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Fields of research

- Thermophysical properties of pure ionic liquids and their liquid phase behavior in mixtures with molecular solvents
- Experimental determination of vapor–liquid equilibria in mixtures containing components of low and high molecular mass
- Data processing with activity coefficient models and equations of state
- Prediction of phase behavior using models based on group contribution methods
- Density functional study of interfacial phase transitions and nanodrops
- Dynamic properties of simple and complex fluids on a molecular scale
- Molecular simulations and perturbation theories for model fluids and fluid mixtures
- Development of equations of state based on molecular theory
- Molecular simulations of solid–liquid interfaces
- Molecular simulations of ionic liquid interfaces
- Mesoscale simulations of polymeric and energetic systems

Applied research

- Technology for the preparation of molecularly imprinted polymeric materials

Research projects

Properties of ionic liquids - experiment and modelling

(M. Bendová, Z. Wagner, bendova@icpf.cas.cz, wagner@icpf.cas.cz; joint project with Queen's University of Belfast, UK and Université Blaise Pascal, France; supported by MEYS, project No. LG12032 and by ICPF)

Ionic liquids (ILs) have been extensively studied for more than two decades now by a number of research teams worldwide. This ever growing class of compounds still remains largely uncharacterized in terms of their thermodynamic properties. To be able to use ionic liquids efficiently in any application, knowledge of their properties as pure compounds and in mixtures with molecular compounds is necessary. A wide range of thermodynamic and physical properties, such as density, viscosity, excess properties and phase behavior is studied not only to facilitate scale-up from a lab bench to a pilot plant, but also to understand the underlying structural effects that influence on the studied macroscopic properties.

Experimentally, thermal properties (heat capacity and phase transitions) in pure ILs using differential scanning calorimetry (DSC) are studied in our group. In mixtures of ILs with molecular solvents, liquid phase behavior is investigated using the following methods:

- cloud-point (nephelometric, synthetic) method [8]
- direct-analytical method [1]
- volumetric method [8]
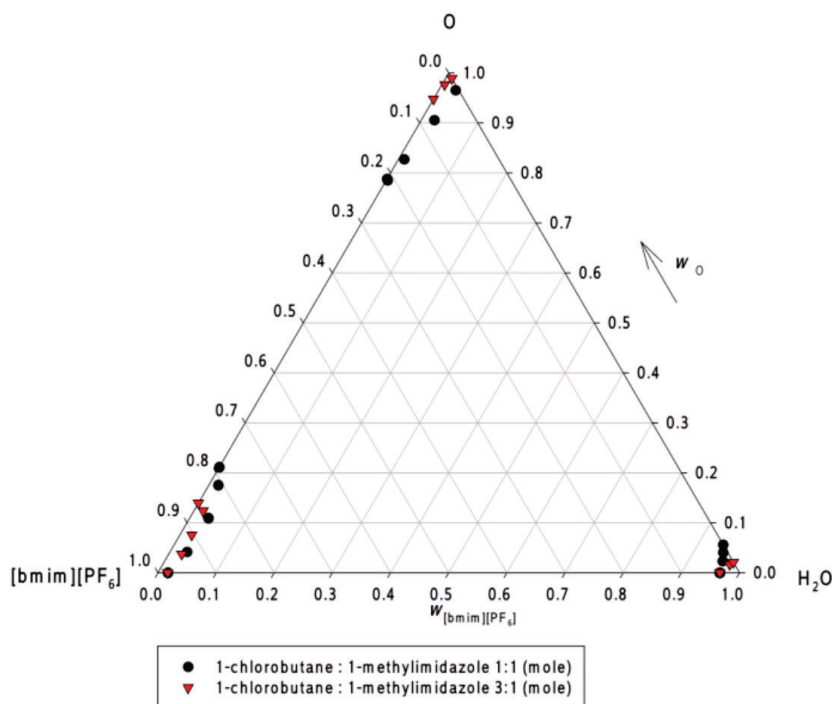
Miscibility gaps in pseudoternary systems 1-butyl-3-methylimidazolium hexafluorophosphate + H_2O + (1-chlorobutane/1-methylimidazole) determined by the cloud-point method

To obtain useful data for the assessment of impact of the studied ionic liquids on environment, the above-mentioned methods are used to measure their mutual solubility with water and 1-octanol and the partitioning coefficient octanol/water K_{OW}. These experiments enable us to assess their hydrophobicity/lipophilicity and hence their tendency to bioaccumulation.

At the same time, experimental work combined with appropriate modelling leads us to a deeper understanding of the influence of the structure of the ionic liquid on its properties. Experiments are complemented with modelling using the COSMO-RS methodology that uses quantum chemistry combined with continuum solvation models for a priori predictions of chemical potentials. Description of experimental data using SAFT-type equations of state provides us with an insight into the molecular structure of the pure ionic liquids and their mixtures. [Refs. 1, 3, 8]


(a)   (b)
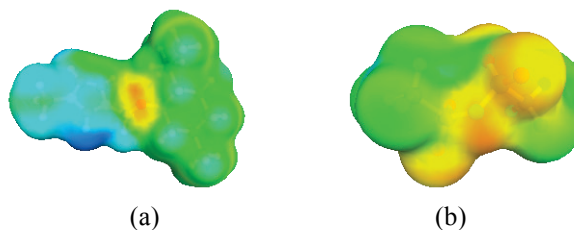
Screening charge density of 1-[(1R, 2S, 5R)-(−)-menthoxymetyl]-3-methylimidazole cation (a) and bis(trifluoromethanesulfonyl)imide anion (b) using COSMO methodology

Vapor-liquid equilibria and thermodynamic properties - experiment and data processing

(I. Wichterle, Z. Sedláková, wichterle@icpf.cas.cz, sedlakova@icpf.cas.cz; supported by ICPF)

a) Systems containing low molecular mass components

Isothermal vapor-liquid equilibrium (VLE) data were measured in binary and ternary systems containing alcohol, hydrocarbon and ketone, namely 2-propanol, isooctane, and 2,4-dimethyl-3-pentanone. The binary VLE data were correlated using the Wilson and nonrandom two-liquid (NRTL) equations by means of a new algorithm and resulting parameters were then used for the calculation of phase behavior in the ternary system and for subsequent comparison with experimental data. Phase and chemical equilibria were isothermally determined in system with chemical reaction (transesterification), namely in the quaternary ethyl ethanoate + ethanol + propyl ethanoate + propanol system and in all six binary subsystems. Good prediction was achieved with use of evaluated NRTL binary parameters; deviations are shown in Figure. [Refs. 11, 12]

a   b
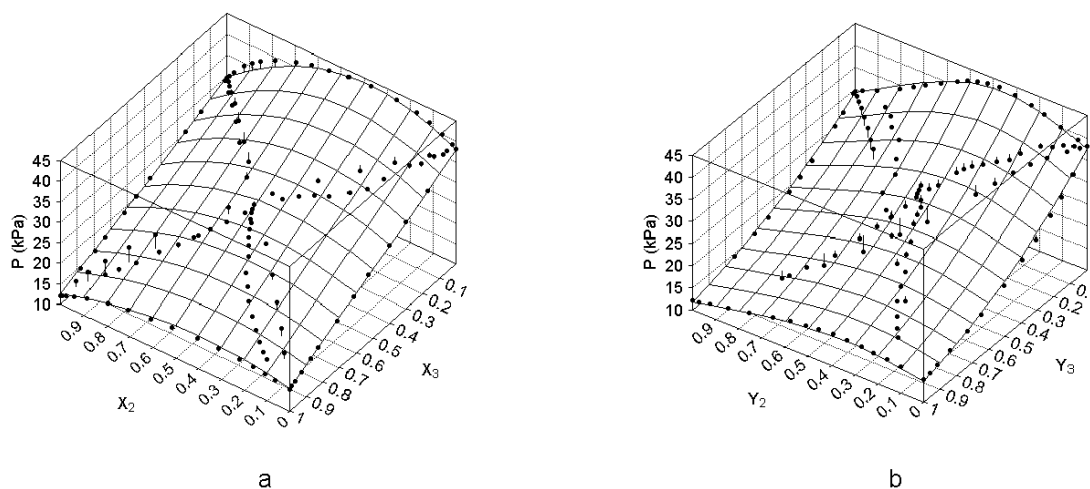
Modified composition variables versus pressure for the ethyl ethanoate (1) + ethanol (2) + propyl ethanoate (3) + propanol (4) system at 348.15 K; (a) liquid phase; (b) vapor phase

b) Systems containing polymers

Vapor-liquid equilibria have been determined in the systems composed of polyacrylic acid with water, and poly(methyl methacrylate) with acetone by ebulliometric (total pressure measurement) method. Ebulliometer has been redesigned (see Figure) and experimental procedure has been upgraded. Experiments have been carried out isothermally and the measured data were correlated by the UNIQUAC equation, and compared with available data. Results were presented at two inter-national conferences.


New design of microebulliometer

c) Prediction of properties of petroleum fluids

A simplified method for characterizing petroleum fluids (crude oil and gas condensate) and for predicting phase equilibria was developed. Vapor-liquid equilibria in such highly complex natural mixtures were calculated by the pseudo-component method, which assumes that each fraction is a mixture of predefined pure components. The required input data include complete TBP (true boiling point) analysis, PNA (paraffin-naphthene-aromatic hydrocarbon) analysis, and density data, preferably for each sub-fraction. Known thermodynamic procedures are used to estimate the critical data, acentric factor, and molecular weight for the model compounds. [Refs. 2, 13]

d) Molar excess volumes

Experimental determination of molar excess volumes in the benzene + *tert*-amyl methyl ether + isooctane and the isooctane + toluene + butan-1-ol systems have been carried out. Data were successfully correlated by means of the ERAS model and the Redlich-Kister equation.
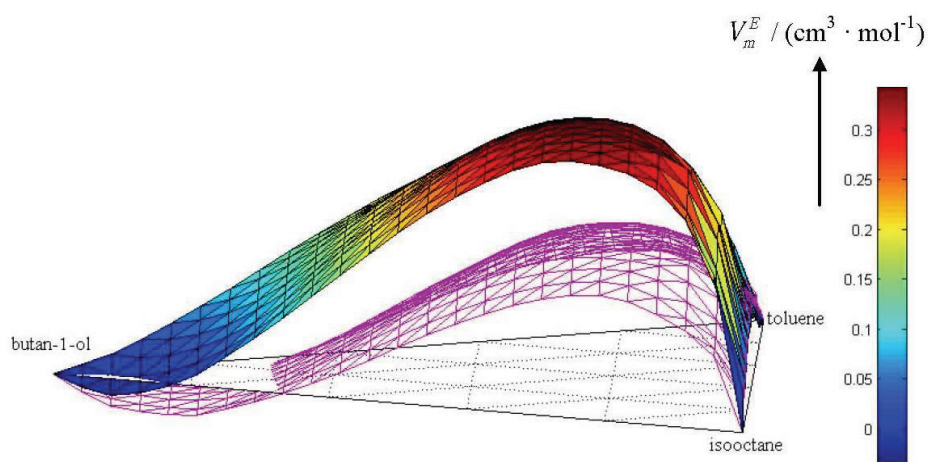

Excess molar volume for the ternary isooctane + toluene + butan-1-ol system at temperature 298.15 K (violet net) and 328.15 K (in colors)

Molecular based studies of fluid systems
(S. Pařez, M. Předota, A. Malijevský, I. Nezbeda, M. Lísal, parez@icpf.cas.cz, predota@icpf.cas.cz, malijevsky@icpf.cas.cz, nezbeda@icpf.cas.cz, lisal@icpf.cas.cz; joint with University of South Bohemia, Ceske Budejovice, with ICT and Imperial College London, UK, and with UJEP; supported by MEYS, KONTAKT II, project No. LH12020, by GA ASCR, projects No. IAA400720802 and IAA200760905, and by GACR, project No. P106/10/1194)

(a) Solid-liquid interfaces

Shear viscosity and relative permittivity of aqueous mixtures were studied in the interfacial region at a planar surface. Profiles of both properties show significant deviations from their bulk values when approaching the surface. Our simulation results provide pieces of information inaccessible by experiment that promote our understanding of peculiar properties of solid-liquid interfaces. [Ref. 10]
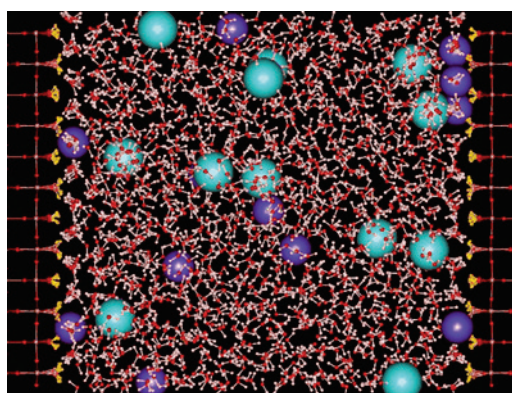
**Water/ions-TiO$_2$ interface**

(b) Confined fluids

The structural and interfacial properties of a nanoscopic liquid drops and bubbles were examined by means of mechanical, thermodynamical, and statistical mechanical approaches. A novel method based on a microscopic density functional theory for calculation of surface tension and Tolman's length of highly curved interfaces was proposed. Further, phase transitions in a microscopic capillary capped at one end were studied by means of fundamental measure density functional theory. [Refs. 16, 18]
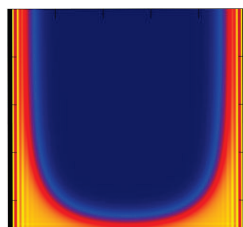
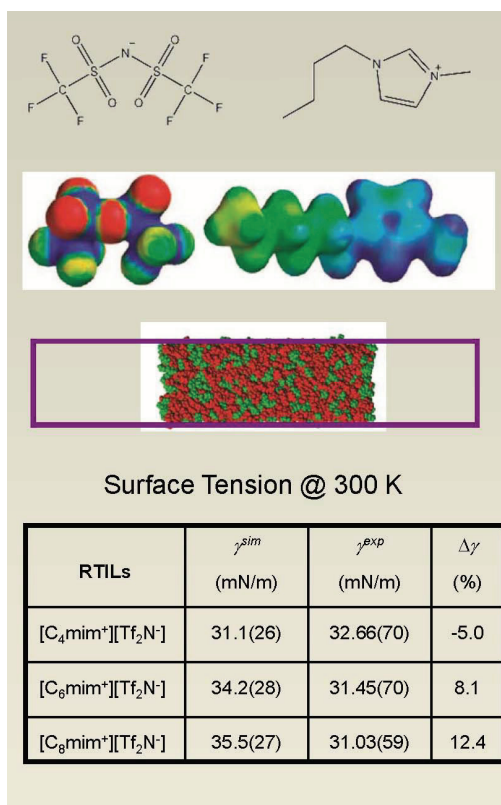**An example of microscopic capillary capped at one end**

(c) Model fluids

A theoretical, molecular-based model for hydration of simple nonpolar solutes has been developed. The model qualitatively reproduces basic features of hydrophobic hydration and temperature dependence of Henry's law constants of noble gases. [Refs. 4, 15]
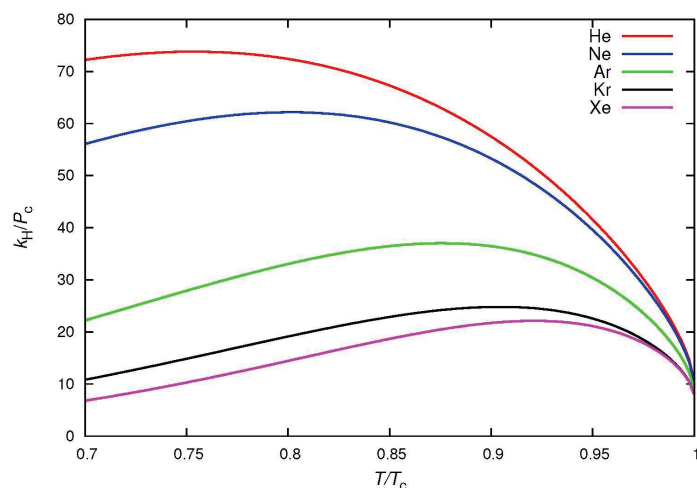
**The reduced Henry's law constant of noble gases predicted
by a theoretical model based on simple interaction potentials**

(d) Ionic liquid interfaces

Molecular dynamics simulations were employed to provide insight into the air-liquid interface for three ILs with a common anion: bis(trifluoromethylsulfonyl) imide, and imidazolium-based cat ions that differ in the alkyl tail length. The air-liquid interface was analyzed using the intrinsic method and of structural and dynamic properties of the interfacial, sub-interfacial and central layers were determined. [Refs. 5, 9]

Surface Tension @ 300 K

| RTILs	γ^{sim} (mN/m)	γ^{exp} (mN/m)	$\Delta\gamma$ (%)
$[C_4mim^+][Tf_2N^-]$	31.1(26)	32.66(70)	-5.0
$[C_6mim^+][Tf_2N^-]$	34.2(28)	31.45(70)	8.1
$[C_8mim^+][Tf_2N^-]$	35.5(27)	31.03(59)	12.4

Molecular dynamics simulations of ILs

Mesoscale simulation studies of polymeric and energetic materials
(M. Lísal, lisal@icpf.cas.cz; joint with US Army Research Laboratory, Aberdeen, USA and Penn State University, State College, USA; supported by MEYS, KONTAKT II, project No. LH12020 and US/CZ bilateral project W911NF-10-2-0039)

   Dissipative particle dynamics simulations were used to study structural and dynamic properties of entangled polymer melts. Mesoscale modelling capability is being develop for studying the dynamic response of reactive materials. [Ref. 14]
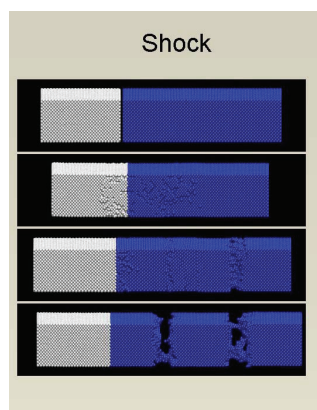
Response of Al/Ni energetic material to shock

International co-operations

Imperial College London, London, UK: Confined fluids

INA, Research and Development, Zagreb, Croatia: Novel technology of molecularly imprinted polymeric materials preparation

Penn State University, State College, PA, USA: Dissipative particle dynamics simulations of adsorption behavior of model proteins on surface

Queen's University Ionic Liquids Laboratory (QUILL), Belfast, UK: Liquid–liquid phase equilibria in systems of ionic liquids

University of Loughborough, Loughborough, UK: Dynamic density functional theory

University of Ontario Institute of Technology, Oshawa, ON, Canada: Macroscopic and molecular-based studies in the statistical mechanics of fluids

U.S. Army Research Laboratory, Weapons and Materials Research Directorate, MD, USA: Mesoscale simulations of energetic and reactive materials

Wrocław University of Technology, Department of Chemical Engineering, Poland: Solubility behavior of chiral ionic liquids in water and 1-octanol, and their tendency to bioaccumulation

Visits abroad

M. Lísal: University of Ontario, Institute of Technology, Oshawa, ON, Canada (1 month)
M. Lísal: Pennsylvania State University, State College, PA, USA (1 month)
A. Malijevský: Imperial College London, London, UK (3 months)
A. Malijevský: University of Loughborough, Loughborough, UK (2 weeks)
S. Pařez: University of Paderborn, Institute of Thermodynamics and Energy Technology, Paderborn, Germany (3 months)
L. Vlček: Vanderbildt University, Nashville, TN, USA (12 months)

Visitors

A. Archer, University of Loughborough, Loughborough, UK

D. Gheorghe Chiscan, Institute of Physical Chemistry I. Murgulescu, Romanian Academy of Sciences, Bucuresti, Romania

D. Dragoescu, Institute of Physical Chemistry I. Murgulescu, Romanian Academy of Sciences, Bucuresti, Romania

Teaching

M. Bendová: ICT, Faculty of Chemical Engineering, postgraduate course "Physical chemistry for technological practice"

J. Jirsák: UJEP, Faculty of Science, courses "Introduction to chemistry", "Physical chemistry", "Physical chemistry seminar" and "Free software in natural sciences"

M. Kotrla, M. Předota: CU, course "Advanced computer simulations in many particle systems"

M. Lísal: UJEP, Faculty of Science, courses "Parallel programming", "Numerical mathematics", "Molecular simulations" and "Mesoscale simulations"

A. Malijevský: ICT, Faculty of Chemical Engineering, courses "Physical chemistry I", "Physical chemistry of the micro-world" and "Introduction to a modern theory of phase transitions"

M. Předota: University of South Bohemia, České Budějovice, courses "Lectures from physics oriented to particle and nuclear physics" and "Selected lectures from physics"

Publications

Original papers

[1]   Bendová M., Sedláková Z., Andresová A., Wagner Z.: Using Partial Least-Squares Regression in Multivariate UV Spectroscopic Analysis of Mixtures of Imidazolium-Based Ionic Liquids and 1-Methylimidazole for Measurements of Liquid-Liquid Equilibria. *J. Solution. Chem.* 41, 2164–2172 (2012).

[2]   Bogdanić G., Pavlíček J., Wichterle I.: Theoretical Background for Predicting the Properties of Petroleum Fluids via Group Contribution Methods. *Procedia Eng.* 42, 1873–1878 (2012).

[3]   Jacquemin J., Bendová M., Sedláková Z., Holbrey J.D., Mullan C.L., Youngs T.G.A., Pison L., Wagner Z., Aim K., Costa Gomes M.F., Hardacre Ch.: Phase Behaviour, Interactions, and Structural Studies of (Amines+Ionic Liquids) Binary Mixtures. *Chem. Phys. Chem.* 13, 1825–1835 (2012).

[4]   Krejčí J., Nezbeda I.: The Critical Temperature and Properties of Real Gas from Low Order Perturbed Virial Expansions. *Fluid Phase Equilib.* 314, 156–160 (2012).

[5]   Lísal M., Posel Z., Izák P.: Air-Liquid Interface of Imidazolium-Based [Tf$_2$N$^-$] Ionic Liquids: Insight from Molecular Dynamics Simulations. *Phys. Chem. Chem. Phys.* 14, 5164–5177 (2012).

[6]   Machanová K., Boisset A., Sedláková Z., Andresová A., Jacquemin J., Bendová M.: Termodynamické vlastnosti směsí iontových kapalin a molekulárních rozpouštědel pro využití v dvoufázové katalýze. (Czech) Thermodynamic Properties of Mixtures of Ionic Liquids and Molecular Solvents for Biphasic Catalysis. *Inovační podnikání a transfer technologií*, příloha 20, V–VII (2012).

[7]   Machanová K., Boisset A., Sedláková Z., Anouti M., Bendová M., Jacquemin J.: Thermophysical Properties of Ammonium-Based Bis{(trifluoromethyl)sulfonyl}imide Ionic Liquids: Volumetric and Transport Properties. *J. Chem. Eng. Data* 57, 2227−2235 (2012).

[8]   Machanová K., Jacquemin J., Wagner Z., Bendová M.: Mutual Solubilities of Ammonium-based Ionic Liquids with Water and with Water/Methanol Mixture. *Procedia Eng.* 42, 1229–1241 (2012).

[9]   Moučka F., Lísal M., Smith W.R.: Molecular Simulation of Aqueous Electrolyte Solubility. 3. Alkali-halide Salts and Their Mixtures in Water and in Hydrochloric Acid. *J. Phys. Chem. B* 116, 5468–5478 (2012).

[10]   Pařez S., Předota M.: Determination of the Distance-Dependent Viscosity of Mixtures in Parallel Slabs Using Non-Equilibrium Molecular Dynamics. *Phys. Chem. Chem. Phys.* 14, 3640–3650 (2012).

[11]   Pavlíček J., Bogdanić G., Wichterle I.: Vapour–Liquid and Chemical Equilibria in the Ethyl Ethanoate + Ethanol + Propyl Ethanoate + Propanol System Accompanied with Transesterification Reaction. *Fluid Phase Equilib.* 328, 61–68 (2012).

[12]   Pavlíček J., Wichterle I.: Isothermal (Vapour + Liquid) Equilibria in the Binary and Ternary Systems Composed of 2-Propanol, 2,2,4-Trimethylpentane and 2,4-Dimethyl-3-Pentanone. *J. Chem. Thermodyn.* 45, 83–89 (2012).

[13]   Sedláková Z., Andresová A., Morávková L., Bogdanić G.: Experiments and Modelling of Liquid–liquid Equilibria in the Mineral Oil + N,N-dimethylformamide System. *Procedia Eng.* 42, 721–725 (2012).

[14]   Sirk T.W., Slizoberg Y.R., Brennan J.K., Lísal M., Andzelm J.W.: An Enhanced Entangled Polymer Model for Dissipative Particle Dynamics. *J. Chem. Phys.* 136, 134903 (2012).

[15]   Škvor J., Nezbeda I.: Percolation Line, Response Functions, and Voronoi Polyhedra Analysis in Supercritical Water. *Condens. Matter Phys.* 15, 23301, 1–8 (2012).

[16]   Malijevský A.: Does Adsorption in a Single Nanogroove Exhibit Hysteresis? *J. Chem. Phys.* 137, 214704 (2012).

Review papers

[17]   Sedláková Z., Wagner Z.: High-Pressure Phase Equilibria in Systems Containing CO_2 and Ionic Liquid of the $[C_nmim][Tf_2N]$ Type. *Chem. Biochem. Eng. Q.* 26, 55–60 (2012).

[18]   Malijevský A., Jackson G.: A Perspective on the Interfacial Properties of Nanoscopic Liquid Drops. *J. Phys.: Condens. Matter* 24, 464121 (2012).