and their transfer properties from water to aqueous solutions of sodium sulphate were also obtained. The transfers calculated are positive and they increase with increasing concentration of sodium sulphate. It could be concluded that 5-aminopentanoic acid can be taken to be a zwitterions molecule with a distance between the charged atomic groups corresponding to the geometric size of the hydration shells of amino and carboxylic groups [2]. Also the results support the structure-making ability of sodium sulphate [5].

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Pure demixing and ferroelectric transition of binary dipolar mixtures

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Recent computer simulation and reference hypernetted-chain (RHNC) studies have shown the existence of a demixing transition for binary mixtures of hard spheres (HS) and dipolar hard spheres (DHS). These works also indicate that the dipole rich phase is not necessarily orientationally ordered.

Our investigations are focussed on demixing of mixtures bidisperse in dipole moment with a reduced total density of $\rho^* = 0.7$, using the RHNC approximation and a modified mean field theory (MFT) approach.

The RHNC theory is applied to the homogeneous and isotropic phase of the system. When we approach the spinodal - the stability border of this phase - from high temperatures, the predominant phase instabilities are indicated by the divergence of some susceptibilities.

We show that the RHNC approximation indicates demixing without ferroelectric transition not only for DHS/HS mixtures but also for the case of two dipolar components (with ratios of the reduced dipole moments up to about $\mu_2^2/\mu_1^2 = 0.2$).

We also present MFT phase diagrams. Contrary to the RHNC results, demixing is always accompanied by a ferroelectric transition in the MFT approach.

Water and other Complex Fluids Confined to Molecularly Thin Films

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The structural and dynamic properties of confined liquids can differ greatly from the bulk when the confinement is of the order of the molecular dimensions. This is of special interest in aqueous systems, as biological interactions between different species (such as ligands and receptors) take place across nanometrically-confined water films, and the properties of such films have been extensively debated. Using a surface-force balance (SFB) with unique sensitivity in measuring shear stresses across thin films we have been able to probe the dynamic properties of water and of aqueous salt solutions confined to subnanometre films. We find a remarkable contrast with the properties of similarly confined non-associating liquids [for preliminary results see:1, 2]. A related issue, central to biolubrication phenomena, is that of the shear and lubrication afforded by polyelectrolyte brushes where both steric and charge effects are important. We present (time permitting) first results on the forces between compressed, charged brushes sliding past each other, contrasting these with neutral brushes on the one hand and adsorbed polyelectrolytes on the other.

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Speed of Sound of Room Temperature Ionic Liquids

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We present results of the speed of propagation of ultrasound waves in three room temperature ionic liquids (RTILs). To the best of the author's knowledge these are the first sets of data available for RTILs.

Very recently, we designed and built a set of novel microcells with internal volumes ranging from 0.2 to 0.8 cm³ using a non-intrusive method for the determination of the speed of sound. Due both to the very small volumes involved and the non-invasive nature of the method, several advantages emerge: (a) study of expensive and/or chemically aggressive liquids are possible; (b) studies performed in metastable regimes; (c) easiness to achieve high pressures. The cells were used to study the pressure and temperature dependence of the speed of sound of three ionic liquids, [C₄mim][NTf₂], [C₄mim][BF₄], and [C₄mim][PF₆], over broad temperature (265<T/K<325) and pressure (1<p/bar<1600) ranges. These data combined with density values were used to calculate various thermodynamic properties such as compressibilities, expansivities, and heat capacities.

Regimes of Negative Pressures: Speed of Sound Measurements

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We present results of the speed of propagation of ultrasound waves in conventional solvents including regimes of absolute negative pressures. To the best of the author's knowledge they constitute the first successful direct and continuous monitoring of a physical property as metastable states of negative pressure develop.

Very recently, we designed and built a set of novel microcells with internal volumes ranging from 0.2 to 0.8 cm³ which use a non-intrusive method for the determination of the speed of sound. Due both to the reduced volumes involved and the non-invasive nature of the method, several advantages emerge: (a) studies of expensive and/or chemically aggressive liquids are possible; (b) studies performed in metastable regimes; (c) easiness to achieve high pressures. The cells were used to study the pressure and temperature dependence of the speed of sound of protonated (test system) and deuterated acetone over broad temperature (265<T/K<340) and pressure (1<p/bar<1600) ranges. Studies in metastable regimes (pressures down to – 80 bar) were performed using acetone, carbon tetrachloride, ethanol, benzene, and water. These data combined with density values were used to calculate various thermodynamic properties both at high and low (negative) pressures, such as compressibilities, expansivities, and heat capacities.

Phase Behaviour of RTILs' Solutions.
A Theoretical and Experimental Study
Including Pressure and Solvent
Isotope Effects

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In spite of the increasing attention that room temperature ionic liquids (RTILs) have recently deserved in respect to their use in synthesis and catalysis, little about their phase behaviour in solution is known.

The current study focuses on solutions of [C₄mim][PF₆] + ethanol and/or water, on those of [C₄mim][NTf₂] + iso-butanol and/or water, and [C₄mim][BF₄] + water. All systems present partial immiscibility not far from room temperature, becoming thus attractive from a technological perspective.

In the search for a more comprehensive understanding of the phase behaviour of RTIL solutions we have followed the phase diagram shifts due to pressure and isotope effects. Phase diagrams will be discussed using a phenomenological approach based on a Flory-Huggins-like g^E -model coupled with the statistical-mechanical theory of isotope effects.

Combination of the model's parameters with the T-p slope of the critical lines enables us to discuss the magnitude and sign of the enthalpic and volumetric excess properties of these mixtures.

The Phase Diagram of (Water + 3-
Methylpyridine) in the Region of
Large Absolute Negative Pressures

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L-L phase splitting in mixtures of water (H/D) + 3-MP at the limit of pure H₂O as solvent and at low pressure are reported for the first time. The phase diagram is encountered at large absolute negative pressure regimes. These studies constitute the first to report phase transitions in (non-polimeric) fluid mixtures at negative pressures, and the values of tension achieved (-350 bar) constitute a record for macroscopically-sized samples.

The overall behavior of mixtures of water (H/D) + 3-MP is successfully interpreted using a simple g^E -model. At critical concentrations, while mixtures of D₂O + 3-MP always present phase separation irrespective of the applied pressure, when the solvent is pure H₂O a miscibility window with the size of 1600 bar emerges. This phenomenon corresponds to an impressive pressure shift of several hundred atmospheres upon (H/D) solvent isotopic substitution. When this effect is projected onto the temperature-solvent isotopic content at atmospheric pressure, a 70 K immiscibility loop is encountered when D₂O acts as the solvent, while total miscibility occurs for concentrations of D₂O lower than 17 wt.%. An entropic effect originated at the relatively large difference in molar volumes between water and 3-MP is responsible for the location of the phase diagram in the low-concentration region of 3-MP. It is again another (subtle) entropic effect that provokes the abnormally large shift in the phase diagram upon isotopic substitution.

Practical expressions to calculate
molar isentropic compressions and
speeds of sound in thermodynamically
ideal binary liquid mixtures

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The ideal molar isentropic compression and the ideal speed of sound for binary liquid mixtures have been expressed in terms of experimentally determinable and frequently tabulated properties of the pure components. On the basis of a recently published expression for the ideal apparent molar isentropic compression (M. I. Davis, G. Douhéret, J. C. R. Reis and M. J. Blandamer, *Phys. Chem. Chem. Phys.*, 2001, 3, 4555), a practical equation was worked out for the calculation of ideal molar isentropic compressions at any composition of binary mixtures. Combining this new expression with the Newton-Laplace equation yields a practical equation for the calculation of ideal speeds of sound. At given temperature and pressure, the following data is required for each of the pure liquid substances forming the mixture: molar mass, density, speed of sound, molar isobaric heat capacity and molar isobaric expansion. These calculations are illustrated with ideal speeds of sound in five organic-organic and one aqueous organic mixtures.

Surface tensions of the ternary system
water + ethyl butyrate + methanol at
303.15 K and atmospheric pressure

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The surface tension is a fundamental property in the design of process units that involve interface heat and mass transfer. In the last few years we have been developed a research program that consists in the experimental determination of surface and interfacial tensions of ternary mixtures and of their binaries constituents. These data has been used to test correlation and prediction methods.

In this work the surface tension in the ternary liquid mixtures water (1)+ ethyl butyrate (2) + methanol (3) as well as of the constituents binaries has been measured at 303.15 K and atmospheric pressure.

Some thermodynamic equations were used to correlate the surface tension of the binary and ternary systems. The majority of these methods are based on the well known Butler equation [1]. For the prediction of this property we have used the methods of Sprow and Prausnitz [2], Fu et al. [3] and Li et al. [4].

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Determination of surface composition in binary mixtures from the parachor parameter

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The knowledge of the surface composition in a liquid mixture is important because many physical and chemical process of interest depend on the surface and not on the bulk composition. Although, usually both compositions differ^[1]. In this abstract we estimate the surface composition of liquid binary mixtures from measurements of their surface tension, σ_{12} and density, ρ_{12} in the whole composition range. For that, we use Sudgen's equation^[2], which relates surface tension and density in a liquid binary mixture. By assuming that the parachor is mole-wise additive^[1] we can rewrite that equation as

$$x_{1S} = \left(\frac{M_1 \cdot M_2}{M_2 \cdot P_1 - M_1 \cdot P_2} \right) \left(\frac{\sigma_{12}^{1/4}}{\rho_{12}} - \frac{P_2}{M_2} \right)$$

where x_{1S} is the mole fraction of the first component at the surface, P_i is the temperature independent parachor parameter, characteristic of any liquid substance, and M_i the molar mass of pure compound i . The parachor for a given compound can be experimentally calculated from their σ and ρ data, or obtained theoretically from additive group contributions, where each structural group has a given P value^[1]. Both methods differ in about 0.1% for the compounds presented here.

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Molecular Simulations of the Sliding Behavior of Double-Walled Carbon Nanotubes

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We report molecular dynamics simulations of the sliding behaviour of double-walled carbon nanotubes. The simulations show that if the inner nanotube is pulled out part of the way and then released, the inner tube exhibits a damped oscillatory behaviour at GHz frequencies. A simple mathematical model, formulated in terms of macroscopic ideas of friction, is shown to predict the observed behaviour to a high degree of accuracy.

The role of associated pairs in the gas-liquid transition of 1:1 electrolyte primitive models

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The role that ionic association plays in the gas-liquid transition of primitive models of electrolytes is still subject of controversy. Even in the most sophisticated theoretical approaches, which include ionic association into pairs [1,2], the transition is considered to be driven by the free ions. However, recent theoretical [3-5] and computer simulation studies [6,7] show that the associated pairs may drive the transition. We present a formalism that naturally introduces an exact description of the ionic fluid as a mixture of associated pairs and free ions, and show that ionic association dominates the thermodynamics of the ionic fluid at low temperatures [8].

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Phase Diagrams of Colloids / Non-ideal polymer mixtures

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Using thermodynamic perturbation theory and simulations, we calculate the free energy and determine the phase diagrams of an effective one-component system, where colloids interact via a recently derived [1] depletion pair-potential induced by interacting polymers. The results are in good agreement with the simulations of the full two-component system [2].

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Krichevskii Functions of Oligomers in Carbon Dioxide from Supercritical Fluid Chromatography

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Retention factors of several oligomers of ethylene glycol (12- to 18-mer), methyl methacrylate (8- to 12-mer), and styrene (4- to 12-mer) were measured by supercritical fluid chromatography in an open tubular capillary column within 371-431 K and 13.9-31.1 MPa. This data set was obtained using a poly(methyl-*n*-octyl siloxane) stationary polymer and carbon dioxide as the mobile-phase fluid. The retention factors are employed here to derive the partial molar volumes of the oligomers at infinite dilution in CO₂. In the conversion of retention data to partial molar volumes, attention has been paid to the effect of dissolution of CO₂ in the stationary polymer. The procedure used in the data reduction has been the same as that described before [1]. The partial molar volumes are subsequently transformed to the Krichevskii functions characterising the short-range, oligomer-CO₂ interactions. The results provide a visual, quantitative scale of relative CO₂-philicities of the oligomers as functions of oligomer composition, temperature, and density of CO₂. The data processing has been supported by the Grant Agency of the Czech Republic (Project No. 203/02/1093).

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Wetting and Drying at Curved Substrates: Non-Analytic Behavior of Interfacial Properties

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We consider the case of complete wetting or drying of a fluid at two curved substrates that have simple geometries, namely a single sphere of radius R_s and an infinitely long cylinder of radius R_c . We combine the well-known mesoscopic effective Hamiltonian approach with exact microscopic sum-rules to show that the substrate-wall surface tension as well as the contact density of the fluid at a hard curved substrate is non-analytic in the curvature. These predictions are general for short-ranged substrate-fluid and fluid-fluid interactions. In order to substantiate these predictions we perform numerical calculations for a model system of a square-well fluid at hard curved wall in the frame work of density functional theory (DFT).

Phase Separation Curve of Dilute Solid ^3He - ^4He Solutions

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The results of numerous investigations revealed an asymmetry of the separation line in the concentration range $^3\text{He} < 30\%$ that was in disagreement with calculations by the theory of regular solutions. Two theoretical models were proposed for explaining the asymmetry of the diagram that gave somewhat different values for the separation line. But the accuracy of the experimental data for low ^3He concentration, where the difference between theories was highest, didn't allow us to choose one of them.

A method is proposed for constructing the separation phase diagram of ^3He - ^4He solid solution on the basis of precision measurements of the pressure jump due to phase separation at constant volume. The technique is implemented on high-quantity samples of the solid solutions, making it possible to obtain reliable and reproducible experimental data with no appreciable hysteresis effects. The line of phase separation constructed from the experimental separation in solid solutions of helium isotopic mixtures. It is found that good agreement with experiment is observed only for the Edvards-Balibar's model [1], which is an extension of the theory of regular solutions with taking into account the differences of the crystal structures (hcp and bcc) of the phases existing in the system.

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Fluid phase transitions at chemically heterogeneous, nonplanar solid substrates: surface versus confinement effects

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The phase behavior of a "simple" Lennard-Jones (12,6) fluid confined between planar substrates has been investigated by means of Monte Carlo simulations in the grand canonical ensemble (GCEMC). The interaction of fluid molecules with the upper wall is purely repulsive and attractive with the lower one. A spherical cap of radius r is embedded in the surface of the upper wall. The cap also attracts fluid molecules. For $r = 0$, that is, in the case of two planar homogeneous substrates, one observes classical prewetting, namely a first-order phase transition from thin to thick films adsorbed on the lower substrate. When $r \neq 0$, that is, when the upper substrate is decorated with a three-dimensional pattern of finite size, system properties are no longer translationally invariant in any spatial dimension. Thus, the grand potential Ω is not a homogeneous function of degree one in any of its extensive variables which precludes a "mechanical" expression for Ω in terms of stresses and conjugate strains. Therefore, in order to determine the phase behavior through plots of Ω versus chemical potential μ we employ a thermodynamic integration scheme under isothermal conditions. We observe a partially condensed phase, where the molecules are preferentially adsorbed in the gap between the spherical cap and the lower substrate, associated with either a thin or a thick film adsorbed on the lower substrate.

Calorimetric study of the effect of a flame retardant on the laboratory soil heating

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To try to minimise the area of the burning zones as well as the fire effects on vegetation and soil, several types of retardants and foams have been used on the wildfire fighting [1].

The aim of this work is to know the effect of a fire retardant on the laboratory heating of a Humic Cambisol: Samples of this soil with different amounts of retardants and without retardant were heated into an oven to different temperatures to simulate medium and high intensity fires.

Differential Scanning Calorimetry is a useful tool to analyse the soil characteristics and therefore it was used to determine the fire effects on soil. The enthalpy of combustion of organic matter and ignition temperature in every soil sample was determined from DSC thermograms in order to be compared.

The obtained results showed that the samples with retardant were less affected by heating than samples without retardant in medium intensity heating, however no differences have been found in high intensity heating.

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Gibbs energy approach for multiphase reactive processes

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Modern simulation programs included with critically evaluated thermochemical databases are commonly used for problem solving for both industrial and natural systems. The classical Gibbs energy approach can be extended to take into account reaction kinetics by setting constraints. In this work, multi-phase thermodynamics have been combined with reactive aqueous solution in order to simulate the chemical and physical equilibrium as well as time-dependent properties. The applications of thermochemical calculations include industrially important oxygen pressurized peroxide-bleaching solution and multiphase calcite system. The knowledge of the pulp- and solution properties along with the results of the model calculations could further be used to improve the optimization of the bleaching process as well as for process control in paper machine.

The properties of fully flexible lennard-jones chains in the solid phase: wertheim theory and simulation

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NpT Monte Carlo simulations were performed for fully flexible Lennard-Jones chains (formed by tangent LJ monomers) in the solid phase. The solid structure of fully flexible chains is obtained by randomly locating the bonds of the chain within a face centered cubic close packed arrangement of atoms. Computer simulations were performed for chains with 3, 4 and 5 monomer units. Wertheim's TPT1 has been extended recently to the solid phase of LJ chains (C.Vega, F.J.Blas and A.Galindo, *J. Chem. Phys.*, 116, 7645, 2002). The simulation results of this work provide a check on the performance of this theory. It is found that Wertheim's TPT1 successfully predicts the equation of state and internal energies of fully flexible LJ chains in the solid phase. Linear rigid Lennard-Jones chains have also been considered. Computer simulations were performed for linear rigid chains in an ordered solid structure. It is found that fully flexible and linear rigid chains present quite different equations of state and different thermodynamic properties in the solid phase.

Excess Molar Volumes of Binary and Ternary Solutions of 2,2,2-Trifluoroethanol, Methanol, Ethanol and Water at 298.15 K and 101 kPa.

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2,2,2-trifluoroethanol aqueous solutions have wide range of applications as cleaning agents, reacting media, refrigerants and fuels. In this work, we report experimental data of excess molar volumes of binary and ternary mixtures containing 2,2,2-trifluoroethanol, methanol, ethanol and water at 298.15 K and 101 kPa. The liquid densities of pure components and mixtures are measured using an electronic densimeter Anton Paar, model: DMA5000 with precision $\pm 5.10^{-6}$ g.cm⁻³ and temperature stability of $\pm 2.10^{-3}$ K.

The experimental excess molar volumes of binary and ternary mixtures are well fitted to the equations:

$$V_{m,ij}^E = x_i x_j \sum_h B_h (x_i - x_j)^h$$

$$V_{m,ijk}^E = \sum_{j>i} V_{m,ij}^E + x_i x_j x_k \Delta_{ijk}$$

The excess molar volumes the ternary aqueous mixtures are predicted by various equations using the general expression:

$$V_{m,ijk}^E = \sum_{i<j} \frac{x_i x_j}{x_i + x_j} V_{m,ij}^E (x_i', x_j')$$

The excess molar volumes of pseudo-binary mixture $V_{m,jk+i}^E$ are predicted along a dilution line using the equation:

$$V_{m,jk+i}^E = V_{m,ijk}^E - (x_j - x_k) V_{m,jk}^E$$

The experimental results are presented in tables and graphs. These systems are not studied experimentally despite their very characteristic thermodynamic properties.

Phase separation and micellization in supercritical CO₂/surfactant systems using lattice Monte Carlo simulations.

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Lattice Monte Carlo simulations are used to study the influence of formulation variables on the micellization and phase equilibria of supercritical CO₂/surfactant systems (scC/S). These simulations are aimed at explaining the trends and characteristics displayed experimentally by such systems.

We use a modified version of Larson's lattice model, which treats the scC/S system as a binary mixture. The CO₂ molecules occupy one lattice point, while the surfactant molecules occupy r lattice points, all on a lattice with coordination number $z = 26$. The surfactant molecules, denoted by H_mT_n , consist of m hydrophilic head segments H and n CO₂-philic tail segments T ($r = m + n$). Vacancies are introduced in order to account for the compressibility of such systems.

Monte Carlo simulations are performed to study the effect of CO₂ density on scC/S systems. A two-phase region is found at low CO₂ density. At high CO₂ density, the surfactants are completely solubilized and form micelles at a surfactant concentration higher than the CMC. Increasing the CO₂ density, we observe an increase in the CMC and a decrease in the micellar size. A study of the micellar shape reveals that the micelles are spherical in our range of surfactant concentration and CO₂ density. Increasing the CO₂ density increases the size of the micellar corona while the size of the micellar core remains constant. Micellar structure calculations show that the micellar core contains mostly surfactant heads while the corona consists of surfactant tails highly solvated by CO₂.

Exploration of the energy landscape of solids using stochastic algorithms

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Understanding the dynamics and thermodynamics of a chemical system in the solid state requires information about the possible stable structures, their thermodynamic weight, and their kinetic stability. From a theoretical point of view this leads us to the global study of the energy landscape of the system.[1] Here, (meta)stable compounds correspond to locally ergodic regions on the landscape that are surrounded by sufficiently high kinetic barriers to provide long-time stability.

In order to identify such regions and to analyze the transitions among them, we have applied and developed several stochastic algorithms. In a first step, we determine as many local minima as possible using short and long simulated annealing runs. Next, we employ the threshold algorithm[2] to determine energetic and entropic barriers. Finally, we use swarms of stochastic quench runs along the threshold runs, to find the so-called characteristic regions[3] of the landscape, which serve as candidates for locally ergodic regions and transition regions. As an example, we are going to present the energy landscape of a simple ionic system MgF₂. We find that the most stable regions correspond to the observed and other chemically reasonable structures. Furthermore, significant entropic barriers are present and the transition regions are quite small compared to the locally ergodic regions in the system.

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Statistical Mechanics of the complex mixture inside E. coli

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Inside a bacterial cell there is a mixture of a few thousand different proteins. The number of proteins with a given charge is a roughly Gaussian function of charge, centered a little below zero, and with a width around ten (in units of the charge on the proton). I have used the charges on E. coli's proteins to estimate the changes in the second virial coefficients of all its proteins as the concentration of a 1:1 salt is increased. The charges on proteins change as an organism evolves, but the central-limit theorem ensures that the variation in the physical properties of the cell is small.

Ionic Liquids: The Bear Necessities

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Green chemistry concerns the reduction of waste from an industrial chemical process to a minimum: it requires the rethinking and redesign of many current chemical processes. The 'dirty' end of the chemical industry, oil refining and bulk chemicals, is remarkably waste conscious: it is the fine chemicals and pharmaceutical companies who are using inefficient, dirty, processes, albeit on a much smaller scale. Volatile organic solvents are the normal media for the industrial synthesis of organics (petrochemical and pharmaceutical), with a worldwide usage of *ca.* £4,000,000,000 p.a. However, the Montreal Protocol has resulted in a compelling need to re-evaluate many chemical processes that have proved otherwise satisfactory for much of this century.

Ionic liquids are becoming recognised as novel solvents for green industrial chemistry, and have been extensively reviewed elsewhere (*e.g.* R.D. Rogers and K.R. Seddon (Eds.), "Ionic Liquids: Industrial Applications for Green Chemistry", *ACS Symp. Ser.*, 818, 2002; R.D. Rogers, K.R. Seddon and S. Volkov (Eds.), "Green Industrial Applications of Ionic Liquids", Kluwer, 2003; P. Wasserscheid and T. Welton (Eds.) "Ionic Liquids in Synthesis", Wiley, 2002. This presentation will illustrate why these are considered as green solvents, both for their lack of vapour pressure, and for the high-yield syntheses with high isomeric selectivity that are possible. Physical properties will be discussed, including polarity, viscosity, and density, along with an overview of recent catalytic and synthetic advances. The need for good physical chemistry input will be highlighted.

Phase behaviour of hyperbranched polymer solutions

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The understanding of the phase behaviour of dendritic polymers, i.e. hyperbranched polymers (HyPol) and dendrimers, is still in its infancy. No systematic thermodynamic investigations on the phase behaviour of dendritic polymer solutions have been reported so far. HyPol represent highly branched, polydisperse macromolecules with a treelike topology and a large number of functional groups. This presentation aims at providing the first extensive experimental study on the low- and high-pressure phase behaviour of HyPol/solvent and HyPol/solvent/supercritical gas systems. The influence of the solvent polarity, the nature and number of polymer functionalities, the degree of polymer branching as well as the polymer and supercritical gas concentration on the phase behaviour of selected HyPol solutions is discussed. Thermodynamic phenomena such as the emergence of the UCST and LCST curves and a remarkably distinct solutropic phase behaviour are presented. Furthermore, the influence of non-volatile mixtures, consisting of HyPol and Ionic Liquids, on the vapor-liquid equilibria of the azeotropic ethanol/water and tetrahydrofuran/ water systems are discussed.

The thermal properties of aqueous Ethanol solutions

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Solar collectors play the most important role for the collection of solar rays. The heat transfer is used in solar collectors for heating systems in various purposes. Therefore, the efficiency of installations depends rather on thermodynamic properties than on heat transfers. However, (p, ρ, T) properties should be taken into consideration. Heat transfer in solar energy systems is usually water. In cold climates the freezing of collector tubes can burst during hard winter freezes and destroy a collector. The solutions of this problem are: to place a heat exchanger between the tank and the collector, or use of the thermo-elastic collectors, turn the system off and drain it during very cold months, and or substances with a low freezing temperature, such as the aqueous solutions of alcohols. Recently, it has become more popular to use aqueous ethanol solutions. The experimental investigation of (p, ρ, T) properties of aqueous solutions of ethanol was carried out by the constant volume piezometer method for obtaining of high pressure measurements. The volume of the piezometer was $350.13 \times 10^{-6} \text{ m}^3$ at room temperature. The experiments were carried out over a temperature range from 298.15 K to 523.15 K, at mole fraction of H₂O $x=0.25$; $x=0.50$; $x=0.75$ from atmospheric pressure up to 60 MPa. The experimental uncertainties are $\Delta T = \pm 3 \text{ mK}$ for temperature, $\Delta P = \pm 5 \cdot 10^{-2} \text{ MPa}$ for high pressure, $\Delta P = \pm 5 \cdot 10^{-4} \text{ MPa}$ for atmospheric pressure, and $\Delta \rho = \pm 3 \cdot 10^{-2} \text{ kg} \cdot \text{m}^{-3}$ for density. A equation of state was derived for correlation of the experimental data of aqueous solutions of ethanol.

The problem of choosing optimal independent components for a chemical system during thermodynamic computations

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The proposed concept of choosing optimal independent components is based on setting an extremum problem on a set of possible thermodynamic bases, the solution of which could pick out an optimal base on one hand, and could give mathematically optimal estimation of equilibrium system composition on the other. We used Monte-Carlo [1] method to examine stability and reliability of thermodynamic equilibrium computation results.

The INFOTHERM [2] (<http://infotherm.nm.ru>) system of thermodynamic computations, which is being developed by us, assumes to have an opportunity to switch between desired bases (optimal in particular) in the existing thermodynamic database.

Theoretically there exists a chance of switching to an «absolute» base, established on subatomic level instead of molecular, i.e. particles forming atomic nucleus and electrons could be considered as base elements.

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The study was supported by RFBR projects 01-07-90122 and 02-05-64135.

Steady gradients of the temperatures and concentration in superfluid ^3He - ^4He solutions

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The temperature and concentration gradients, $\text{grad}T$ and $\text{grad}X$ are measured in a superfluid ^3He - ^4He mixture with an initial concentration 9.8% of ^3He in the temperature range of 70-500mK. The gradients have been produced by a steady thermal flow Q and registered by two thermometers and two capacitive - concentration gauges which are placed at 1 cm interval between them. The dependencies of $\text{grad}T$ and $\text{grad}X$ on Q and temperature are investigated at Q values from 0.1 to 20 $\mu\text{W}/\text{cm}^2$.

The onset of the convection is observed where the dependencies $\text{grad}T(Q)$ and $\text{grad}X(Q)$ deviated from the linear region. It is shown that the relationship between the steady values of $\text{grad}T$ and $\text{grad}X$ in the superfluid solutions is in agreement with a theoretical model followed from the temperature and concentration dependencies of the osmotic pressure. We found the thermal diffusion ratio of the solution to be responsible for the thermal diffusion coefficient temperature dependence. The relaxation processes of concentration and temperature in superfluid ^3He - ^4He solutions are also studied.

Simulating Microheterogeneous Fluids

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Accurate knowledge of phase equilibria and other thermophysical properties of complex mixtures is of enormous importance for the chemical industry. However, given only the molecular architecture of the molecules (types of atoms and their connectivity) and the experimental conditions (temperature, pressure, and overall composition), the quantitative prediction of phase equilibria and thermophysical properties remains one of the grand challenges for the field of molecular simulation.

Configurational-bias Monte Carlo simulations in the Gibbs ensemble and the TraPPE force field are used to investigate (i) structure and solvation in wet or dry 1-octanol, (ii) partitioning between water/methanol mixtures and n-hexadecane, and (iii) the interfacial properties of saturated 1-butanol/water mixtures.

Freezing in Narrow Pores

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Confinement within a nanoporous material is known to lead to a number of novel phenomena on freezing. The freezing temperature may increase or decrease relative to the bulk value, and new phases may appear depending on factors such as the size and shape of the pores and the interactions between the confined fluid and the nanoporous material. Such new phases include contact layer phases and hexatic phases. In addition to the fundamental scientific interest, such phenomena are of considerable practical importance in areas related to nanofabrication, lubrication, adhesion, nanotribology, development of novel materials for energy storage and distribution of pollutants in soil. Freezing in porous media has also been widely employed in the characterization of porous materials using the method of thermoporometry. Recent molecular simulation results, and experimental studies based on dielectric measurements and differential scanning calorimetry, will be presented. A broad understanding of the phenomena involved for simple systems can be gained by viewing the freezing behavior as resulting from the competition between fluid-wall and fluid-fluid forces, with perturbations due to other variables. Global phase diagrams will be presented for slit-shaped pores, and where possible comparison with experiment will be made. For sufficiently narrow slit pores hexatic phases are observed in the simulations. Measurement of the nonlinear dielectric effect for carbon tetrachloride and aniline in activated carbon fibers show strong evidence for crystal/hexatic and hexatic/liquid transitions, with transition temperatures in good agreement with the simulation results.

Phase boundaries and aggregation in mixed micellar solutions

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In the last years mixed surfactant systems are paid much attention, largely due to their various technological applications. Data on the critical micellar concentration (CMC), the micellar solution - solid phase and micellar solution - liquid crystal phase boundaries, alongside viscosity data in systems containing two surfactants are considered. Results of experimental measurements and model calculations, performed by the author and collaborators, are presented for mixed aqueous solutions of dodecylsulfates, sodium ethoxydodecylsulfate, dimethyldodecylamine oxide [1-3]. The dependence of the precipitation temperature on the relative content of two surfactants spans a wide range of the gross surfactant concentration. Special attention is paid to synergistic effects in mixtures of anionic and semi-polar surfactants, where the dependence of the precipitation temperature, CMC and viscosity on the relative surfactant content and pH is rather complicated. The model description using the pseudo-phase approach addresses prediction of the properties of ternary systems on the basis of data for aqueous solutions of the pure surfactants. Effects of non-ideal behavior of mixed micelles and chemical interactions are considered. Feasibility of semi-empirical approaches accounting for molecular characteristics of surfactants is discussed.

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Simulating the adsorption and diffusion of hydrocarbons in zeolites

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Catalysis in zeolites involves the adsorption and diffusion of reactants to the active site, the conversion and subsequently the diffusion and desorption of the product molecules. Hence, knowledge on the adsorption and diffusion of adsorbed molecule is essential in understanding the overall catalytic activity of zeolites. Since experiments at reaction conditions of the molecules of interest are very difficult, molecule simulations might be an attractive alternative. In this lecture it is shown that using molecular simulations one can obtain accurate data on both the thermodynamics and diffusion of linear and branches hydrocarbons in zeolites.

We use these insights obtained from molecular simulations to shed some light on questions related to the product distribution obtained in various zeolite. We demonstrate the lack of experimental data on the thermodynamics of adsorption makes it every difficult to interpret the experimental data. We provide an alternative mechanism of inverse shape selectivity.

Stockmayer fluids under the influence of porous materials

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The influence of different porous materials on the phase behaviour of Stockmayer fluids is investigated by using integral equation theory (Reference Hypernetted Chain and Mean Spherical Approximation) in combination with the replica method. The Stockmayer fluid particles (which interact with dipolar and Lennard-Jones potentials) are exposed to a) a hard sphere matrix, b) a hard sphere matrix with an additional Lennard-Jones fluid-matrix potential, c) a dipolar hard sphere matrix. When the system is cooled down from the homogeneous, isotropic high temperature phase, a borderline is found below which no numerical solution is possible. We interpret this borderline as the spinodal line of the high temperature phase.

In model a) the position of the spinodal line is shifted towards lower temperatures compared to the bulk for the low fluid density area, where a liquid-vapour transition is found. In model b) and c) an additional shift towards higher fluid densities is observed. At high fluid densities a ferroelectric transition (marked by a divergence of ϵ) is found for model a) and b) at significantly higher temperatures compared to the bulk. In model c) only an increase of ϵ can be seen.

Besides the influence of the different matrices on the spinodal line, the behaviour of the thermodynamical properties and the fluid structure is investigated.

Thermodynamics of DMAGaS-DMAAIS ferroelectrics in microscopic description considering Gaussian fluctuations

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This study is aimed on a microscopic model description of thermodynamic properties of ferroelectrics of DMAGaS and DMAAIS family. Elaborated earlier four-state model considers ordering processes in the subsystems of dimethyl-ammonium groups as the main reason of the sequence of phase transitions in the mentioned crystals. Obtained in the mean field approximation thermodynamic characteristics of the model (spontaneous polarization, occupancy of orientational states, dielectric susceptibility, phase diagrams) are in a good agreement with experimental data [1,2].

To enhance precision of description in the vicinity of the paraphase – ferroelectric phase transition point fluctuations of polarization are taken into account in Gaussian approximation. A generalization of self-consistent Onyszkiewicz approach suiting the four-state model is developed. Numerical calculations show that such an enhanced approximation decreases the temperature of the phase transition and does not involve any dramatic changes comparing to the mean field approximation.

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Legitimacies change of properties of binary systems on an example of solutions formed by n-alcohols and complex ethers of organic acids.

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Determination of connection between the thermodynamic functions of solutions and molecular characteristics of components is a topical problem of current development of the thermodynamic theory. The contributions of intermolecular interactions to the thermodynamic functions of pure n-alkyl etanoates, n-alkyl propanoates, n-alkyl butanoates and their binary mixtures with ethanol, n-propanol, and n-butanol (25 binary systems in total) are calculated. It is found that these contributions to the Helmholtz energy, internal energy and entropy are linearly dependent on the molar substance mass in the homological series. It is shown that the Helmholtz energy, molar volume and refraction in the case of binary solutions of constant molar concentration formed by common solvent and representatives of homological series are linearly dependent on the molar component mass in the homological series. The corresponding equations are given. Similar regularities have been observed for the following systems: methyl etanoate–n-alkyl etanoates, methyl propanoate–n-alkyl propanoates, methyl butanoate–n-alkyl butanoates, benzene–n-alkyl benzenes (methylbenzene, ethyl benzene, n-propyl benzene, n-butyl benzene), benzene–fluoro benzene, benzene–chloro benzene, benzene–1-bromo-benzene, benzene–iodobenzene (unpublished data). There are solid grounds for supposing that the aforementioned linear dependencies of the properties of the solutions formed by common solvent and the representatives of homologous series on the molecular mass are of the most general character.

Fluctuations and decay of nematic disclination lines with integer strengths

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Topological line defect of the nematic liquid crystal is the disclination line with winding number (strength) $1/2$. Disclination lines with integer strengths are not topological, since they can be continuously transformed to defectless structures via the escape in the third dimension. Besides, any disclination line with strength $1/2$ is energetically unstable towards the decay to disclinations with lower strengths. There is a question, however, concerning its local stability. In one elastic constant approximation, we solve the fluctuation problem of the complete tensor order parameter for a straight disclination line with a general integer strength. In all cases we find growing fluctuation eigenmodes of both types - leading to the decay or the escape. For any topologically allowed decomposition there exists at least one growing mode, provided that none of the resulting winding numbers is too high.

The time constant of the fluctuations associated with the escape is one or two orders of magnitude larger than for the decay - a disclination decays before it has a chance to escape. The decay of strength ± 1 disclination line to a repelling pair of $\pm 1/2$ lines is studied numerically including hydrodynamics [1], showing that the flow effect is substantial and even increases with the interdefect separation. The contribution of the advective transport to the defect speed is larger than that of the director reorientation.

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Thermodynamics of Clay Swelling

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Clay minerals consist of negatively charged sheets, with counter ions in between to compensate for the charge deficiency. Understanding the influence of temperature, external pressure and humidity on the sorption of water molecules is crucial for clay swelling. We applied a combination of molecular dynamics and Monte Carlo simulations, using the TIP4P model, to predict this swelling behavior. During our simulations, we fixed the temperature and volume, as well as the water chemical potential. We studied the crystalline swelling domain (basal spacing $< 20 \text{ \AA}$) within the experimental scope of relative dry and wet conditions. We computed the average water content and the average pressure perpendicular to the clay layers and integrated the later to obtain the free energy. Our results show that the pressure oscillates as a function of the basal spacing, in agreement with experiments and simulations from the literature. The minima of the free energy curves indicate the spacings of stable layered hydrates and their values agree with experimentally measured spacings. By adjusting the relative water vapor pressure, we observe successive formation of stable layered hydrates. Our calculated pathways of swelling and shrinking are not similar, in accordance with the experimental hysteresis phenomenon. Quantitatively, we predict that the vice versa transition from the one- towards the two-layer hydrate occurs at lower relative water vapor pressure compared with experiments. We explain this by the sensitivity of the system with respect to the water content. Addition of only a few extra water molecules may have a substantial effect. Fine-tuning of the model parameters should give better agreement on this point.

Group contribution method with SAFT EOS applied to Vapour liquid equilibria of various hydrocarbon series.

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A new group contribution method is built using the SAFT (Statistical Associating Fluid Theory) equation of state (EOS), in order to describe the thermodynamic properties of hydrocarbon series. The method is developed for vapor-liquid equilibrium (VLE) calculations for a large number of hydrocarbons, with the use of several group parameters. SAFT models are chosen for the physical meaning of their parameters. These can be related to the molecular structure. Two versions of the SAFT EOS are used in this work: SAFT equation of state, proposed by Chapman, *et al*¹ and SAFT-VR (SAFT Variable Range) equation of state, proposed by Gil-Villegas, *et al*². The present group contribution method consists in calculating the equation of state parameters (dispersion energy ϵ , segment diameter σ , chain length m and square-well range parameter λ for SAFT-VR) using group contribution rules. In this paper, we have treated pure components of four hydrocarbon families: *n*-alkanes, *alkyl*-benzenes, α -olefins and *1*-alkanols. The obtained results are compared with the classical approach (by fitting each molecule parameters on its own properties) and seem to be nearly equivalent. The proposed method is also compared with other predictive approaches, and presents reasonable results.

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Crystallization kinetics and ramanspectroscopical studies on the system Na^+ , $\text{Mg}^{2+}/\text{Cl}^-$, $\text{SO}_4^{2-}/\text{H}_2\text{O}$

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Parallel studies on the crystallization kinetics of the salts from the system Na^+ , $\text{Mg}^{2+}/\text{Cl}^-$, $\text{SO}_4^{2-}/\text{H}_2\text{O}$ and Ramanspectroscopic studies on the respective saturated solutions were undertaken at 25°C. Four association species between the Mg^{2+} and SO_4^{2-} ions were established to correspond to $\nu_1(\text{SO}_4^{2-})$ Raman bands at 980, 990, 1003 and 1021 cm^{-1} . They were assigned to free non-associated sulfate ions, solvent separated ionic pairs, direct ionic pairs $\text{Mg}^{2+}\text{—OSO}_3$ and SO_4^{2-} group containing oxygen bounded simultaneously to two Mg^{2+} ions, respectively. The water activity calculated by Pitzer method shows a direct correlation with the ionic association.

The crystallization kinetics of NaCl , Na_2SO_4 , $\text{Na}_2\text{SO}_4\cdot\text{MgSO}_4\cdot 4\text{H}_2\text{O}$ and $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ is examined in relation with the structure of the respective saturated four-component solutions. It is established that the highest crystallization rate and lowest supersaturation required for nucleation belong to salts in whose saturated solutions there is a sufficient concentration of structural entities able to be incorporated unchanged or with small changes into the crystal structure.

The work was financially supported by the Centre of Excellence CESUM-BS, EC Contract ICA1-CT-2000-70031.

Maximum Energy Deposition at Wire Explosion

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Recently the importance of the initial resistive phase of wire explosion is becoming evident. The interest to the initial phase is manifested both by investigators of later stages of explosion, and by material scientists. The expansion rate and uniformity of the wire at later plasma phase of explosion strongly depend on the amount of energy deposited in the wire during this heating phase. On the other hand, the increase of energy deposition extends the range of matter states accessible for investigations.

The above reasons emphasize the problem of estimating the theoretical limits to the energy deposition and the values of the circuit and wire parameters, which allow to approach this limits. We address these issues by means of the nucleation theory of wire explosion and compare our results with experimental data. Also we applied our technique to the estimation of the average size of metal particles formed after explosion. A good agreement between our estimations and direct experimental measurements validates our approach.

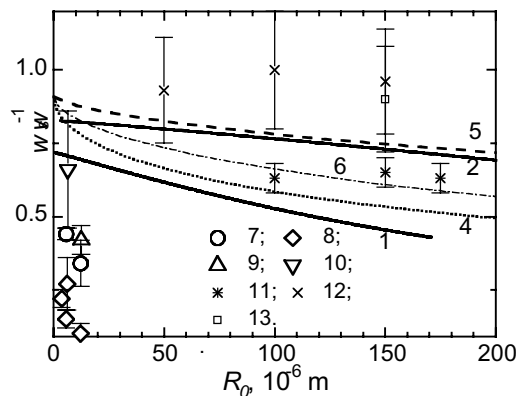


Fig.1. The maximum deposited energy versus the initial radius calculated for *Al*, *Cu*, and *W*.

Modeling of liquid-liquid phase equilibrium in aqueous solutions of Poly(ethylene glycol)

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Solutions of poly(ethylene glycol) (PEG) in water have been used in biochemistry and biochemical engineering to separate and purify biological products, biomaterials, proteins, and enzymes from the complex mixtures in which they are produced. PEG/water solutions show a phase diagram of closed-loop type. Increase of the MW raises the UCST and lowers the LCST, and the region of immiscibility expands.

In this work a simple activity coefficient model, referred to as EFV/UNIFAC model, is used for the correlation and prediction of LLE in aqueous solutions of PEG. Interaction parameters between the solvent molecule and the repeating unit (segment) of the polymer are determined and their values are used to predict the effect of the polymer molecular weight on the solvent/polymer partial miscibility. The influence of the end groups is taken also into consideration and is proven to be extremely significant. The interaction parameters of the end group with the segment and the solvent molecules are estimated separately from VLE and LLE data of low molecular weight compounds.

Critical anomalies of the density and isobaric heat capacity for binary mixtures.

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Several recent studies [1-3] have been devoted to the investigation of the amplitude of the density ρ and isobaric heat capacity C_p anomalies for binary mixtures in the vicinity of the liquid-liquid critical point. It has been suggested [1] that these quantities can be related from knowledge of the density at the critical point ρ_c , the critical exponent of C_p α and the slope of the critical line $(dT/dp)_c$.

An experimental study of these two magnitudes was carried out for four binary critical mixtures in order to obtain the critical amplitudes R^+ and A^+ of ρ and C_p , respectively. Taking the literature values of $(dT/dp)_c$ [5], R^+ values were calculated and compared to their experimental counterparts. This revealed the calculated value to be greater than the experimental ones for all cases. Some authors [1] have suggested that this behaviour is expected since the relations deduced between R^+ and A^+ are not rigorously valid in the experimentally accessible region.

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Acoustical Measurements of Thermodynamic Properties

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Modern experimental techniques allow the speed of sound to be measured in gases and liquids with high accuracy over wide ranges of temperature and pressure. The use of spherical acoustic resonators for measurements on gases is now routine, and high-precision transient measurement techniques are available for liquids. At Imperial College, we have applied these methods to a number of pure fluids and mixtures at temperatures between 100 K and 475 K with pressures as high as 30 MPa in gases and 200 MPa in liquids. The total uncertainty of the measurements typically ranges from better than 0.001 per cent for a pure gas at pressures near 1 MPa to about 0.05 per cent for a liquid mixture at 200 MPa. Results for a number of fluids, illustrating the capabilities of the measurement techniques, will be presented.

The primary motivation for measuring the speed of sound is to gain information about other thermal and caloric properties of the fluid. A variety of techniques have been developed for this purpose including applications of molecular theory, in which model intermolecular potential-energy functions are fitted to acoustic data, and methods based solely on the integration of rigorous thermodynamic relations. These methods and typical results will be presented. Finally, some industrial applications acoustic sensors will be mentioned.

Study of Thiocyanates in Water/DMF Mixtures by Raman Spectroscopy

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The aim of the present work is the application of Raman spectroscopy in order to obtain information regarding the ionic interactions in solutions of NaSCN, KSCN and NH₄SCN in water/DMF mixtures.

In the C-S stretching region (700-780 cm⁻¹), in solutions of pure water till the composition 50 mass % DMF, a single band appears at about 749-750 cm⁻¹, which is assigned to the C-S stretching mode of the hydrated free SCN⁻ ions. In the mixtures with high DMF content (80 mass % DMF) two bands were observed which are ascribed to the solvated by both water and DMF, free SCN⁻ ions (743-745 cm⁻¹) and to the ion-paired Na⁺NCS⁻ (752 cm⁻¹), K⁺NCS⁻ (752 cm⁻¹), NH₄⁺NCS⁻ (755 cm⁻¹). The ion-paired band was observed at higher frequency than the free SCN⁻ band and is assigned as an N-bonded thiocyanate ion-pair. In pure DMF two bands were observed which are ascribed to the free SCN⁻ ions surrounded by DMF molecules (733 cm⁻¹) and to the ion-paired Na⁺NCS⁻ (752 cm⁻¹), K⁺NCS⁻ (752 cm⁻¹), NH₄⁺NCS⁻ (755 cm⁻¹).

In the C-N stretching vibrational region (2000-2150 cm⁻¹) a single band was observed for all the investigated salts in all solvent mixtures. The band splitting of the C-N stretching mode is smaller than for the C-S band, as C-N bond is a triple bond.

Low temperature heat capacities of GaSe and Ga₂Se₃

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The gallium selenides are promising optoelectronic and thermoelectric converters. Their specific features are connected to a layered structure. These compounds intercalated by alkaline and alkaline earth metals can be used as accumulators of solar and electrical energy. The heat capacity of gallium selenide was studied earlier using adiabatic calorimetry [1], but the data were obtained starting only from 60.62 K and are characterized by a rather wide scatter (up to 1%) of experimental points. No heat capacity measurements of Ga₂Se₃ were carried out earlier. The heat capacities curves ($C_p(T)$) of the gallium selenides were determined in this work in an adiabatic calorimeter in the temperature range 10-325 K based on 88 C_p values for GaSe and 103 values for Ga₂Se₃. Uncertainty in the C_p are $\pm 0.25\%$ in the range of temperature 50-300 K and are more substantial (up to 2%) in the temperature range 14.15-50 K. The smoothing of the $C_p(T)$ was made using a spline-approximating software of the IVTANTHERMO Databank. $C_v(T)$ curves and Debye temperature of GaSe and Ga₂Se₃ were calculated based on obtained experimental C_p data.

K.K. Mamedov, I.G. Kerimov, V.N. Kostryukov, M.I. Mehtiev. 1967, .1, P.441-442

This work was supported by RFBR. Grant 02-03-33086.

Molecular simulation of H₂S-containing mixtures

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The design of improved processes for producing H₂S-rich natural gases faces a general scarcity of experimental data, because of the high toxicity and corrosive character of H₂S. We apply here Monte Carlo simulation to predict thermodynamic properties for these systems.

A first step was the selection of intermolecular potentials from the literature for water, H₂S, CO₂ and methane on the basis of pure component properties. A second step involved the comparison of experimental and predicted phase diagrams of binary mixtures of the methane-H₂S-water system. This involved Gibbs ensemble simulations, either biphasic or triphasic. A third step involved the prediction of volumetric and enthalpic properties of the CO₂-H₂S system at high pressure, using different combining rules.

A satisfactory agreement was found with available experimental data. We have thus been able to use molecular simulation to perform predictions for conditions where data were lacking (high pressures, ternary phase diagrams, excess properties). The study illustrates that Monte Carlo simulation is now able to contribute significantly to process development.

Small angle X-Ray scattering from 5CB-Laponite compounds

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The interactions between anisometric particles and a liquid crystalline solvent in the nematic phase are studied. The liquid crystal is 5CB, 4-pentyl-4-cyanobiphenyl and as model platelet Laponite is used, which has a particle diameter of about 25 nm, a thickness of 1 nm and is naturally hydrophilic. The particles are made organophilic by treatment with dimethyldioctadecylammonium bromide. The treated clay was suspended in the liquid crystal by heating above the transition temperature, combined with sonicating for 7 hours (Method 1) or 30 min (Method 2).

Long-term colloidal stability was not observed - A few particles would be expelled from the nematic immediately, and most of the suspension would settle within a day (Method 1) or two days (Method 2). The samples also showed very different behaviour in 10 μm thin glass cells. A Method 1 mixture cools from the isotropic phase into a scattering nematic phase. A Method 2 mixture cools into a clear state, indicating homeotropical alignment. The resulting suspensions were characterised using Small Angle X-Ray Scattering (SAXS). The samples were cooled from the isotropic phase in a ~ 1 T magnetic field. For samples prepared by the two methods with the same Laponite concentration, the data recorded are significantly different. We will report on the data fitting and our conclusions.

Gravity versus entropy in suspensions of charged colloids

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It is common practice to view charge-stabilised colloidal suspensions (i.e. mixtures of highly charged colloidal particles, cations, anions, and a molecular solvent) as effective one-component systems of colloidal particles, which interact with effective (ion and solvent mediated) potentials. According to the classic DLVO theory, the effective interaction between two identical charged colloids is given by the sum of van der Waals attractions and screened-Coulomb repulsions. The electrostatic screening is performed by the salt ions, which form a diffuse cloud around any colloidal surface. Under conditions of extremely low salt concentrations of the order of micromolars, where the screening length is of the order of a colloidal diameter, one expects, in any case, a breakdown of pairwise additivity, i.e. many-body interactions become important. Moreover, in the presence of external potentials (e.g. earth's gravity) one can also expect a breakdown of the ionic cloud structure, as the salt entropy does not favor localisation of salt in the vicinity of the colloids at the bottom of the suspension. In this contribution we generalise the DLVO theory (including the so-called volume terms that describe the many-body character) to inhomogeneous situations. The theory seems to be able to explain some recent sedimentation experiments, and can be used to study gas-liquid interfaces, wetting, and perhaps even nucleation.

Computer simulation of the macroscopic pitch in systems of chiral spherocylinders

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One of the major driving forces behind the formation of liquid crystalline phases is the minimisation of the excluded volume between a pair of particles. The gain in entropy from the increase in accessible volume more than compensates for the loss of orientational disorder. Though all mesogenic molecules possess a rigid non-spherical core some liquid crystals possess a chiral geometry. This imparts a chirality on the bulk phase which is strongly temperature dependent. The effect of this molecular chirality on the bulk phase behaviour is examined by simulating a system of hard spherocylinders of aspect ratio $L/D = 5$ with a central chiral interaction. For sufficiently large values of the chiral interaction parameter, a chiral nematic (and even a blue phase) is found. The problem with the use of the standard periodic boundary conditions for such systems is that the chiral pitch of the phase corresponds to the dimension of the simulation box. As a consequence the chiral pitch shows no dependence on the temperature, which is in stark contrast with experimental findings. One can circumvent this problem by confining the system between parallel hard walls, thus breaking the symmetry of the twist between the two ends of the box. We present a detailed study of the order parameters, the chiral pitch, and the chiral correlation functions for the bulk and confined system together with the profiles of the density and the order parameters. It is gratifying to see that the pitch increases with increasing temperature as is often seen experimentally; for values of the chiral interaction which are similar to the kinetic energy, a pitch of the order of hundreds of nanometers is observed.

Thermodynamic properties of alkyl-tert-alkyl ethers and thermodynamic functions of their synthesis

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Alkyl-tert-alkyl ethers having high octaine ratings are lately considered as antidetonating components of the motor fuels. Some of the key thermodynamic properties of four promising ethers $i\text{-C}_3\text{H}_7\text{OC}_4\text{H}_9\text{-t}$, $n\text{-C}_3\text{H}_7\text{OC}_4\text{H}_9\text{-t}$, $i\text{-C}_4\text{H}_9\text{OC}_4\text{H}_9\text{-t}$, and $\text{C}_2\text{H}_5\text{OC}_5\text{H}_{11}\text{-t}$ have been studied by experimental and calculation methods. The low temperature heat capacities, the temperatures and enthalpies of the transitions and fusion were measured by adiabatic calorimetry. Saturated vapour pressure and boiling temperatures were determined by comparative ebulliometry over the moderate pressure range $13 < (p/\text{kPa}) < 100$. The enthalpies of vaporization were measured calorimetrically at $T = 298.15$ K. On the basis of vapour pressure data and density of liquids, the critical parameters and some transport properties of ethers were calculated by corresponding states law. Extending the vapour pressure to the whole range of the liquid phases and thermodynamic analysis of equilibrium reactions of the synthesis of ethers were carried out using the set of obtained experimental values and the literature data on the ideal gas heat capacity and enthalpies of formation. Values of equilibrium constants, enthalpies and maximum temperatures of reactions have been obtained. Enthalpies of reactions were found to be the same for the alkyl-tert-butyl ethers with the number of C-atoms in molecules equal $n_C \geq 7$.

This work was financially supported by the Russian Foundation for Basic Research (project. No 02-02-17009)

The phase diagram of a model of charged hard spheres: the restricted primitive model

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The global phase diagram of a charged hard sphere system, made of positive and negative ions of the same size is determined from computer simulations. Thermodynamic integration and Einstein crystal calculations are used to determine the free energies of the different possible solid structures. Gibbs-Duhem integration is used to trace the full coexistence curves between the different phases involved. Three different solid structures are found to be stable for the considered model; namely, a caesium chloride structure (CsCl), a substitutionally disordered close packed structure which is faced centered cubic (fcc), and a tetragonal ordered structure with an fcc arrangement of atoms if the charge of the ions is not considered. At high temperatures, freezing occurs into the substitutionally disordered close packed structure. This solid structure undergoes an order-disorder transition at low temperatures transforming into the tetragonal solid (F.Bresme, C.Vega and J. L. F.Abascal, *Phys.Rev. Lett.*, 85, 3217, (2000)). At low temperatures freezing occurs into the caesium chloride structure (CsCl) which undergoes a phase transition to the tetragonal structure at high pressures. The tetragonal solid is the stable solid phase at low temperatures and high densities. In a narrow range of temperatures direct coexistence between the fluid and the tetragonal solid is observed. Several triple points are found for the restricted primitive model.

Solid-fluid phase behaviour of model attractive chain molecules

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The first order perturbation theory (TPT1) of Wertheim has proved very successful in the modelling of fluid phases of hard chain-like molecules. In the context of the statistical associating fluid theory (SAFT), it has been shown to be also very effective in modelling the fluid phase behaviour of chain-like molecules with attractive interactions, and it is now commonly used to model chain fluids of industrial interest. In this contribution we present a simple extension of the approach, which allows us to take into account solid as well as fluid phases of attractive chain molecules. In the implementation of the original TPT1 approach the only information required to describe the properties of the chain fluid are the properties (the equation of state and structure) of a reference monomer fluid. It turns out that this statement is also true in the solid phase. In this way we derive an equation of state phase suitable for fluid and solid phases of chain molecules [1]. We study the global (solid-liquid-vapour) phase diagram of Lennard-Jones chain molecules of varying chain lengths, and compare our results with computer simulations. Excellent agreement is found in terms of the pressure, internal energy and free energy of the systems considered. In agreement with experimental data, asymptotic limits for the critical and triple temperatures are obtained as the chain length increases, although the inherent flexibility of the TPT1 model means that the calculated fluid range is greater than seen experimentally.

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Description of PVT behaviour of hydrofluoroethers using PC SAFT EOS

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In the last few years, many papers have been devoted to the thermophysical characterization of hydrofluoroethers. The reason for this is that these compounds are suitable to replace other halocarbonated fluids in many practical applications. Thus, from a theoretical point of view, an accurate description of the thermodynamic behaviour of these fluids is essential, but due to their molecular size and structure most classical EOS fail to yield good estimations.

In this work, compressed and saturated liquid densities of several pure hydrofluoroethers have been used to calculate the characteristic parameters of PC SAFT EOS. Saturation curves were then calculated using these parameters. These properties were described with good accuracy.

In addition, a group contribution scheme is proposed in order to estimate the pure compound PC SAFT parameters on an additive basis taking into account the functional groups involved in this type of molecules. This contributing method was checked by reproducing the trend of parameters calculated by other authors for linear alkanes and ethers. Then, characteristic parameters were extrapolated for other hydrofluoroethers, obtaining a good description of their saturation curves when experimental data were available for comparison.

Three-site extended primitive models of water and methanol

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Primitive models of associating liquids result from realistic 'parent' models by simplifying their essential features and neglecting the remaining ones (repulsions are represented by hard body interactions and hydrogen bond is mimicked by a square-well attraction). To determine optimal parameters of the primitive models, we have developed a general methodology, which is based primarily on the parameters of the realistic OPLS potential and on the requirements of steric incompatibility. Using this method, we have constructed three-site extended primitive models of water and methanol, and examined their properties by Monte Carlo simulations. We have found that the structural properties, as described by site-site correlation functions, bonding angle distributions, and the number of hydrogen bonds per molecule, are in very good semi-quantitative agreement with their realistic counterparts. This fact proves that the primitive models parametrized by our procedure are able to capture the most important features of the hydrogen bonding. Due to the form and parameters of their potential, they are also well suited for the theoretical description by the thermodynamic perturbation theory of Wertheim.

Thermodynamic properties of primitive models from theory and simulations

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The thermodynamic properties of the recently introduced three-site extended primitive models of water and methanol are computed by means of the thermodynamic perturbation theory of Wertheim (TPT) and the results are compared with simulation data. While theoretical description of the thermodynamic behavior of the reference system of pseudohard bodies by standard hard body equations of state has proven to be very precise, available theories (e.g. RAM) for the structural properties of such substances lack the desired accuracy. Therefore, to assess the performance of TPT itself, we have determined the structure of the reference system from computer simulations. Since the oxygen interaction sites of the considered models can form double bonds, we have used the second order TPT for the perturbation part. We have found that the full theory performs well, but the resulting expressions for the thermodynamic properties are rather complex. For this reason, we have proposed approximations that simplify the resulting expressions and retain accuracy in the most interesting range of the thermodynamic conditions.

Polyelectrolyte-surfactant complexes

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Polyelectrolyte chains and ionic surfactants in solution aggregate towards complexes that exhibit conformational, structural and dynamical features much different from the pure polyelectrolyte or surfactant phases [1,2]. New materials based on this polyelectrolyte - surfactant complexation display extraordinary properties that are interesting for a wide range of applications [2].

While a rich variety of complex structures is revealed experimentally, a systematic theoretical understanding is still missing. Here, we undertake the analysis of the self-assembly of a single polyelectrolyte chain with ionic surfactants at low concentration including a full treatment of the long-ranged Coulomb interaction. In our MC simulation [3] we observe a molecular bottle brush structure of the resulting polyelectrolyte-surfactant-complex. The neutral surfactant tails significantly stabilize the backbone stretching of the polyelectrolyte over a much wider range of Coulomb coupling than is observed for a poly-electrolyte with simple counterions. Adding salt to the complex, the ionic surfactant molecules that are condensed onto the polyelectrolyte chain are replaced by salt microions. Increasing the salt concentration a weakening of the complex and a reduced backbone stretching results.

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Grand Equilibrium: vapour-liquid equilibria by a new simulation method

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In the present work, a new efficient method for molecular simulations of fluid phase equilibria was developed, the *Grand Equilibrium method* [1]. It can be applied to a variety of cases, including liquid-liquid equilibria, but is especially suited for the determination of vapor-liquid equilibria of mixtures. The Grand Equilibrium method combines high accuracy with easiness to use and compares favorably to alternatives like the Gibbs Ensemble Monte Carlo or the NpT + test particle method.

Independently of the number of components, one NpT simulation for the liquid and one independent subsequent pseudo grand canonical simulation for the coexisting phase (typically a gas phase) is performed. Only very rough estimates on the equilibrium are required for reliable and fast convergence. For extreme cases, where highly dense, strongly interacting liquids are involved, the Grand Equilibrium method can be combined with expanded ensemble methods to yield highly accurate results [2].

The method is presented and compared to standard methods using examples for real binary and ternary mixtures, also for difficult conditions [3].

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Thermodynamic modeling of CO₂ absorption into aqueous solutions of MDEA

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The objective of the present work is to develop a thermodynamically rigorous VLE model that represents the system CO₂/MDEA/H₂O. For that purpose the LCVM EoS/G^E model [1] was extended for electrolyte solutions. The electrolyte-LCVM model combines the *t-m* Peng-Robinson equation of state and the extended UNIQUAC equation, where the long range ion-ion interactions are represented by a Debye-Hückel term. The short-range ion-molecule and molecule-molecule interactions were represented by the combinatorial and the residual term of extended UNIQUAC and the adjustable parameters were regressed from experimental VLE data found in literature. The model uses as mixing rule a linear combination of the Vidal and Michelsen mixing rules and takes into consideration the simultaneously chemical and phase equilibria. The obtained results are very satisfactory and they are compared with results obtained from a simplified model [2].

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Chemical Potentials and Phase Equilibria of Lennard-Jones Mixtures: A Self-Consistent Integral Equation Approach

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In vapor-liquid equilibria of liquid mixtures where a supercritical component is present, many conventional correlations fail due to the ambiguities in deciding the reference fugacity for this substance at the temperature and pressure and the state of matter (liquid state) involved. This is particularly serious when the activity coefficient models are used (NRTL, UNIQUAC, Wilson, etc.) Since at the given temperature, the supercritical component is gaseous, not a liquid, it does not have a "vapor pressure". Therefore the pure state cannot be used as reference, and the activity coefficient is ill-defined. In this paper, we used the integral equations for the molecular distribution functions, as given by the Ozstein-Zernike (OZ) equations in statistical mechanics, to calculate for mixtures of hydrocarbons (say, A+B species) the contributions from individual components, including the supercritical components, and determine the partial chemical potentials ($\mu_A = x_A \mu_{AA} + x_B \mu_{BA}$) and partial pressures ($P_A = x_A P_{AA} + x_B P_{BA}$). These statistical mechanical quantities are then characterized with respect to the state conditions and used as standards to test different Ansatzes (assumptions) used in literature. We find that these partial chemical potentials, not being analyzed thus far, are powerful tools for elucidating the phase behavior of vapor-liquid equilibria.

Ionspecific Effects in Diffuse Double Layers - A Local Balance Approach

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Ionspecific, or Hofmeister, effects are omnipresent in biology and colloid chemistry. Important examples include the stability of nucleic acid complexes and micelle formation. Generally, such effects arise from a number of specific interactions of ions with charged interfaces. We describe these interactions by a modified Poisson-Boltzmann theory that takes into account the excluded volumes, polarizabilities and activities of ions and solvent within an electrical double layer [1,2]. The theory provides a set of differential equations that are solved numerically without further approximations. The results are used to investigate the influence of volume effects, dielectric saturation, polarization and self-atmosphere potentials on the surface potential and the electrostatic energy of a charged surface. It is found that the combination of dielectric saturation of the solvent and specific excluded volumes of the ions leads to distinct counterion specific effects. The competition between different counterions is investigated. It is shown that, at sufficiently high surface charge densities, divalent ions are displaced from the immediate vicinity of a charged surface by smaller monovalent ions.

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Polymer solutions: Modelling of $\chi(\varphi, N)$

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The availability of new experimental techniques has revealed that the Flory-Huggins interaction parameter χ depends on N , the number of polymer segments, even as φ , the volume fraction of the solute approaches unity; furthermore $\chi(\varphi)$ may pass through pronounced minima [1]. In order to account for these observations, the Flory-Huggins theory is rephrased in two respects. The new approach starts from infinitely dilute solutions (instead of the regime of high polymer concentration) and thus accounts explicitly for chain connectivity. Moreover it allows for the ability of chain molecules to modify their conformation in response to changes in composition.

In this manner one obtains the following expression for g , the *integral* Flory-Huggins interaction parameter

$$g = \alpha / ((1 - \nu)(1 - \nu\varphi)) - \zeta(1 + (1 - \lambda)\varphi)$$

α and ζ refer to infinite dilution; α stands for the reduced residual Gibbs energy of mixing in the absence of conformational changes and ζ for the conformational response (becoming zero under theta conditions); these two quantities are linearly interdependent. The parameter ν accounts for the fact that the deviation from non-combinatorial behaviour varies with composition. The influences of N are exclusively contained in the parameter λ , which is on the order of 1/2.

The above relation describes ($T=\text{const}$) liquid/vapor and liquid/liquid equilibria quantitatively by means of only two adjustable parameters.

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Macromolecules **28** (1995) 4975

Advances in steam mixture research

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Information about the strength of the interaction between water vapour and the polar fluids NH_3 or SO_2 or HCl or CH_3OH can be gained from flow calorimetric experiment. Quasi-chemical association theory yields the binding energy of the complex formed by the unlike molecules if values of the self association energy of the pure components are available. For the $\text{H}_2\text{O}-\text{H}_2\text{O}$ interaction the self association energy can be obtained from thermodynamic measurements on water with non-polar fluids of known potential, For NH_3-NH_3 analysis of virial coefficients of the ammonia-nitrogen mixture gives the necessary information. For $\text{HCl}-\text{HCl}$ the extent of self association can be obtained from potential surfaces fitted to microwave measurements on Ar-HCl jet-beams. Binding energies from gas phase mixing calorimetry are related to the Boltzmann weighted average of the potential and are about 20% less than those obtained by ab-initio calculations. Structural information on the van der Waals complexes allows calculation of the rotational partition function and hence the entropy and free energy. This information can be used to improve the analysis of the thermodynamic measurements.

Wetting of a symmetric binary mixture in a slit pore

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We consider the wetting behavior of a symmetric binary mixture between two planar, parallel, non-selective, attractive walls (slit pore). Using a lattice-gas model and field-density representation for the intrinsic free-energy functional, we obtain a closed expression for the grand-potential density which is minimized numerically [1]. For sufficiently large wall separations we observe wetting phenomena qualitatively similar to those obtained by (continuous) density functional theory or Monte Carlo computer simulations at a single wall [2]: For weakly attractive walls there are no first-order wetting transitions. Intermediate attraction induces a mixed film coexisting with a demixed bulk phase at low temperatures. For strongly attractive walls a demixed film wets the substrates even at zero temperature, eventually changing to mixed one with increasing temperature via first- or second-order transitions. By varying the size of the pore some of these effects change. For example, smaller pores weaken or even inhibit the formation of the mixed film. Moreover, demixing of the wetting film may be supported by increasing the pore size.

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Unified Density Functional Theory of Complex Fluids

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I will present a unified density functional theory of complex fluids that is able to take into account thermodynamic nonideality due to both inter- and intra-molecular interactions quantitatively. This density functional theory is based on recent achievements in engineering-oriented statistical-thermodynamic theories of bulk fluids, the statistical associating fluid theory (SAFT) in particular, and a modification of Rosenfeld's fundamental measure theory (FMT) for inhomogeneous hard spheres. The central idea is that the excess Helmholtz energy functional can be approximated by that corresponding to the unbonded monomeric system and an additional term taking into account the effect of bond connectivity on inter-segmental interactions. The excess Helmholtz energy functional for the monomeric system includes contributions from hard-sphere repulsion represented by the modified FMT, from van der Waals attraction calculated from the energy equation using the radial distribution function of bulk fluids, from electrostatic interactions represented by the variational mean-sphere approximation, and from associations represented by an extension of SAFT for inhomogeneous systems. The excess Helmholtz energy functional due to chain connectivity depends on the cavity correlation functions of the monomeric reference fluid. I will discuss applications of the unified density functional theory to structural and thermodynamic properties of various complex fluids including colloids and polymers in the bulk or under confinement.

Free-volume theory of the freezing of polydisperse hard-sphere mixtures

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The freezing of hard-sphere mixtures of arbitrary polydispersity is studied within a van der Waals-like free-volume approximation. The present theory is simple enough to allow for a thorough numerical investigation of all the polydispersity effects on the order-disorder transition of hard spheres. Within this context we have studied the influence on the order-disorder transition of the initial preparation, the subsequent fractionation and the possible terminal polydispersity. It is found that the order-disorder transition occupies a finite domain of the initial density-initial polydispersity plane and the frontier of this domain is determined. Considerable variation within this domain is found with respect to the initial density, while the influence of the specific form of the initial size-distribution is found to be only marginal.

Absolute Reference State Measures of Activity Coefficients in Natural Hydrocarbon Mixtures

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The reported technique simultaneously measures the activity coefficient of many petroleum fluids hydrocarbon components. For each component, the chemical potential difference between two different fluids is determined. These two fluids do not need to be in contact. The principle relies on an isotherm liquid-liquid phase equilibrium between Φ_1 (mixture under study) and a reference solvent $S = \Phi_{\text{Ref}}$, where dissolved hydrocarbons should not associate (concept of thermodynamic infinite dilution in reference solvent S). This requirement is fulfilled with methanol/water mixtures. GC-MS coupling is used for quantitating hundreds of the oil components dispersed as infinite dilution traces in solvent S. Complex mixture experimental data can be compared with the predictions of semi-empirical mixing rules such as UNIFAC. Experimental non idealities are more than ten times higher than the theoretically expected ones. Results exhibit the existence of a very rich phenomenology of solvation and order transitions, especially on the paraffins dispersed either in crude oils or in refined cuts.

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MD study of viscoelastic surfactant bilayer membranes

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Molecular dynamics simulations were performed for bilayers formed by cationic surfactants [CH₃(CH₂)₇CH=CH(CH₂)₁₂N⁺(C₂H₄OH)_n(CH₃)_{3-n}]Cl⁻ (n=0,1,2,3) in water. The numbers of surfactant and water molecules were 242 and around 4000, respectively. The effect of the head group chemistry and salt addition on the properties of the bilayer was investigated. All MD simulations were done using the GROMACS package [1,2]. Significant penetration of water and counter-ions inside the hydrophobic core, not registered in computer simulations for anionic surfactants [3], was observed. Radial distribution functions, density profiles, surface area per surfactant molecule, lateral diffusion coefficients were calculated. The effect of salt addition on packing and thickness of the bilayer was studied. The importance of specific features of interaction of the head group with counter ions was stated. The results are of value for developing thermodynamic models of aggregation.

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Phase Transitions of Binary Hard-Sphere Mixtures by Use of a Simple Analytical Equation of State

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Recently we have proposed a unified analytical equation of state (EOS) [1] for solid-liquid-vapor states of matters, and examined the thermo-dynamic properties of argon, carbon dioxide, and methane, as well as binary mixtures of methane and carbon dioxide. Also it has been demonstrated that the EOS can be applied for the solid-fluid transition of hard spheres, by eliminating the attractive part of the EOS. The present work is an extension of the earlier calculations of pure hard spheres, and here we examine the phase behavior of binary hard-sphere mixtures.

The hard-sphere EOS employed in this study is :

$$P = \frac{RT}{V-b} \left(\frac{V-d}{V-c} \right)^k, \text{ where } k=1 \text{ or } 2. \text{ } b, c, \text{ and } d$$

are proportional to a hard-sphere volume, and their mixing rule is a quadratic form in mole fraction, with a "non-additive" mixing parameter, m_{ij} (zero for $i=j$). The b parameter is given:

$$b(\text{mix}) = \sum_{i,j=1}^2 \frac{(b_i + b_j)}{2} (1 - m_{ij}) x_i x_j. \quad \text{Similar}$$

mixing rules are applied to c and d . It is shown that various fundamental phase-transition behaviors can be simulated: ideal or near ideal, azeotropic (max. and min.), eutectic, and peritectic types. While stable solid-fluid and solid-solid transitions occur generally, stable fluid-fluid separations can only exist under certain conditions.

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Swelling and electro-mechanical effects of swollen liquid crystal elastomers with low molecular weight liquid crystals

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We experimentally investigated the swelling behavior of swollen liquid crystal elastomers (LCEs) in two anisotropic solvents such as low molecular weight liquid crystals, 5CB and MBBA. The length of LCEs by swelling expanded more than 1.8 times of its initial length which depended on the director orientation. The volume change of swollen LCEs has been investigated as function of temperature and several phase transitions were observed in both optical and differential scanning calorimetry measurements [1]. Electro-mechanical effects of swollen LCEs were also investigated in detail and drastic decrease of the critical field for electro-mechanical effects, 1/4000 lower than dry LCEs was obtained. The response time of shape change is in msec levels. On the basis of these results we conclude that the swollen LCEs have the potential to make a wide variety of fast, variable amplitude, low voltage driven artificial muscles.

Reference

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Energy and structure of 3-1 valent ionic system : A Monte Carlo study

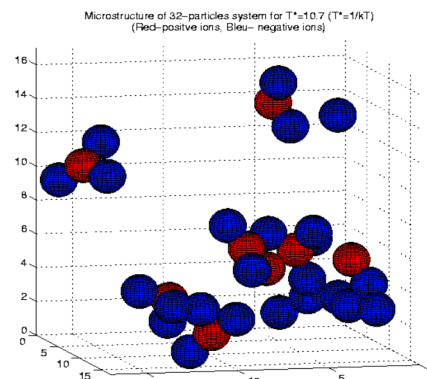
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An asymmetric 3-1 valent ionic system was studied by Monte Carlo method. Study was done in both NVT and NPT ensembles. Three isotherms were calculated; undercritical, near-critical and overcritical. Liquid-vapor phase transition is checked out. The character of radial distribution functions and thermophysical properties were used to follow the microstructure of the system. At high temperature a second order phase transition is checked out. There's structuration in neutral groups with four ions forming an equilateral triangle; the positive ion is in the center (Figure). At this point the heat capacity has a non-monotone character.



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Prediction of phase equilibria for hydrocarbon-water-methanol systems

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In this work, three thermodynamic models have been evaluated and compared to the experimental dew point data for hydrocarbon-water-methanol systems. The three models are: (1). The DBR method that is integrated in commercial software, DBR Hydrate and PVT Pro. This method uses the Peng-Robinson equation of state (PR EOS) with temperature dependent interaction parameters (k_{ij} and l_{ij}). (2). The UNIFAC-based SRK EOS with the MHV2 mixing rule developed by Dahl et al. (3). The EOS-CR (equation of state-chemical reticular) method with the UNIFAC model developed by Blanco et al. and Avila et al.

The three models were applied to predict dew point temperatures for C_1 -H₂O-CH₄O, C_2 -H₂O-CH₄O and C_3 -H₂O-CH₄O mixtures. The DBR, SRK-MHV2 and EOS-CR models give very good and comparable predictions with AADs of 1.3, 1.2 and 1.9 K, respectively. The three models were also used to predict water dew points for nine SNG-water-methanol systems. The AADs of the predicted water dew temperature by using the DBR, SRK-MHV2 and EOS-CR models are 0.9, 1.5 and 1.2 K, respectively.

The three models have comparable accuracies to predict water dew points for hydrocarbon-water-methanol systems. The SRK-MHV2 model gives worse predictions for systems containing multi-hydrocarbons than for those containing a single hydrocarbon. Although the SRK-MHV2 and EOS-CR models are much more complicated, the DBR model gives relatively better results than the other two models for the systems containing multi-hydrocarbons.

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