EMLG-JMLG Annual Meeting 2010

Complex liquids
Modern trends in exploration, understanding and application

September 5–9, 2010
Lviv, Ukraine

PROGRAMME & ABSTRACTS

Lviv – 2010

Organizers

European Molecular Liquids Group

Japanese Molecular Liquids Group

Institute for Condensed Matter Physics
of the National Academy of Sciences of Ukraine
Lviv, Ukraine

Ivan Franko National University of Lviv
Lviv, Ukraine

Lviv Polytechnic National University
Lviv, Ukraine

Supported by

National Academy of Sciences of Ukraine
Organisation for the Prohibition of Chemical Weapons
Uarnet

Meeting Chair

Myroslav Holovko
Institute for Condensed Matter Physics, Ukraine

Vice-Chair

Wojciech Gadomski
University of Warsaw, Poland

Scientific Advisory Committee

Yuriy Bobalo, (Polytechnic National University, Ukraine)
Philippe Bopp, (University of Bordeaux, France)
Richard Buchner, (University of Regensburg, Germany)
Leonid Bulavin, (Kyiv National University, Ukraine)
Vladimir Durov, (Moscov State University, Russia)
Fumio Hirata, (Institute for Molecular Science, Japan)
Ralf Ludwig, (University Rostock, Germany)
Ivo Nezbeda, (Czech Academy of Sciences, Czech Republic)
Ihor Mryglod, (National Academy of Sciences of Ukraine, Ukraine)
Maurizio Musso, (University of Salzburg, Austria)
Gabor Palinkas, (Hungarian Academy of Sciences, Hungary)
Maria Ricci, (University of Roma 3, Italy)
Hajime Torii, (Shizuoka University, Japan)
Ivan Vakarchuk,(Ivan Franko National University of Lviv, Ukraine)
Toshio Yamaguchi, (Fukuoka University, Japan)
Jack Yarwood, (Sheffield Hallam University, UK)
Ihor Yukhnovskii, (National Academy of Sciences of Ukraine, Ukraine)
Anatolij Zagorodny, (National Academy of Sciences of Ukraine, Ukraine)

Organizing Committee

Chairman

Taras Bryk
Institute for Condensed Matter Physics, Ukraine

Co-Chairmen

Vasyl Vysochanskii
Ivan Franko National University of Lviv, Ukraine,

Petro Kostrobiy
Lviv Polytechnic National University, Ukraine

Secretary

Andrij Trokhymchuk
Institute for Condensed Matter Physics, Ukraine

Members of the Organizing Committee

Yuriy Blazhyevskyi, (Institute for Condensed Matter Physics, Ukraine)
Maksym Druchok, (Institute for Condensed Matter Physics, Ukraine)
Ivan Klevets, (Institute for Condensed Matter Physics, Ukraine)
Ivan Kravtsiv, (Institute for Condensed Matter Physics, Ukraine)
Olesya Mryglod, (Institute for Condensed Matter Physics, Ukraine)
Mykola Patsahan, (Institute for Condensed Matter Physics, Ukraine)
Petro Yakibchuk, (Ivan Franko National University of Lviv, Ukraine)

The European Molecular Liquids Group (EMLG) and the Japanese Molecular Liquids Group (JMLG) are interdisciplinary groups covering the molecular aspects of fluids in Physics, Chemistry and Biology. The European group was founded in 1982 and was joined by the Japanese group in 1996.

Annual meetings have been organized since 1982 in different countries with varying focus in order to cooperate internationally and to coordinate activities in this field. Traditionally, a special issue of the Journal of Molecular Liquids covers the scientific contributions to the meetings.

The EMLG-JMLG annual meeting 2010 is aimed to present the most recent progress in experiment, theory and computer simulations of complex liquids.

Main topics

- General aspects
- Electrolyte and polyelectrolyte solutions, ionic liquids
- Liquids under confinement and at interfaces, colloids
- Macromolecular and bilogical liquids
- Anisotropic liquids

Contacts

EMLG-JMLG 2010
Institute for Condensed Matter Physics
of the National Academy of Sciences of Ukraine
1 Svientsitskii Str., 79011 Lviv, Ukraine

E-mail: `emlg2010@icmp.lviv.ua`

Tel.: +38 032 2761978

Fax: +38 032 2761158

URL: `http://emlg2010.org.ua`

EMLG-JMLG Annual Meeting 2010

Complex liquids

Modern trends in exploration, understanding and application

Programme

September 5–9, 2010

Lviv, Ukraine

Monday, September 6, 2010

1^{st} Morning Session 9.00 – 10.45

9.00 – 9.20 **Opening address**

Chaired by Richard BUCHNER

9.20 – 10.05 **Polyelectrolytes in water: How the presence of hydrophobic groups modifies the ion–specific effects**
Vojko VLACHY, University of Ljubljana, Slovenia

10.05 – 10.25 **Chemical reactions of biological proteins in solution by time-resolved diffusion method**
Masahide TERAZIMA, Kyoto University, Japan

10.25 – 10.45 **Aqueous alkali halide solutions: can osmotic coefficients be explained on the basis of the ionic sizes alone?**
Yuriy KALYUZHNYI, Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

10.45 – 11.15 COFFEE

Monday, September 6, 2010

2nd Morning Session 11.15 – 13.00

Chaired by Philippe BOPP

11.15 – 12.00	**Thermal behavior, structure and dynamics of liquids and electrolyte solutions confined in mesoporous materials** Toshio YAMAGUCHI, Fukuoka University, Japan
12.00 – 12.20	**One– and two–mode behavior of the ν(C=O) band in N,N–dimethylformamide isotopic mixtures: DMF/DMF–d$_1$, DMF/DMF–d$_6$, and DMF/DMF–^{13}CO** Maria Grazia GIORGINI, Universitá di Bologna, Italy
12.20 – 12.40	**Scaled particle theory for a hard-sphere fluid confined in different model matrices** Wei DONG, Ecole Normale Supérieure de Lyon, France
12.40 – 13.00	**Transient absorption and fluorescence measurements of polymer liquids and gels** Wojciech GADOMSKI, University of Warsaw, Poland
13.30 – 15.00	LUNCH

Monday, September 6, 2010

1^{st} Afternoon Session 15:00 – 17.00

Chaired by Hajime TORII

15.35 – 16.20	**Critical casimir forces** Siegfried DIETRICH, Max Planck Institut for Metals Research, Stuttgart, Germany
16.20 – 16.40	**Dipolar interaction and molecular ordering in liquid propylene carbonate: anomalous dielectric susceptibility and Raman non-coincidence effect** Alexander BRODIN, National Techn. Univ. of Ukraine “Kyiv Polytechnic Institute”, Ukraine
16.40 – 17.00	**Viscosity calculations of simple liquids using the transient time correlation function formalism** István BORZSHÁK, Nyugat-magyarországi Egyetem, Szombathely, Hungary
17.00 – 17.30	COFFEE

Monday, September 6, 2010

2^{nd} Afternoon Session 17.30 – 18.55

Chaired by Ralf LUDWIG

17.30 – 18.15 **Transport coefficients: a path to explorate convex (colloidal and polyelectrolyte solutions) and concave (clays, porous media) systems**
Pierre Turq, Université Pierre et Marie Curie, Paris, France

18.15 – 18.35 **Shear relaxation and ionic transport of imidazolium-based ionic liquids**
Tsuyoshi YAMAGUCHI, Nagoya University, Japan

18.35 – 18.55 **Understanding the solubility of gases in ionic liquids from molecular simulations**
Daniela KERLÉ, University of Rostock, Germany

Tuesday, September 7, 2010

Morning Session 9.00 – 10.45

Chaired by Gabor PALINKAS

9.00 – 9.45	**Inelastic X-Ray Scattering study of the high frequency dynamics in liquids** Giancarlo RUOCCO, “Sapienza” Universitá di Roma, Italy
9.45 – 10.05	**First-principles molecular dynamics simulations of supercritical water: the importance of dispersion corrections** Ari Paavo SEITSONEN, University of Zurich, Switzerland
10.05 – 10.25	**Intermolecular charge flux induced by the OH stretching mode of water and its effect on the intermolecular vibrational coupling** Hajime TORII, Shizuoka University, Japan
10.25 – 10.45	**Breast cancer diagnosis and dynamics of lipids by Raman imaging and femtosecond spectroscopy** Halina ABRAMCZYK, Technical University of Łódź, Poland
10.45 – 11.15	COFFEE
11.00 – 13.00	POSTER SESSION

Chaired by: Michael PROBST

13.30 – 15.00	LUNCH
15.00 – 18.00	EXCURSION

Wednesday, September 8, 2010

1st Morning Session 9.00 – 10.45

Chaired by Toshio Yamaguchi

9.00 – 9.45	**Statics and dynamics of colloidal particles in liquid crystals** Oleg LAVRENTOVICH, Kent State University, Kent, Ohio, USA
9.45 – 10.20	**Structure and dynamics of Magnetic Fluids** Regine Perzynski, Université Pierre et Marie Curie, Paris, France
10.20 – 10.40	**Influence of molecular size and shape of the nematogenic substances on the liquid crystal phase equilibrium** Santiago LAGO, University Pablo de Olavide, Seville, Spain
10.40 – 11.00	**Dispersions of multiwalled carbon nanotubes in liquid crystals: new challenges to molecular theories of anisotropic soft matter** Longin LISETSKI, Institute for Scintillation Materials, NAS of Ukraine, Kharkiv, Ukraine
11.00 – 11.30	COFFEE

Wednesday, September 8, 2010

2^{nd} Morning Session 11.15 – 13.00

Chaired by Wojciech Gadomski

11.30 – 12.15	**Statistical mechanics of molecular liquids reveals elementary processes in life phenomena** Fumio HIRATA, Institute for Molecular Science, Okazaki, Japan
12.15 – 12.35	**Simple lattice models of complex systems** Alina CIACH, Institute of Physical Chemistry, PAS, Warsaw, Poland
12.35 – 12.55	**Theoretical and simulation results for some model simple fluids (bulk and confined) with structural, thermodynamic and dynamic anomalies** Orest PIZIO, Instituto de Quimica, UNAM, Mexico City, Mexico
12.55 – 13.15	**An equilibrium study of urea denaturation of trp-cage miniprotein** Dietmar PASCHEK, Universität Rostock, Germany

13.30 – 15.00 LUNCH

Wednesday, September 8, 2010

Afternoon Session 15.30 – 17.15

Chaired by Halina ABRAMCZYK

15.30 – 16.15	**Stimuli-responsive nanostructured materials** Sergiy MINKO, Clarkson University, Potsdam, New York, USA
16.15 – 16.35	**The liquid-liquid phase transitions in ionic solutions: criticalität, crossover and complete scaling** Wolffram SCHRÖER, University of Bremen, Germany
16.35 – 16.55	**Effect of methanol on microphase separation of ionic liquids** Toshiyuki TAKAMUKU, Saga University, Japan
16.55 – 17.15	**Diffusion of imidazolium based ionic liquids in different polar solvents** Eliane SCHMIDT, University of Rostock, Germany
17.15 – 17.35	**Multiscale simulations of the self-assembly of liquid crystalline dendrimers** Jaroslav ILNYTSKYI, Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine
19.00 – 22.00	BANQUET

Thursday, September 9, 2010

1st Morning Session 9.00 – 11.00

Chaired by Igor MRYGLOD

9.00 – 10.00	**Supramolecular chemistry for molecular liquids, solutions and assemblies** Jean-Marie LEHN, Université de Strasbourg and Collège de France, Paris, France
10.00 – 10.20	**Entropy driven self-assembly mechanism** Marcelo LOZADA-CASSOU, Mexican Petroleum Institute, Mexico City, Mexico
10.20 – 10.40	**Microheterogenity of alcohol-water mixtures: experimental and simulation study** Franjo SOKOLIĆ, University of Split, Croatia
10.40 – 11.00	**Nanosize supramolecular aggregates in methanol: from melting point to supercritical state** Vladimir DUROV, Moscow State University, Russia
11.00 – 11.30	COFFEE

Thursday, September 9, 2010

2^{nd} Morning Session 11.30 – 13.15

Chaired by Myroslav HOLOVKO

11.30 – 12.15	**Multiscale methods for nanochemistry and biophysics in solution** Andrij KOVALENKO, National Institute for Nanotechnology, Edmonton, Canada
12.15 – 12.35	**Towards calculation of hydration free energy** Volodymyr SERGIIEVSKYI, Max-Planck-Institute for Mathematics in the Sciences, Leipzig, Germany
12.35 – 12.55	**On the structure of aqueous electrolyte solutions** Laszlo PUSZTAI, Research Institute for Solid State Physics and Optics, HAS, Budapest, Hungary
12.55–13.15	**EMLG-JMLG assembly**
13.30 – 15.00	LUNCH

LIST OF POSTERS

1. **Ultrafast dynamics of lipids at the phospholipid - water interface**
   Abramczyk H., Technical University of Łódź, Poland
2. **The invesigation of concentration features of molecular water–alcohol solutions**
   Atamas N., Kyiv Taras Shevchenko University, Ukraine
3. **Dielectric permittivity of the mixture of non-polar particles**
   Blazhyevskyi Yu., Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine
4. **Static and transport properties at the base for development of an all-atom force field for ethylene glycol**
   Cordeiro M.N.D.S., REQUIMTE/University of Porto, Portugal
5. **Application of recursive sequences and diagram technique in the theory of associated liquids**
   Durov V.A., Moscow State University, Russia
6. **Ion association in aqueous alkali formate solutions**
   Eiberweiser A., Universität Regensburg, Germany
7. **Temperature and density effects on structural features of near- and supercritical diluted aqueous lithium chloride solutions**
   Fedotova M., Institute of Solution Chemistry, RAS, Ivanovo, Russia
8. **Ir spectroscopic study of the local stucture of water rich phase in ternary water–scCO$_2$ –NaCl system**
   Fedotova M., Institute of Solution Chemistry, RAS, Ivanovo, Russia
9. **On the calculation of structural and thermodynamic characteristics of ion hydration in the framework of RISM approach**
   Fedotova M., Institute of Solution Chemistry, RAS, Ivanovo, Russia

10. **Structure of water and methanol-water mixture at high-temperatures and high-pressure by energy dispersive X-ray diffraction combined with EPSR modeling**
    FUJIMURA K., Fukuoka University, Japan

11. **Influence of confinement on solvation dynamics of ethanol in water by Raman spectroscopy and transient fluorescence spectroscopy**
    GADOMSKA B., University of Warsaw, Poland

12. **Volumetric properties of peptides from Voronoi tessellation analysis of hydration shells**
    GEIGER A., Universität Dortmund, Germany

13. **Effects of cryoprotectants on the hydrophobic hydration of small apolar solutes in aqueous solutions**
    HECKHAUSEN S., University of Rostock, Germany

14. **Dynamics of water in aqueous salt solutions**
    HOLZMANN J., University of Rostock, Germany

15. **The structure of Ag^+, Ca^{2+} and Y^{3+} hydration in confinement in nanometer scale over the temperature range of 298 – 190 K**
    ITO K., Fukuoka University, Fukuoka, Japan

16. **Translational and rotational dynamics of methanol and nickel chloride – methanol solutions: quasi-elastic neutron scattering** *vs* **molecular dynamics simulations**
    KALUGIN O.N, V.N. Karazin Kharkiv National University, Ukraine

17. **Liquid-gas phase behavior of polydisperse dipolar hard-sphere fluid**
    KALYUZHNYI YU., Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

18. **Phase behavior of a simple model of ferocolloidal dispersion**
    KALYUZHNYI YU., Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

19. **Hydration structure of pyridine molecule studied by neutron diffraction with isotopic substitution method**
    KAMEDA Y., Yamagata University, Japan
20. **Molecular dynamics simulation of n–butanol from glacial state to supercritical conditions**
    KISELEV M., Institute of Solution Chemistry, RAS, Ivanovo, Russia
21. **Spinodal decomposition in nematic liquid crystals filled with nanoparticles**
    KLESHCHONOK A.V., Taras Shevchenko National University of Kyiv, Ukraine
22. **Dipole glass state in hydrogen bonded ferro-antiferroelectric mixed compounds**
    KORYNEVSKII M., Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine
23. **Maier-Saupe nematogenic system near hard wall**
    KRAVTSIV I., Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine
24. **Structural behaviour of associating polymers through dielectric properties using TDR**
    KUMBHARKHANE A.CH., Swami Ramanand Teerth Marathwada University, Nanded, India
25. **Generalized relations for partial conductivities in ionic liquids**
    KUPOROV V., Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine
26. **Second virial coefficients of prolate and oblate molecules interacting through nematogenic intermolecular potentials**
    LAGO S., University Pablo de Olavide, Seville, Spain
27. **Liquid crystal colloids**
    LEV B., Bogolyubov Institute for Theoretical Physics, NAS of Ukraine, Kyiv, Ukraine

28. **Light-induced effects in cholesteric mixtures containing photoactive nematics: challenges to molecular theories of helical twisting**
    Lisetski L., Institute for Scintillation Materials, NAS of Ukraine, Kharkiv, Ukraine
29. **Molecular dynamics simulations of the thermocapillary effect at model liquid-liquid interfaces**
    Maier H., Technical University Darmstadt, Germany
30. **On the problem of a consistent description of kinetic and hydrodynamic processes in dense gases and liquids**
    Markiv B., Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine
31. **Acoustic spectra in dissipative hemodynamics taking into account erythrocytes size and shape**
    Matskevych V.T., National Science Center “Kharkiv Institute for Physics and Technologies”, Ukraine
32. **Green functions and polarization features of acoustic waves in uniaxial and biaxial nematic liquid crystals**
    Matskevych V.T., National Science Center “Kharkiv Institute for Physics and Technologies”, Ukraine
33. **Structure and thermodynamics of simple fluids under extreme conditions**
    Melnyk R., Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine
34. **X-ray diffraction studies of liquid-solid composites**
    Mudry S., Ivan Franko National University of Lviv, Ukraine
35. **Selektive coatings via the method of sol-gel technology for solar collectors**
    Musiy R., L.M. Lytvynenko Institute of Physical-Organic Chemistry and Coal Chemistry, NAS of Ukraine, Lviv, Ukraine
36. **The approach for large scale simulation on the solution confining flucutuation**
    Nakada M., Niigata University, Japan

37. **Frequency dependence of velosity and absorption of longitudinal, shear and thermal waves in the electrolyte solutions**
    ODINAEV S., Osimi M.S. Tajik Technical University, Dushanbe, Tajikistan

38. **Investigation of frequency dispersion of the viscosity coefficients of simple liquids depending on the thermodynamic parameters of a state**
    ODINAEV S., Osimi M.S. Tajik Technical University, Dushanbe, Tajikistan

39. **Processed algorithms for multiple time scale molecular dynamics**
    OMELYAN I.P., Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

40. **Phase equilibria in size- and charge-asymmetric primitive models of ionic fluids**
    PATSAHAN O.V., Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

41. **A hard sphere fluid in one- and two- dimensional disordered porous media**
    PATSAHAN T., Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

42. **Conformational vibrations of ion lattice in DNA solution**
    PEREPELYTSYA S.M., Bogolyubov Institute for Theoretical Physics, NAS of Ukraine, Kyiv, Ukraine

43. **Optical Kerr effect measurements of methanol and acetone mixtures**
    POLOK K., University of Warsaw, Poland

44. **Helium - no molecular liquid but an interesting solvent**
    PROBST M., Innsbruck University, Austria

45. **Solubility in water of chlorophenols and chloroanisoles as an example of hydrophilicity and hydrophobicity with practical consequences**
    SEGURA D., University Pablo de Olavide, Seville, Spain

46. **Self-assembly in liquid crystalline suspensions 5CB filled by aluminsilicate discs**
    Shaydyuk Y., Institute of Physics, NAS of Ukraine, Kyiv, Ukraine
47. **Dynamics of protic and aprotic ionic liquids: what distinguishes ethylammonium nitrate from imidazolium ils?**
    Sonnleitner T., Universität Regensburg, Germany
48. **Miicrosolvation of the oh radidal in high temperature water - molecular dynamics study**
    Szala-Bilnik J., Technical University of Łódź, Poland
49. **Structural and thermodynamic properties of discrete potential fluids in first-order mean spherical approximation**
    Trokhymchuk A., Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine
50. **Statistical mechanical theory for model of water and hydration**
    Urbic T., University of Ljubljana, Slovenia
51. **The monomer density profiles of real polymer chains in confined geometries**
    Usatenko Z., Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine
52. **The new force field model for imidazolium-based ionic liquids**
    Voroshylova I., V.N. Karazin Kharkiv National University, Ukraine
53. **Development of the QM/MM/RISM theory: Application to the intercalation of proflavine with solvated DNA**
    Yoshida N., Institute for Molecular Science, Okazaki, Japan
54. **Polymers in crowded environment: shape anisotropy**
    Blavatska V., Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine
55. **Orientational correlations in molecular liquids containing tetrahedral molecules**
    Pusztai L., Research Institute for Solid State Physics and Optics, HAS, Budapest, Hungary

EMLG-JMLG Annual Meeting 2010

Complex liquids

Modern trends in exploration,
understanding and application

Keynote Lectures

September 5–9, 2010

Lviv, Ukraine

Polyelectrolytes in water: How the presence of hydrophobic groups modifies the ion–specific effects

V. Vlachy

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Ljubljana, Slovenia

Polyelectrolytes are by definition polymers containing groups that can ionize in an appropriate solvent. Since they contain both ionic and hydrophobic groups, they resemble certain biological materials, such as nucleic acids and proteins. Aliphatic x,y–ionenes are alkyl polymer chains in which methylene groups are separated by ionic charges. They can be prepared with varying degrees of hydrophobicity; for example, the 3,3–ionene contains three methylene groups between the quaternary nitrogen atoms. For the 6,6–ionene there are six methylene groups between the charges, which makes it a much weaker polyelectrolyte. They are soluble in water and can therefore be studied by standard methods of the solution chemistry, such as osmometry, calorimetry, conductometry, and others [1,2]. Ionenes can therefore be test substances to help one understand the ion-specific and hydrophobic effects when a more complex bio-polyelectrolyte is dissolved in water. We will present the results for the osmotic coefficient, enthalpy of dilution, heat capacity, partial molar volume, dielectric relaxation, conductivity, and transport numbers in 3,3–, 4,5–, 6,6–, and 6,9–ionenes with fluoride, bromide, chloride, and iodide counterions. Many of these data are yet unpublished. We will show how the increased length of the hydrophobic chain between the polyion's charges modifies the counterion–polyion interaction. Most interestingly: the effect is highly ion–specific; presence of hydrophobic groups affects differently the ionene solutions with fluoride, than solutions with bromide (or chloride and iodide) ions. The experimental results will be discussed in view of the explicit water molecular dynamics simulations of 3,3– and 6,6–ionene oligoions with various counterions [3].

1. C. Pohar, K. Arh, V. Vlachy, J. Phys. Chem. B, **106**, 9967 (2002).
2. M. Lukšič, B. Hribar-Lee, V. Vlachy, R. Büchner, Macromolecules, **42**, 4337 (2009); Phys. Chem. Chem. Phys. **11**, 10053 (2009).
3. M. Druchok, V. Vlachy, K.A. Dill, J. Chem. Phys., 130, 134903 (2009); J. Phys. Chem. B, **113**, 14270 (2009).

Thermal behavior, structure and dynamics of liquids and electrolyte solutions confined in mesoporous materials

T. Yamaguchi
Department of Chemistry, Faculty of Science and Advanced Materials Institute, Fukuoka University, Nanakuma, Jonan-ku, 814-0180 Fukuoka, Japan

Liquids and solutions in confinement and/or interface play an important role in natural environments, such as sedimentation in clays, in biological systems like membrane proteins, and in industrial applications such as separation columns and fuel cells. In particular, water confined in pores of 21 Å diameter or less is stable in the liquid state in a temperature range down to 140 K; resultantly, low temperature confined water has drawn much attention as a model of non freezable water in biological system. Thus, the thermal, structural and dynamic properties of liquids and solutions under nanometer-scale confinement at a molecular level are essential for understanding their roles and the underlying mechanisms of processes going in the systems. These properties of liquids and solutions in confinement would originate from both confinement, i.e. pore size, and a balance between intermolecular forces and the molecule-surface interaction. This talk reviews the results of our studies on the thermal, structural and dynamic properties of molecular liquids, water, methanol, and acetonitrile with different hydrogen bonding nature and of aqueous electrolyte solutions confined in mesoporous vitreous silica MCM-41 with different pore sizes, cross-linked dextran polymer Sephadex G15, and activated carbons as revealed by differential scanning calorimetry, FTIR, X-ray and neutron diffraction, dielectric relaxation, quasi-elastic neutron scattering and neutron spin- echo measurements.

1. T. Yamaguchi, H. Hashi, S. Kittaka, J. Mol. Liq., **129**, 57-62 (2006).
2. S. Kittaka, S. Ishimaru, M. Kurahashi, T. Matsuda, T. Yamaguchi, Phys. Chem. Chem. Phys., **8**, 3223-3231 (2006).
3. T. Yamaguchi, K. Yoshida, P. Smirnov, T. Takamuku, S. Kittaka, S. Takahara, Y. Kuroda, M.-C. Bellissent-Funel, Eur. Phys. J. Special Topics **141**, 19-27 (2007).
4. K. Yoshida, T. Yamaguchi, S. Kittaka, M.-C. Bellissent-Funel, P. Fouquet, J. Chem. Phys. **129**, 054702-1-11 (2008).
5. S. Kittaka, K. Sou, T. Yamaguchi, K. Tozaki, Phys. Chem. Chem. Phys., **11**, 8538-8545 (2009).

Critical casimir forces

S. Dietrich[a,b]

[a] *Max Planck Institut for Metals Research, Stuttgart, Germany*
[b] *Institute for Theoretical and Applied Physics, University of Stuttgart, Stuttgart, Germany*

Long-ranged correlations in a fluid near its critical point lead to clearly identifiable effective forces acting on confining walls. The corresponding universal scaling functions are discussed for different boundary conditions and geometries. The theoretical predictions are compared with high precision experimental data for He^4 and He^3/He^4 wetting films near the superfluid phase transition as well as with synchrotron scattering data from classical binary liquid mixtures. Direct measurements and applications for colloidal suspensions are discussed.

Transport coefficients: a path to explorate convex (colloidal and polyelectrolyte solutions) and concave (clays, porous media) systems

P. Turq,[a] J. François,[b] M. Jardat,[a] E. Dubois[a] and O. Bernard[a]

[a] *Univeristé Pierre et Marie Curie, Bat. F74 CC51 4 Place Jussieu, 75005, Paris, France*
[b] *Dufrêche Université de Montpellier2/ICSM*

Transport coefficients such as electrical mobilities or diffusion coefficients can be measured on a collective or on an individual basis; bulk electrolyte or single ion conductivities, collective or individual diffusion coefficients. We determine transport coefficients of different colloidal and micellar systems, as well as natural polyelectrolytes such as soil natural organic matter, by several experimental methods: electrical conductance, electrophoretic mobilities (optic and acoustic zetametry), diffusion coefficients: individual by NMR, collective by dynamic light scattering. The results can be compared to the predictions of different mesoscopic theoretical models , such as MSA dynamic and brownian dynamics. In any case counterion condensation is a major factor which has to be taken in to account for a proper quantitative description of the system.

Analogous results can be inferred for concave media.

1. G.M. Roger, S. Durand Vidal, O. Bernard, P. Turq, T.M. Perger and M. Bester Rogac J. Phys. Chem. B, 2008 , **112**, 16529-16538

Inelastic X-Ray scattering study of the high frequency dynamics in liquids

G. Ruocco

Dipartimento di Fisica, "Sapienza" Università di Roma, Italy

The recent development of the Inelastic X-ray Scattering (IXS) technique allows the experimental determination of the dynamic structure factor, S(Q,E), of topologically disordered systems in an exchanged momentum (Q) and frequency (ω) region not accessible before (1-10 nm^{-1}, 1-10 meV). The possibility to measure the S(Q, ω) functions in the mesoscopic (Q- ω) region, and to compare them with those calculated by Molecular Dynamics (MD), has allowed to clarify several general characteristics of the high frequency collective excitations of glasses and liquids. Recent results on this topic will be presented and discussed –using the case of liquid water as prototypical —with particular attention to i) the propagating or not–propagating nature of the high frequency excitations; ii) the origin of their attenuation; iii) the existence and location of a propagation threshold; iv) the existence of transverse–like excitations; v) the role of these excitations in determining the anomalous thermal and transport properties of disordered materials.

Statics and dynamics of colloidal particles in liquid crystals

O. Lavrentovich

*Liquid Crystal Institute and Chemical Physics Interdisciplinary
Program Kent State University, Kent, OH 44242, USA*

Liquid crystals (LCs) produce a rich variety of complex 3D structures that are easily changed by external fields, boundary conditions, embedded particles, etc. In the latter case of a liquid crystal with colloidal inclusions (liquid crystal colloid), the equilibrium is often achieved by introducing topological defects in the director field, stabilized by surface anchoring at interfaces [1]. This report reviews the basic properties of liquid crystal colloids such as elastically-mediated interactions of colloidal particles and then presents recent experiments on the dynamics of particles in the nematic and smectic liquid crystals driven by AC and DC electric fields [2-4]. The 3D director structure around the particles is visualized by fluorescence confocal polarizing microscopy (FCPM). The electric field causes translation and rotation of the colloids. The underlying mechanisms include specific liquid crystal effects such as backflow (coupling of director reorientation and mass flow) and mechanisms of general nature, such as electrophoresis, dielectrophoresis, electrorotation and hydrodynamic interaction between the particle and a confining wall. These general mechanisms acquire new, sometimes unexpected, facets when the action is staged inside a liquid crystal.

The work has been supported by NSF DMR, DOE, W.M. Keck Foundation, CMPND.

1. H. Stark, *Physics of colloidal dispersions in nematic liquid crystals*, Phys. Reports, **351**, 387 (2001).
2. O. P. Pishnyak, S. Tang, J. R. Kelly, S. V. Shiyanovskii, O. D. Lavrentovich, *Lift and bidirectional motion of colloidal particles in an electrically-driven nematic liquid crystal.* Phys. Rev. Let., **99**, 127802 (2007).
3. A. Jakli, B. Senyuk, G. Liao, O.D. Lavrentovich, *Colloidal micromotor in smectic A liquid crystal driven by DC electric field*, Soft Matter **4**, 2471-2474 (2008).
4. O.D. Lavrentovich, I. Lazo, O. P. Pishnyak, *Electrophoresis of dielectric and metal particles in liquid crystals* (in preparation, 2010).

Statistical mechanics of molecular liquids reveals elementary processes in life phenomena

F. Hirata

Institute for Molecular Science, 38, Nishigo-naka, Myodaiji, 4448585 Okazaki, Japan

"Molecular recognition" is an essential elementary process for protein to function. The process is a thermodynamic process which is characterized with the free energy difference between two states of a host-guest system, namely, associated and dissociated states. The time to reach the chemical equilibrium depends on the height of free energy barrier in between the two states. It is readily understood that the structural fluctuation of protein gives a big effect on the free energy barrier. In that respect, the "molecular recognition" is a thermodynamic process which is conjugated with the structural fluctuation of protein.

We have been developing a new theory concerning the molecular recognition, based on the 3D-RISM/RISM theory which is a statistical mechanics of liquids. The theory has successfully "probed" small ligands such as water molecules and ions bound in a small cavity of protein. [1-3]

In the lecture, we present our recent work on the conduction mechanism of small ligands in molecular channels including aquaporin and a proton channels in virus.

1. T. Imai, R. Hiraoka, A. Kovalenko, F. Hirata, J. Am. Chem. Soc. (Communications), 1**27** (44), 15334 (2005).
2. Y. Kiyota, et. al., J. Am. Chem. Soc. (Communications), **131**, 3852 (2009).
3. N. Yoshida, T. Imai, S. Phongphanphanee, A. Kovalenko, and F. Hirata, J. Phys. Chem. B (Feauture Article), **113**, 873 (2009).

Stimuli-responsive nanostructured materials

S. Minko

Department of Chemistry & Biomolecular Science, Clarkson University, Potsdam, NY, USA

Response to stimuli is one of the major life processes, by which living systems interact with the external environment. Advances in nanotechnology have focused on designing "responsive to stimuli" or "smart" materials that mimic many processes found in living systems.

The talk addresses our recent results on the synthesis, study, interesting applications and prospects of nanostructured polymer and colloidal systems for the fabrication of smart responsive surfaces, membranes, sensors with various transduction mechanisms, micro/nanoactuators, and capsules. We also use surface modification of nanoparticles with a stimuli-responsive shell for a new intriguing opportunity to turn on and off and tune interactions between nanoparticles, allowing control of the directed self-assembly with external stimuli/signals. The stimuli responsive polymeric and hybrid systems demonstrate strong advantages for the fabrication of robust multifunctional and multiresponsive materials and nanodevices.

Supramolecular chemistry for molecular liquids, solutions and assemblies

J.-M. Lehn

ISIS, Université de Strasbourg and Collège de France, Paris, France

The properties of molecular liquids, solutions and assemblies are of supramolecular nature as they result from the interactions between the molecular components. Some early work on the dynamics of molecular liquids finds significance in the supramolecular aspects of condensed phase. Basic principles of supramolecular chemistry will be presented in relation to the generation of organized molecular assemblies through molecular recognition processes and their structural, dynamic and functional properties. They provide perspectives in the exploration of the behaviour of molecules in liquids.

Multiscale methods for nanochemistry and biophysics in solution

A. Kovalenko[a,b]

[a] *National Institute for Nanotechnology, 11421 Saskatchewan Dr., Edmonton, AB, T6G 2M9, Canada*
[b] *Department of Mechanical Engineering, University of Alberta, Edmonton, AB, T6G 2G8, Canada*

Predictive modeling of nanosystems in solution should derive their properties from the chemical functionalities of the constituents, while operating at length scale up to hundreds nanometers and time scale up to milliseconds and more, which requires multiscale treatment. Their molecular modeling requires long-time description of millions molecules which is by far not feasible with ab initio methods, challenging for molecular simulations, and problematic for continuum solvation theories that are phenomenological and thus non-transferable. Statistical-mechanical, three-dimensional molecular theory of solvation (a.k.a. 3D-RISM) operates with 3D distributions of species in the statistical ensemble rather than with trajectories of individual molecules and predicts from the first principles the solvation structure and thermodynamics of nanosystems[1]. It properly accounts for chemical functionalities by representing both electrostatic and non-polar features of the solvation structure, such as hydrogen bonding, solvophobicity, salt bridges, structural solvent, associative and electrochemical effects, and is promising as a core part of multiscale modeling of nanosystems in solution. We have coupled the 3D-RISM-KH theory with ab initio quantum chemistry methods in a self-consistent description of electronic structure, optimized geometry, and chemical reactions in solution[1,2] and have extensively validated this multiscale method against experimental data for solvation thermochemistry, conformational equilibria, and activation barriers for various nanosystems in different solvents[2]. We have also coupled the 3D-RISM-KH theory contracting solvent degrees of freedom with MD simulation of biomolecules in the Amber molecular dynamics package[3]. This included several accelerating schemes and multi-time steps up to 20 fs to enable simulation of large biomolecules. The method allows one to study biomolecular processes on extremely long timescales. It also replaces the MM/PB(GB)SA post-processing using empirical non-polar terms with statistical-mechanical, MM/3D-RISM-KH evaluation of the solvation thermodynamics[3,4]. This talk presents the above multiscale methods and their application to explain experimental results for the electronic and solvation structure of ionic liquids[5]; mechanisms of self-assembly, conformational stability and solvent-driven supramolecular chirality of synthetic organic rosette nanotubular architectures[6]; aggregation of β–sheet Amyloid oligomers[4]; and function-related properties of GroEL chaperon[7].

1. A. Kovalenko, 3D-RISM theory for molecular liquids and solid-liquid interfaces, in: Molecular Theory of Solvation, F. Hirata (ed.), Kluwer, Dordrecht, 2003, pp.169-275; (and refs. therein)
2. S. Gusarov, T. Ziegler, A. Kovalenko, J. Phys. Chem. A **110**, 6083 (2006); D. Casanova, S. Gusarov, A. Kovalenko, T. Ziegler, J. Chem. Theory Comput. **3**, 458 (2007).
3. T. Luchko, S. Gusarov, D.R. Roe, C. Simmerling, D.A. Case, J. Tuszynski, A. Kovalenko, J. Chem. Theory Comput., (2010), (in press).
4. N. Blinov, L. Dorosh, D. Wishart, A. Kovalenko, Biophys. J. **98**, 282 (2010).
5. M. Malvaldi, S. Bruzzone, C. Chiappe, S. Gusarov, A. Kovalenko, J. Phys. Chem. B **113**, 3536 (2009).
6. T. Yamazaki, H. Fenniri, A. Kovalenko, ChemPhysChem. **11**, 361 (2010); R.S. Johnson, T. Yamazaki, A. Kovalenko, H. Fenniri, J. Am. Chem. Soc. **129**, 5735 (2007); J.G. Moralez, J. Raez, T. Yamazaki, R.K. Motkuri, A. Kovalenko, H. Fenniri, J. Am. Chem. Soc. Comm.**127**, 8307 (2005).
7. T.M. Stumpe, V. Pande, N. Blinov, D. Wishart, A. Kovalenko, (submitted).

EMLG-JMLG Annual Meeting 2010

Complex liquids

Modern trends in exploration,
understanding and application

Plenary Lectures

September 5–9, 2010

Lviv, Ukraine

Chemical reactions of biological proteins in solution by time-resolved diffusion method

M. Terazima,[a] Y. Kawaguchi,[a] Y. Nakasone,[a] and S. Tokutomi[b]

[a] *Kyoto University, Sakyo-ku, 606-8502 Kyoto, Japan*
[b] *Osaka Prefecture University, Japan*

Solution dynamics is quite important for revealing molecular mechanisms of chemical reactions of biological molecules. For that purpose, a variety of time-resolved spectroscopic methods have been developed. However, in spite of extensive efforts, detection of time-development of intermolecular interaction, which is essential for understanding the mechanism and function of biological molecules, has been almost impossible. In this respect, we have succeeded in detecting the temporal change in the intermolecular interaction by using a time-resolved detection of diffusion. We used the pulsed laser induced transient grating (TG) method for the measurements in time domain. We applied this technique to the photochemical reactions of various proteins. Here we will present recent studies on phototropin in particular for the reverse reaction of this protein, which will provide us information on protein folding reaction in solution.

Phototropins (phot1, phot2) are well known as the blue light receptors for phototropism, stomatal opening and chloroplast relocation. The photochemical reaction of a plant blue-light photoreceptor Arabidopsis phototropin 1 (phot1)-LOV2 domain with a linker region (phot1LOV2-linker) has attracted significant interest since the discovery of this protein. Phots consist of two photoreceptive domains LOV1 and LOV2 at their N terminus, Ser/Thr kinase domain at their C terminus, and a linker domain that connects the LOV2 domain and the kinase domain. Each of the two LOV domains noncovalently binds a single flavin mononucleotide as a chromophore. Upon photoillumination of the chromophore, we discovered that the main conformational change involves the unfolding of the alpha-helix present in the linker region and this change is closely linked to biological function. The unfolded state of this linker should undergo a return to the folded conformation via a dark reversion process, but when does this occur? The restoring dynamics of the linker domain induced by a reverse reaction of the phot1LOV2-linker construct was investigated by the time-resolved diffusion method using two-step excited transient grating method. Following the disruption of the covalent bond between the cysteinyl and flavin, the unfolded conformation was observed to fold with a time constant of 13 ms. The rate is considerably (10000 times) slower than the helix formation rate measured for an alpha-helical polypeptide in solution. This slow rate suggests that an inter-domain interaction between the LOV domain and the linker is important and the LOV domain acts as a template to facilitate the folding of the linker into an alpha-helix conformation. We will discuss this reaction by considering the solution dynamics.

Aqueous alkali halide solutions: can osmotic coefficients be explained on the basis of the ionic sizes alone?

Yu. Kalyuzhnyi,[a] V. Vlachy[b] and K. Dill[c]

[a] *Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine*
[b] *Ljubljana University, Slovenia*
[c] *University of California, San Francisco, USA*

We use the AMSA associative mean spherical theory of associative fluids, to study ion–ion interactions in explicit water. We model water molecules as hard spheres with four ff-center square-well sites and ions as charged hard spheres with sticky sites that bind to water molecules or other ions. We consider alkali halide salts. The choice of model parameters is based on two premises: (i) The strength of the interaction between a monovalent ion and a water molecule is inversely proportional to the ionic (crystal) diameter. Smaller ions bind to water more strongly than larger ions do, taking into account the asymmetry of the cation-water and anion-water interactions. (ii) The number of contacts an ion can make is proportional to. In short, small ions bind waters strongly, but only a few of them. Large ions bind waters weakly, but many of them. When both a monovalent cation and anion are large, it yields a small osmotic coefficient of the salt, since the water molecules avoid the space in between large ions. On the other hand, salts formed from one small and one large ion remain hydrated and their osmotic coefficient is high. The osmotic coefficients, calculated using this model in combination with the integral equation theory developed for associative fluids, follow the experimental trends, including the unusual behavior of cesium salts.

One– and two–mode behavior of the ν(C=O) band in N,N–dimethylformamide isotopic mixtures: DMF/DMF–d_1, DMF/DMF–d_6, and DMF/DMF–^{13}CO

H. Torii,[a] M.G. Giorgini[b] and M. Musso[c]

[a] *Department of Chemistry, School of Education, Shizuoka University, 836 Ohya, 422-8529 Shizuoka, Japan.*
[b] *Dipartimento di Chimica Fisica ed Inorganica, Universitá di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy*
[c] *Fachbereich Materialwissenschaften, Abteilung Physik und Biophysik, Universität Salzburg, Hellbrunnerstraße 34, A-5020 Salzburg, Austria.*

Observation of the Raman spectrum of some binary isotopic liquid mixtures may cause a great surprise: the spectral merging of the bands associated with a given normal mode having slightly different intrinsic frequency in the two neat liquids, to only one band with a frequency located in between (one-mode behavior). It was noticed in the Raman spectrum of the amide I [ν(C=O)] band of formamide-d_2/formamide-d_3 liquid mixtures [1]. Both the overlap of the two bands and the dynamical D/H exchange could be excluded as possible origins of merging. The onset of this phenomenon requires the occurrence of very critical spectral conditions, because, while it is observed in the amide I band of the formamide-d_2/formamide-d_3 [1] mixtures, it is absent in the same mode of the analogous formamide/formamide-^{13}CO mixtures [1] where the two-mode behavior is observed. To unveil the origin of this phenomenon and recognize which and how spectral conditions discriminate between the observation of the one- or two mode behavior, a computational procedure has been envisaged [2] based on the parametrization of the vibrational modes in a liquid coupled by transition dipole coupling mechanism (TDC). It is well known, in fact, that the ν(C=O) mode in liquid carbonyl compounds, and more notably in the amide I band present in amides, is affected by intermolecular resonant vibrational coupling as manifested by the frequency splitting between the Raman aniso- and isotropic components (termed noncoincidence effect, NCE), particularly large (15 cm^{-1}) in these carbonyl compounds. It has been found [3] that the ingredient for the onset of the one-mode behavior is the extent of resonance condition (the magnitude of the resonant coupling compared with the separation of the wavenumber positions) between the vibrations of the two species and their bandwidths. With the present investigation we intend to analyse and discuss the one-/two-mode behaviour of the amide I band in isotopic mixtures of N,N-dimethylformamide (DMF) in the light of the general results obtained in [3] on the basis of a parametric analysis of a coupled oscillator system. Among the results (isotropic Raman spectra) obtained for the three types of isotopic mixtures under study, DMF/DMF-^{13}C=O, DMF/DMF-d$_1$ and DMF/DMF-d$_6$, the latter system unambiguously indicates the occurrence of one-mode behavior (complete merging) of the ν(C=O) band whereas the first system unambiguously displays the two mode behavior (complete separation) of these bands.

1. Mortensen A., Faurskov Nielsen O., Yarwood J., Shelley V., J. Phys. Chem., **99**, 4435-4440, (1995)
2.Torii H., J. Phys. Chem. A, **110**, 4822-4832,(2006)
3.Torii H., Osada Y., Iwami M., J. Raman Spectrosc., **39**, 1592-1599, (2008)

Scaled particle theory for a hard–sphere fluid confined in different model matrices

W. Dong,[a] T. Patsahan[b] and M. Holovko[b]

[a] *Laboratoire de Chimie, UMR 5182, CNRS, Ecole Normale Supérieure de Lyon, 46, Allée d'Italie, 69364 Lyon Cedex 07, France*

[b] *Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine*

Despite intense investigations during the last two decades, no analytical result has been available for any non trivial off–lattice model for fluids in random porous media until very recently. In a recent work [1,2], we presented a first formulation of scaled particle theory (SPT) for a hard sphere fluid in a hard sphere matrix or in an overlapping hard sphere matrix. The agreement between this SPT and simulation [3] is fine (errors$\leq$ 20%). However, we have identified some inconsistencies in this first formulation of SPT (named as SPT1 hereafter). For example, in the limit of one single big matrix particle, i.e., $R_0 \to \infty$(R_0: radius of matrix particle), $\rho_0 \to \infty$ (ρ_0 : matrix density) with η_0 remaining finite ($\eta_0 = 4\pi\rho_0 R_0^3/3$), the fluid-matrix system becomes in fact a fluid in contact with a flat hard wall. In this case, the fluid chemical potential, μ_1, the fluid pressure, P , and the contact fluid-fluid radial distribution function, $g_{11}(2R_1)$(R_1 : radius of fluid particle), should reduce to their corresponding results for a bulk fluid and $\rho_1 g_{10}(R_1+R_0) = P$ should hold (ρ_1: fluid density; $g_{10}(R_1 + R_0)$: contact fluid-matrix radial distribution function). SPT1 does not give the appropriate results in the limit of one single big matrix particle. In this presentation, we will show how these inconsistencies in SPT1 can be remedied and give a new formulation of SPT (named as SPT2) for a HS fluid in a HS matrix or in an overlapping HS matrix [4]. We carried out also some grand canonical ensemble Monte Carlo simulations in order to make more extensive comparison with our SPT2. In the majority of cases, SPT2 improves significantly the accuracy of different thermodynamic properties. We will briefly talk about also the possible extension of SPT2 to multi-component systems and some specific difficulties in these cases.

1. M. Holovko and W. Dong, J. Phys. Chem. B, **113**, 6360, (2009).
2. W. Chen, W. Dong, M. Holovko and X.S. Chen, J. Phys. Chem. B (in press).
3. A. Meroni, D. Levesque and J.J. Weis, J. Chem. Phys. **105**, 1101 (1996).
4. T. Patsahan, M. Holovko and W. Dong, *Fluids in porous media: Scaled particle theory*, (publication in preparation).

Transient absorption and fluorescence measurements of polymer liquids and gels

W. Gadomski and P. Piątkowski

Laboratory of Physicochemistry of Dielectrics and Magnetics,
Department of Chemistry, University of Warsaw, ul. Żwirki i Wigury
101, 02-089 Warsaw, Poland

Herewith we present the optical characteristics of three polymer liquids, based on PPV derivatives, which are used as a matrix for semiconductor quantum dots PbS, both in the liquid and in the gel state. The transient fluorescence measurements of polymers exhibit strong dependence of the exciton lifetimes in polymers on the concentration of the nanocrystals. It appears that the fluorescence lifetimes increase with the increase of the PbS nanocrystal concentration, which suggests that the surface interaction of polymer with quantum dot stabilizes the emerging exciton. The transient absorption measurements, in turn, allow to establish how the nanocrystal interaction with the matrix influences the lifetime of the quantum dot excited state and the flow of the charge from quantum dot to the polymer.

Dipolar interaction and molecular ordering in liquid propylene carbonate: anomalous dielectric susceptibility and Raman non-coincidence effect

A. Brodin[a] and P. Jacobsson[b]

[a] *National Technical University of Ukraine "Kyiv Polytechnic Institute", Kyiv, Ukraine*
[b] *Chalmers University of Technology, Göteborg, Sweden*

Dielectric constant of non-associating fluids normally exhibits a $1/T$ temperature dependence according to Curie's law. Kirkwood correlation factor in such cases is close to unity and almost independent of the temperature. Recent broadband dielectric studies of a well-known solvent propylene carbonate (PC) revealed anomalous behavior of its loss spectrum, whose amplitude somewhat increases at high temperatures contrary to Curie's law, while it is known from the literature that its Kirkwood factor is close to unity. We analyze the origin of this discrepancy and find, based on recent literature data, that the Kirkwood factor of PC is strongly temperature dependent and significantly differs from unity, which signals the presence of temperature dependent molecular ordering. We find other signatures of this ordering in vibrational spectra of PC, where it leads to splitting of molecular vibrations due to interaction between the transition dipoles of neighboring molecules (the so-called non-coincidence effect). Spectroscopic and dielectric results agree well with each other and reveal the presence of significant temperature-dependent anti-parallel dipolar arrangement. Based on these results, it is likely that other polar liquids with large and localized molecular dipoles, albeit traditionally classified as non-associating, in fact do possess significant local molecular order due to dipolar interactions.

Viscosity calculations of simple liquids using the transient time correlation function formalism

I. Borzsák

Nyugat-magyarországi Egyetem, Károlyi Gáspár tér 4, 9700
Szombathely, Hungary

Calculation of the strain rate dependent shear viscosity is of considerable theoretical and industrial interest. Most fluids, subjected to planar Couette flow (the velocity gradient is perpendicular to the flow direction), exhibit Newtonian behaviour, which means the shear viscosity is independent of strain rate up to a certain crossover strain rate, typically given by the inverse of the longest relaxation time in the fluid, which for simple fluids is the translational relaxation time. Beyond the crossover strain rate, shear thinning occurs: the viscosity decreases with increasing strain rate. This crossover point is usually at a strain rate which is too high to be accessed by experimental measurement, but also — due to the poor signal-to-noise ratio at low strain rates — too low to calculate using steady state (SS) nonequilibrium molecular dynamics (NEMD) simulation. The calculation of the strain rate dependent shear viscosity is reported here for several simple model fluids using the transient time correlation function (TTCF) formalism. The TTCF formalism is perhaps the simplest nonlinear generalization of the Green-Kubo relations. Its numerical accuracy is similar to the Green-Kubo calculations at equilibrium, but the TTCF method is capable of calculating the viscosity over several orders of magnitude in strain rates with the same level of accuracy. The particles of the model fluids interact via a Lennard-Jones type of potential. Both the TTCF method and the resulting viscosities for the fluids are discussed in detail.

Shear relaxation and ionic transport of imidazolium-based ionic liquids

Ts. Yamaguchi, S. Miyake and S. Koda

Nagoya University, Furocho B2-3(611), Chikusa, 464-8603 Nagoya, Japan

We shall present our experimental and theoretical studies on the frequency-dependent shear viscosity and ionic mobilities of representative imidazolium-based ionic liquids.

On experimental side, we developed a shear impedance spectrometer based on QCM-D technology, which enables us to determine the complex shear viscosity from 5 to 205 MHz [1]. The shear impedance spectroscopy was then applied to four representative imidazolium-based ionic liquids, [Cnmim][PF6] with n = 4, 6, 8 and [C4mim][TFSA], where n stands for the length of alkyl chain. Comparing the shear relaxation spectra of [C4mim][PF6] at 283 and 298 K, the normalized spectra agree with each other when the frequency is shifted by multiplying the zero-frequency shear viscosity, which indicates that the increase in the relaxation time is the principal reason for the increase in the zero-frequency shear viscosity with decreasing temperature. The difference between the shear viscosities of [C4mim][PF6] and [C4mim][TFSA] is also explained by the relaxation time. On the other hand, the increase in the relaxation time with lengthening the alkyl chain of the cation is larger than that in the zero-frequency shear viscosity. In addition, the relaxation time distribution becomes broader with lengthening the alkyl chain. Comparing the shear relaxation spectrum with the frequency-dependent electric conductivity determined by dielectric spectroscopy, the relaxation of conductivity is faster than that of shear viscosity, indicating the partial decoupling between shear viscosity and electric conductivity.

On theoretical side, the dynamic properties of [C2mim]Cl were calculated at 400K with mode-coupling theory for molecular liquids based on the interaction-site model [2]. The static structure required as the input function is taken from an MD simulation. The theory captures the characteristics of the slow dynamics of the ionic liquid. In particular, the relaxations of shear viscosity and electric conductivity appear in 100 MHz region as have been observed in experiments. The theoretical analysis shows that the dielectric relaxation observed in 100 MHz region is mainly ascribed to the translational modes of ions, contrary to the conventional assignment of the reorientational relaxation of the cation. The relaxation of electric conductivity is faster than the shear relaxation as is observed in the experiment. The frequency-dependent self-diffusion coefficients of ions possess the relaxation time similar to the shear viscosity. Therefore, the decoupling between the shear viscosity and electric conductivity is ascribed to the correlation between the ionic motions.

1. T. Yamaguchi, S. Miyake and S. Koda, J. Phys. Chem. B, in press (2010)
2. T. Yamaguchi and S. Koda, J. Chem. Phys. **132**, 114502 (2010)

Understanding the solubility of gases in ionic liquids from molecular simulations

D. Kerlé, D. Paschek and R. Ludwig

Physical Chemistry, University of Rostock, Dr.-Lorenz-Weg 1, D-18055 Rostock, Germany

Ionic liquids (ILs) are organic salts with a low melting point ($< 100°$ C) and represent a relatively new class of non-molecular materials with unique properties and various potential applications. The solvation process of gases in ILs is of fundamental interest for gas separation processes and flue gas decontamination. In particular the phase behaviour of carbon dioxide with ILs might be important for the development of potential carbon sequestration applications. The imidazolium-based IL 1-n-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([CnMIM][NTf2]) with varying chain length n = 2, 4, 6, 8 is investigated by molecular dynamics simulations. Previous we have shown that our force field describes structural and thermodynamic properties of the neat IL very well. Now we demonstrate that also the solubility of light gases like carbon dioxide, oxygen, nitrogen, hydrogen and the noble gases is very well reproduced. The solubility is calculated from free energies of solvation, determined by Widom-Particle-Insertion technique. While experiments are difficult and time consuming, this method is rather quick and provides hints on the solvation mechanism. A large temperature range from 300 K to 500 K is examined. Carbon dioxide shows an "anomalous" temperature dependence of the solvation in ILs at infinite dilution that is characterized by counter-compensating negative entropies and enthalpies of solvation.

1. Köddermann T., Paschek D., and Ludwig R., *Molecular Dynamics Simulation of Ionic Liquids: A Reliable Description of Structure, Thermodynamics and Dynamics.* ChemPhysChem. **8**, 2464-2470, (2007)
2. Kerlé D., Ludwig R., Geiger A., and Paschek D., *On the Temperature Dependence of the Solubility of Carbon Dioxide in Imidazolium-based Ionic Liquids.* Journal of Physical Chemistry B. **113**, 12727-12735 (2009)
3. Kerlé D., Ludwig R., and Paschek D., *On the Temperature and Chain Length Dependence of the Solubility of Llight Gases in Imidazolium-based Ionic Liquids.* Angewandte Chemie, in preparation

First-principles molecular dynamics simulations of supercritical water: the importance of dispersion corrections

A.P. Seitsonen,[a] G. Ferlat[b] and R. Vuilleumier[c]

[a]*Physikalisch-Chemisches Institute, University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzerland*
[b]*IMPMC, University Paris VI, 140 rue de Lourmel, 75015 Paris, France*
[c]*ENS, France*

Kohn-Sham density functional theory, with local density approximation or present-day generalized gradient approximation exchange-correlation functionals, either gives sporadic results or fails completely to account for London dispersion forces. In the case of water, this results in an overestimated melting temperature and an overstructured liquid in the simulations. Considerable efforts have been made to address this shortfall and several proposals have been made in the literature, such as the dispersion-corrected atom-centered potentials (DCACP) [1] or the empirical Grimme corrections [2]. The effect of such corrections have been adressed recently in ambient water [3,4] and it has been found that they largely correct for the previous shortfalls. The importance of dispersion corrections is expected to be even larger at low densities as in supercritical water. We have performed first-principles molecular dynamic simulations of water at densities of 1. (ambient) and 0.7 g.cm^{-3} (supercritical) at different temperatures. We shall present the effect of dispersion corrections on the structural and dynamical properties.

1. I-C. Lin, M.D. Coutinho-Neto, C. Felsenheimer, O.A. von Lilienfeld, I. Tavernelli, and U. Rothlisberger, Phys. Rev. B, **75**, 205131 (2007)
2. Stefan Grimme, Jens Antony, Stephan Ehrlich, and Helge Krieg, J. Chem. Phys. **132**,154104 (2010)
3. Jochen Schmidt, Joost VandeVondele, I.-F. William Kuo, Daniel Sebastiani, J. Ilja Siepmann, Jürg Hutter and Christopher J. Mundy, J. Phys. Chem. B, **113** (35), 11959, (2009)
4. I-Chun Lin, Ari P. Seitsonen, Maurcio D. Coutinho-Neto, Ivano Tavernelli and Ursula Rothlisberger, J. Phys. Chem. B, **113** (4), 1127, (2009)

Intermolecular charge flux induced by the OH stretching mode of water and its effect on the intermolecular vibrational coupling

H. Torii

Shizuoka University, Chem / Educ, 836 Ohya, 422-8529 Shizuoka, Japan

It is well known that the OH stretching mode of water has a significantly larger IR intensity in the liquid state than in the isolated state. This IR intensity enhancement is recognized as induced by hydrogen bonding, but its electronic structural aspect has not been well clarified. Meanwhile, the OH stretching mode of liquid water is known to have a strong intermolecular vibrational coupling, giving rise to the large noncoincidence effect and the rapid vibrational excitation transfer between molecules. The latter effect is observed as a rapid decay of transient IR absorption anisotropy. This strong intermolecular vibrational coupling is often explained by the transition dipole coupling (TDC) mechanism, in which the dipole derivative (the square of which is proportional to the IR intensity) plays a crucial role. The purpose of the present study is twofold. One is to analyze the electronic structural aspect of the IR intensity enhancement of the OH stretching mode of water upon hydrogen bonding. It is shown that a charge flux of a significant magnitude is induced between molecules, and its effect on the IR intensity is larger than that of the intramolecular charge flux. The other is to examine the effect of this intermolecular charge flux on the intermolecular vibrational coupling. The reason for the strong intermolecular vibrational coupling is shown from the electronic structural viewpoint, and the extent of validity of the TDC mechanism is discussed.

Breast cancer diagnosis and dynamics of lipids by Raman imaging and femtosecond spectroscopy

H. Abramczyk,[a] B. Brożek-Płuska,[a] J. Surmacki,[a] J. Jablonska[b] and B. Kordek[b]

[a] *Technical University of Łódź, Wroblewskiego str. 15, 93-590 Łódź, Poland*
[b] *Medical University of Łódź, Poland*

Optical methods such as Raman spectroscopy, Raman imaging, Fourier Transform infrared (FTIR), femtosecond laser spectroscopy, fluorescence microscopy are new tools for chemical analysis of biological and biomedical samples. These new techniques are non-destructive and less expensive when compared with the immonostaining method for detection of specific proteins. Raman imaging belong to the most up-to-date and promising trends in medical diagnostics as an optical alternative to conventional biopsy. The Raman method is non-invasive, and it provides in situ real-time analysis of a pathological tissue, e.g. during routine physical examination. The most important feature of Raman spectra is that they act as very sensitive biochemical markers through the unique vibrational fingerprint spectra. Raman imaging is a novel method for research of medical diagnostics of human breast cancer and has a potential as an optical biopsy to replace the conventional biopsy [1-2].

The goal of the paper is to present Raman biomarkers for breast tissue cancer diagnosis that would have the ability to accurately characterize breast cancer tissue and distinguish between normal, malignant and benign types. The second aim is to present the "optical biopsy" by Raman imaging for normal and malignant breast tissues of the same patient. The presented paper involves recent results based on 150 patients by Raman spectroscopy and Raman imaging obtained so far by our group. The results prove that there is a high level of possibility for applying Raman imaging in the medicine as a diagnostic tool.

The results demonstrate that lipid molecules play a key role in activity of biological membranes and decide about the health-disease balance in breast tissue pathology. We report energy dynamics at the water/lipid interface. Femtosecond infrared (IR) two-color and bleaching pump-probe experiments were employed to investigate vibrational relaxation dynamics of C-H strech modes in the lipid alkyl chains of 2,3-Dipalmitoyl-sn-glycero-1-phosphocholine (DPPC) and O-H stretch mode of water at the water/lipid interface for a controlled humidity of the sample.

1. H. Abramczyk, J. Surmacki, B. Brożek-Płuska, Z. Morawiec, M. Tazbir, *The Hallmarks of Breast Cancer by Raman Spectroscopy*, J. Mol.Struc. 924-926, 175-182, (2009)
2. H. Abramczyk, B. Brożek-Płuska, K.Kurczewski, Z. Morawiec, M.Tazbir, *Breast tissue Diagnostics by Raman Spectroscopy*, J. Mol. Liquids, **141**,145-148, (2008)

Multiscale simulations of the self-assembly of liquid crystalline dendrimers

J. Ilnytskyi,[a] M.R. Wilson,[b] J.S. Lintuvuori[b] and L.M. Stimson[c]

[a] *Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine*
[b] *Department of Chemistry, University Science Laboratories, South Road, Durham, DH1 3LE, UK*
[c] *University of Western Ontario, 1151 Richmond Street North, London (ON), Canada*

Multiscale modelling of the self-assembly of liquid crystalline dendrimers (LCDr) in a bulk is performed. As the first stage, molecular dynamics simulations have been carried out to study the structure of a generation three model LCDr in solution on a semi-atomistic level. The model dendrimer is immersed in a mesogenic solvent composed of Gay-Berne particles, which can form isotropic, nematic and smectic-A phases. Markedly different behavior results from simulations in the different phases, with the dendrimer changing shape from spherical to rodlike in moving from isotropic to nematic solvents. The change in structure of the dendrimer is mediated by conformational changes in the flexible chains, which link the terminal mesogenic moieties to the dendrimer core [1,2]. Based on these findings, a coarse-grained simulation model for LCDr is developed. It allows, for the first time, for a successful molecular simulation study of a relation between the shape of a polyphilic macromolecular mesogen and the symmetry of a macroscopic phase. The model dendrimer consists of a soft central sphere and 32 grafted chains each terminated by a mesogen group. The mesogenic pair interactions are modelled by the recently proposed soft core spherocylinder model [3]. Coarse-grained molecular dynamics simulations are performed on a melt of 100 molecules in the anisotropic-isobaric ensemble. The model LCDr shows conformational bistability, with both rod-like and disc-like conformations stable at lower temperatures. Each conformation can be induced by an external aligning field of appropriate symmetry that acts on the mesogens (uniaxial for rod-like and planar for disc-like), leading to formation of a monodomain smectic A or a columnar phase, respectively. Both phases are stable for approximately the same temperature range and both exhibit a sharp transition to an isotropic cubic-like phase upon heating. We observe a very strong coupling between the conformation of the LCDr and the symmetry of a bulk phase, as suggested previously [4,5]. The study reveals rich potential in terms of the application of this form of coarse-grained modelling to the study of molecular self-assembly of liquid crystalline macromolecules.

1. M.R. Wilson, J.M. Ilnytskyi and L.M. Stimson, J. Chem. Phys. **119**, 3509 (2003)
2. M.R. Wilson, L.M. Stimson, J.M. Ilnytskyi, Liquid Crystals **33**, 1167 (2006)
3. J.S. Lintuvuori and M.R. Wilson, J. Chem. Phys. **128**, 044906 (2008)
4. I.M. Saez and J.W. Goodby, J. Mater. Chem. **15**, 26 (2005)
5. I.M. Saez and J. W. Goodby, Liquid Crystalline Functional Assemblies and Their Supramolecular Structures **128**, 1 (2008)

Influence of molecular size and shape of the nematogenic substances on the liquid crystal phase equilibrium

S. Lago,[a] F. Gámez,[a] P.J. Merkling,[a] B. Garzón[b] and C. Vega[c]

[a] *Dpt.Sistemas Físicos, Químicos y Naturales, Univ.Pablo de Olavide, Ctra Utrera Km 1, 41013 Seville, Spain*
[b] *Univ.CEU San Pablo, Madrid, Spain*
[c] *Dpto. Química Física I, Univ.Complutense, Madrid, Spain*

Most chemical molecules with important applications are poorly modelled if considered as spherical because their principal moments of inertia are different. Hovewer, it is very frequent that one of them is markedly different from the other two moments and the molecules are called oblate or prolate whether the differing moment is the biggest or the least, respectively. For sake of simplicity, we call the corresponding liquids as oblate molecular liquids (OML) and prolate molecular liquids (PML). If the molecular anisotropy is large enough, mesophases (liquid crystals) between the solid and the liquid state may appear. The relation between the global phase diagram and the intermolecular potential is relatively well-known for prolate models and we can assign the features of the intermolecular potential to the appearance of different macroscopic phases. The behavior is far less understood for OML. Recently, we have performed Gibbs ensemble Monte Carlo (GEMC) simulations and proposed a perturbation theory for oblate fluids reproducing vapor-liquid equilibrium in a satisfactory way. Even more recently, we have applied a Parsons- Lee theory to OML obtaining very good results for hard OML not too thick. We present here the main results from our works, considering the possible extensions to more complicated systems.

1. F. Gámez, B. Garzón, S. Lago, P. Merkling and C. Vega, Mol.Phys. **106**, 1331-1339, (2008)
2. F. Gámez, S. Lago and P.J. Merkling, Chem.Phys.Lett. (in press) doi:10.1016/j.cplett.2010.05.094

Dispersions of multiwalled carbon nanotubes in liquid crystals: new challenges to molecular theories of anisotropic soft matter

L. Lisetski,[a] S.S. Minenko,[a] V.V. Ponevchinsky,[b] M.S. Soskin,[b]
A.I. Goncharuk[c] and N.I. Lebovka[c]

[a] *Institute for Scintillation Materials, STC "Institute for Single Crystals", NAS of Ukraine, 60 Lenin Ave., 61001, Kharkiv, Ukraine*
[b] *Institute of Physics, NAS of Ukraine, Kyiv, Ukraine*
[c] *Institute of Biocolloidal Chemistry, NAS of Ukraine, Kyiv, Ukraine*

Recently, great attention has been attracted by the anisotropic soft matter systems including particles of different size, shape and aspect ratio. Among the most interesting are dispersions of multi-walled carbon nanotubes (NT) in liquid crystalline (LC) media displaying many interesting and unexpected features and presenting stimulating challenges to molecular theories of anisotropic liquids. For theoretical consideration, two different types of LC+NT dispersions can be assumed. At low NT concentrations, each NT aligns several molecular layers of nematic molecules on a short-range scale. On the long-range scale, nematic as an anisotropic fluid orients the NTs formally considered as non-mesogenic dopants. In real systems, NTs show a strong tendency for aggregation in a LC medium. Above a certain concentration of NTs ("percolation threshold"), the spanning network arises and grows with time through incorporation of individual NTs from the quasi-homogeneous dispersion. The aggregates in the vicinity of percolation threshold are of fractal nature. These ramified aggregates capture surrounding LC molecules, and their volume becomes by 2-2.5 orders greater than the total volume of the NTs involved. It was shown by methods of singular optics that such anisotropic microsized LC cladding initiates strong speckled scattering with induced optical singularities. One can conceive of these aggregates as of large quasi-macroscopic particles in the nematic matrix.

We studied dynamics of NT aggregate formation in freshly prepared (by ultrasonication) dispersions of 5CB + multi-walled carbon NTs (0.01-0.1 wt %). Several different methods were used: (a) microscopic observation of microstructure, (b) light transmission changes at the point of nematic-isotropic phase transition (Ti), (c) differential scanning calorimetry of phase transition peaks, (d) temperature and concentration dependences of electrical conductivity, and conductivity vs. applied voltage behavior in the Freedericks transition geometry, (e) measurement of birefringent structure of LC cladding around NT aggregates and induced optical singularities. The obtained results were in reasonable agreement and could be explained by the proposed tentative model. The individual NTs are gradually assembled into fractal aggregates with 5CB molecules incorporated into the “micropores” of the “skeleton” formed by a loose NT arrangement. For example, at 0.1% wt of NTs the aggregates formed after several hours of incubation effectively behave like micron-sized small particles occupying up to 20-40% of the bulk nematic volume. Higher concentration and higher aspect ratio of NTs strongly favor the aggregation, while in general the behavior was similar. The obtained results were compared with other systems involving anisotropic micro- and nanoparticles dispersed in a LC matrix(e.g., plate-like particles of organomodified montmorillonite, self-assembling aggregates of anthraquinone dyes in 5CB, etc.).

Simple lattice models of complex systems

A. Ciach

Institute of Physical Chemistry, Polish Academy of Sciences,
Kasprzaka 44/52, 01-224 Warsaw, Poland

Collective phenomena in systems containing particles that self-assemble into different non-homogeneous structures exhibit similar properties, despite different physical origin of interactions. Universal properties of a class of such systems can be described by highly simplified models that capture key properties of the (effective) interactions. Phase transitions and structural properties for a few such generic models will be described. The models include:(i) a triangular lattice model for particles that interact with short-range attraction and long-range repulsion potential (SALR), and are adsorbed on different surfaces; this can be a toy model for protein rafts on biological membranes, since 'rafts' and 'stripes' correspond to thermodynamically stable structures in different conditions (ii) simple cubic lattice model for water, predicting all major anomalies and (iii) simple lattice model for alcohol (polar molecules) predicting orientational ordering of molecules into zig-zag chain-like clusters.

Theoretical and simulation results for some model simple fluids (bulk and confined) with structural, thermodynamic and dynamic anomalies

O. Pizio[a] and S. Sokołowski[b]

[a] *Instituto de Quimica, UNAM, 04510 Mexico City, Mexico*
[b] *Faculty of Chemistry, Maria Curie-Sklodowska University, Lublin, Poland*

We discuss a set of our original results for some soft-core model simple fluids in the bulk and under confinement. The results follow from the Ornstein-Zernike integral equations of the first and of the second order as well as from computer simulation techniques.

An equilibrium study of urea denaturation of trp–cage miniprotein

D. Paschek,[a] D. Canchi[b] and A. Garcia[b]
[a] *Institut für Chemie der Universität Rostock, Satower Str. 164a, D-18059 Rostok, Germany*
[b] *Rensslear Polytechnic Institute, Troy, NY 12180, USA*

Urea is commonly used to denature proteins and its molecular mechanism is a subject of considerable debate.

Previous simulation studies have sought to elucidate the mechanism of urea denaturation by focusing on the pathway of denaturation, rather than examine the effect of urea on the folding/unfolding equilibrium.

Extending our previous simulation work [1, 2], we report the reversible folding/unfolding equilibrium of Trp-cage miniprotein in presence of urea using all-atom replica exchange molecular dynamics (REMD) simulations, compiling more than 30 microseconds worth of trjecory data. The simulations capture the experimental linear dependence of unfolding free energy on urea concentration.

We now have a picture for how urea denatures proteins. We find that the denaturation is essentially driven by favorable direct interaction of urea with the protein, through both electrostatic and van der Waals forces. The unfolded ensemble depends qualitatively on urea concentration, with greater urea concentration favoring conformations with greater solvent exposure. The unfolded state is also characterized by a more favorable interaction with urea than the folded ensemble, which provides an enthalpic driving force for unfolding.

Using present simulation techniques and parallel computing power, we have characterized the protein-solvent inter- actions in a two-solvent system and studied the effects on protein conformation. This study can be easily extended to other denaturants to obtain insights into their mechanism. A challenging extension will be to study the compensating effect on protein stability in a mixed–osmolyte system, for e.g Urea–TMAO–Water.

1. D. Paschek, H. Nymeyer, and A. E. Garcia, J. Struct. Biol. **157**, 524 (2007).
2. D. Paschek, S. Hempel, and A. E. Garcia, Proc. Natl. Acad. Sci. USA **105**, 17754 (2008).

The liquid-liquid phase transitions in ionic solutions: criticalität, crossover and complete scaling

W. Schröer,[a] J. Köser,[a] V.R Vale[a] and B. Radtke[b]

[a] *Department Biology and Chemistry, University Bremen, Leobener Str. NWII, D-28359, Bremen, Germany*
[b] *Technical Thermodynamics, University Bremen, Germany*

The critical properties of phase transitions of fluids and fluid mixtures are known to agree with that of the 3d–Ising model. Although mean–field criticality was presumed because of the long–range nature of the Coulomb potential and stated by some measurements of the liquid–liquid phase transition of ionic solutions, it is now almost certain that the phase transitions in ionic systems also belong to the Ising universality class. This is stated by experiments investigating the liquid-liquid phase transition of ionic solutions and simulations on the model systems of charged hard spheres.

In this paper we report measurements of the viscosity, of the coexistence curve and the static and dynamic light scattering of various solutions of ionic liquids, including such in alkanes alcohols, arenes, arenhalides and water. All data show Ising critical behaviour with indications of crossover to mean-field criticality. Is in variance to theoretical estimates, the crossover is shifted towards larger separations from the critical temperature with increasing dielectric permittivity of the solvent, thus stating Pitzer's observation.

In variance to the Ising model the phase diagrams are highly asymmetric. Furthermore, the diameter, which is the mean value of the compositions in the coexisting phases, is non-linear in variance to the predictions of mean-field theories but also to the observations on noble gases.

The asymmetry, which is analysed using complete scaling theory, is found to decrease with increasing dielectric permittivity of the solvent.

Effect of methanol on microphase separation of ionic liquids

T. Takamuku,[a] T. Shimomura[a] and K. Fujii[b]

[a] *Saga University, Honjo-machi, 840-8502, Saga, Japan*
[b] *The University of Tokyo, Japan*

The previous molecular dynamics (MD) simulations on 1-alkyl-3-methylimidazolium (Cnmim+)-based ionic liquids have shown that microphase separation occurs in the ionic liquids [1,2]. Thus, the positively charged imidazolium ring and anion form polar domains in pure ionic liquids, while the alkyl chains of the imidazolium cations aggregate to form nonpolar domains. The other MD simulations on Cnmim+NO_3–water systems have revealed that microphase separation of the ionic liquids is loosened by addition of water [3]. The polar domains are gradually disrupted by intruding water aggregate formed around NO_3-. The repulsive force acts between Cnmim+. This leads to the weakening of the interaction among the alkyl chains in the nonpolar domains. However, effects of a molecular liquid on microphase separation of imidazolium-based ionic liquids have not been corroborated by experimental results.

In the present investigation, we have made small-angle neutron scattering (SANS) measurements on methanol solutions of Cnmim+ bis-(trifluoromethanesulfonyl)amide (TFSA-) with varying the alkyl chain length from n = 4 to 12 to observe the heterogeneous mixing of the Cnmim+TFSA–CD_3OD solutions. In addition, the interactions of methanol–methanol, Cnmim+ –methanol, and TFSA–methanol have been evaluated by means of attenuated total reflectance infrared (ATR-IR) spectroscopy and 1H and 13C NMR.

The SANS measurements revealed that the heterogeneity of the Cnmim+TFSA- -methanol solutions, except for C4mim+TFSA-, is most enhanced at methanol mole fraction of xCD_3OD = 0.97 over the entire range. Thus, the mole fraction of the maximum heterogeneity of the solutions is independent of the alkyl-chain length. In contrast, the magnitude of the maximum heterogeneity of the solutions is larger in the order of the alkyl-chain length from n = 4 to 12. ATR-IR and NMR measurements showed that the hydrogen bonds among methanol molecules are conspicuously evolved in the solutions above xCH_3OH = 0.8. The increase in the concentration of the hydrogen-bonded methanol with increasing xCH_3OH does not significantly depend on the alkyl-chain length. On the basis of these results, the loosening of the polar and nonpolar domains in the ionic liquids with increasing methanol content will be discussed at the molecular level.

1. J.N.C. Lopes, M.F.C. Gomes and A.A.H. Padua, J. Phys. Chem. B, **110**, 16816., (2006)
2. A.A.H. Padua, M.F.C. Gomes and J.N.A.C. Lopes, Acc. Chem. Res., **40**, 1087, (2007)
3. W. Jiang, Y. Wang and G.A. Voth, J. Phys. Chem. B, **111**, 4812., (2007)

Diffusion of imidazolium based ionic liquids in different polar solvents

E. Schmidt, A. Heintz, R. Ludwig

University of Rostock, Dr.-Lorenz-Weg 1, 18059 Rostock, Germany

The solvation behaviour of ionic liquids in different solvents is very important for industrial applications. Solvent-solute-properties can be observed by their binary diffusion coefficients which can be measured by the fast and accurate Taylor dispersion technique.

Here, using the Taylor dispersion technique, we present diffusion coefficients of the ionic liquids [C_2MIM][$EtSO_4$], [C_4MIM][$OcSO_4$], [C_2MIM][NTf_2] and [C_4MIM][NTf_2] in water [1], methanol and acetonitrile in a temperature range between 288 K and 313 K. Furthermore we calculated the activation energies and the prefactors of the Arrhenius plots and show that the temperature dependence of the diffusion is characteristic for the solvents.

In order to support our experimental results we also present MD simulations of [C_2MIM][NTf_2] and [C_4MIM][NTf_2] in water, methanol and acetonitrile using the force field parameters of the imidazolium-based ionic liquids from T. Köddermann [2]. With the help of this method we are able to calculate binary diffusion coefficients via self diffusion coefficients and the comparison between the simulated and the measured values is very good. The advantage of MD is the molecular view into the solutions. We show that depending on the solvent the solution contains neutral aggregates of ion pairs and solvated ions as diffusive species.

1. Heintz A., Lehmann J. K., Schmidt E., Wandschneider A. J. Solution Chem. **38**, 1079 - 1083 (2009).
2. Kddermann T., Paschek D., Ludwig R. Chem Phys Chem **8**, 2464 - 2470 (2007).

Entropy driven self-assembly mechanism

M. Lozada-Cassou, G. Odriozolaand and F. Jímenez Ángeles

Mexican Petroleum Institute, Mexico City, Mexico

Self-assembly mechanisms are studied through many-body physics methods, i.e., integral equation theories and Monte Carlo simulations. Simple models for self-assembly of DNA, confined into phospholipid bilayers, and key-lock enzymatic catalytic reactions are considered. This last theoretical study inspired self-assembly experiments of ad-hoc design colloids, with an excellent qualitative agreement with our proposed key-lock mechanism.

Microheterogenity of alcohol-water mixtures: experimental and simulation study

B. Kežić,[a] M. Mijaković,[a] L. Zoranić,[a] F. Sokolić,[a] A. Asenbaum,[b]
C. Pruner,[b] E. Wilhelm[b] and A. Perera[c]

[a] *Department of Physics, Faculty of Science, University of Split, Teslina 12, 21000 Split, Croatia*
[b] *Section for Experimental Physics, Department of Materials Science and Physics, University of Salzburg, Hellbrunnerstrasse 34, A-5020 Salzburg, Austria*
[c] *Laboratoire de Physique Théorique de la Matiére Condensée (UMR CNRS 7600), Université Pierre et Marie Curie, 4 Place Jussieu, F75252 Paris, Cedex 05, France*

Liquid water and liquid alcohols are both hydrogen-bonded. However, while water possesses a three-dimensional hydrogen-bonded network, alcohols show chain and ring association. Thus, investigation of mixtures of these two liquids are of considerable interest, in particular, when results are subsequently compared with those obtained for aqueous solutions of higher alcohols, where phase separation may be observed.

Indeed, the anomalous negative excess entropy characteristic for aqueous mixtures of lower alcohols containing hydrophobic groups may be successfully discussed by invoking molecular scale segregation of the components across the entire composition range [1]. Such local immiscibility or microheterogeneity, is observed in the experimental as well as in the simulations results [2,3]. In this study we investigate the microheterogeneity in the water-alcohol system focusing on the clustering properties.

Previous Brillouin scattering measurements of the alcohol-water mixtures were mostly done with a single-pass Fabry-Perot spectrometer [4,5]. Here, we present Brillouin scattering measurements over the full composition range, using a 6-pass tandem Fabry-Perot interferometer with a finesse of about 80, and FWHH of about 90 MHz of the instrumental function. The molecular dynamics simulations were done using the Dlpoly2.14 package. We calculated: the clustering parameters, such as cluster distribution for the clusters that are made of each component and the clusters that are mixed; and differentiate the hydrogen - bonded clusters and the sterical clusters. We also studied the static correlations such as sites radial distribution functions and Kirkwood-Buff integrals, which are directly connected with the compressibility. At the end we compared the simulation results with the results of the experiments.

1. S. Dixit, J. Crain, W.C.K. Poon, J.L. Finney and A.K. Soper, Nature, **416**, 829, (2002); (b) A.K. Soper, L. Dougan, J. Crain and J.L. Finney, J. Phys. Chem. B, **110**, 3472, (2006)
2. Y. Seshimo, Y. Ike and S. Kojima, Jpn. J. of Appl. Phys., **47**, No 5, (2008)
3. L. Zoranić, F. Sokolić, A. Perera, J. Chem. Phys., **127**, 024502, (2007)
4. K. Negishi, M. Yamazaki, and Y. Torikai, Japan. J. Appl. Phys., **6**, 1016, (1967)
5. A. Asenbaum and M. Sedlacek, Acustica **30**, 109 (1974)

Nanosize supramolecular aggregates in methanol: from melting point to supercritical state

V.A. Durov and I.Yu. Shilov

Department of Chemistry, Moscow State University, Moscow, Russia

Quasichemical models [1,2] provide a unified molecular approach to describe the supramolecular structure and properties of liquid systems in a wide range of parameters of state, with negligible computational cost. This approach gives a new insight into long-range molecular correlations due to specific interactions (e.g. hydrogen bonding).

Mean squares of distances between oxygen atoms of terminal molecules of chain-like aggregates are considered as characteristics of length scale of connectivity and correlations of molecules in liquid. Equations for number-, weight- and z-average mean-square distances between oxygen atoms of terminal molecules of chain-like aggregates of alcohols as functions of structural and thermodynamic parameters of aggregation are derived.

Mean-square distance between oxygen atoms of terminal molecules of chain-like aggregates of methanol is calculated as function of the number of molecules. Temperature dependence of number-, weight- and z-average distances between oxygen atoms of terminal molecules of chain-like aggregates of methanol is calculated in the wide range from melting point to critical point [3]. The average size of the aggregates of methanol at ambient conditions is found to be about several nanometers, while approaching melting point it can reach tens of nanometers.

This work was supported by the Russian Foundation for Basic Research, project N 10-03-01164 and by the Program of Ministry of Education and Science of the Russian Federation “Development of scientific potential of higher education institutions (2009-2010)”, project N 2.1.1/3305.

1. V.A. Durov, Pure Appl. Chem., **76**, 1 (2004).
2. V.A. Durov, J. Mol. Liq., **118**, 101 (2005).
3. V.A. Durov, I.Yu. Shilov, J. Mol. Liq., **136**, 300 (2007).

Towards calculation of hydration free energy

V.P. Sergiievskyi and M.V. Fedorov

Max-Planck-Institute for Mathematics in the Sciences, Inselstrasse 22, 04103 Leipzig, Germany

Hydration Free Energy (HFE) is one of the fundamental quantities in Physical Chemistry of solutions. It allows to predict many properties of compounds, such as solubility, pKa, constants of complex formation. Application of HFE prediction methods are found in pharmacology. For screening large drug-candidate datasets the drug-design industry needs fast method for prediction HFE with the acceptable method accuracy 1-2 kcal/mol. Promising tool for such task is the integral equation theory, in particular Reference interaction site model (RISM) [1]. It is a compromise between slow MD or MC simulations and fast, but too-much simplified polarizable continuum models. Although RISM is much faster than MD/MC simulations, the standard algorithms of solving the RISM equation are not fast enough for effective screening of large molecule sets.

In the work [2] it was shown, that the multi-grid method, applied to the equation for the monoatomic spherical particles, reduces the computational cost of standard algorithm up to several dozen times. Now we applied the multi-grid technique to a more common case: RISM equations for polyatomic solvent. It was shown, that RISM multi-grid solver is stable for all investigated physically-reasonable systems and give more than 30 times speed-up of the standard algorithm. With the new algorithm the time to calculate Hydration Free Energy of the typical drug-like molecule (20 atoms) is about 15 sec instead of several minutes with the standard algorithm. Recently performance of the new multi-grid RISM solver for prediction Hydration Free Energy of drug-like bioactive compounds was studied.[3] It was shown, that RISM Hydration Free Energy calculations with structures and partial charges obtained by the QM methods give a good correlation with experiment, and after simple atom-type parametrization are able to give RMSD about 1.2 kcal/mol. This shows the perspective to use the efficient RISM-based method for calculating HFE in industrial applications.

1. Chandler D. and Andersen H.C., J. Chem. Phys., **57**(5):1930-1937, (1972)
2. Fedorov M.V. and Hackbusch W., Preprint, 88, Max-Planck-Institut fuer Mathematik in den Naturwissenschaften (2008)
3. David S. Palmer, Volodymyr P. Sergiievskyi, Frank Jensen, Maxim V. Fedorov, accepted for publication in J. Chem. Phys., Manuscript No.: A10.04.0425R

On the structure of aqueous electrolyte solutions

L. Pusztai,[a] V. Mile,[a] O. Gereben[a] and O. Pizio[b]

[a] *Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, Konkoly Thege ut 29-33, 1121, Budapest, Hungary*
[b] *Instituto de Quimica, UNAM, 04510 Mexico City, Mexico*

The microscopic structure of cesium and rubidium halide (e.g., CsCl, CsF, CsBr, CsI, RbCl) solutions, as a function of concentration, has been investigated via neutron and X-ray diffraction, EXAFS and molecular dynamics (MD) simulation. As a means of combining all these techniques, total structure factors from diffraction experiments and partial radial distribution functions from MD have served as input simultaneously for Reverse Monte Carlo (RMC) structural modeling. Based on this approach, it has been shown that, surprisingly, ion-water correlations, as described by several interatomic potential sets, can be consistent (within errors!) with diffraction data. On the other hand, water-water correlations from MD are much less reliable. Finally, a detailed description of the structural parameters, such as the (distribution of the) number of first neighbors and angular distributions within the first coordination shell, will be provided.

Structure and dynamics of Magnetic Fluids

G. Mériguet, G. Demouchy, E. Dubois, M. Jardat andR. Perzynski

Univeristé Pierre et Marie Curie, Bat. F74 CC51 4 Place Jussieu, 75005, Paris, France

Ionic aqueous ferrofluids, which are aqueous dispersions of magnetic nanoparticles electrostatically stabilized, present a phase diagram analogous to that of molecular systems with a gas-like phase, fluid, liquid and solid ones, a coexistence curve with a critical point. Thanks to an osmotic compression method, it is possible to prepare dispersions with tuned interparticle interactions, in a well-defined state that can be localized inside this well-known phase diagram. The experimental control parameters determining the state of interaction inside the dispersion, are the osmotic pressure and the ionic strength. We explore here the structural and the dynamical properties of repulsive dispersions based on $\gamma-Fe_2O_3$ nanoparticles stabilized by citrate species. The structure and the dynamics isotropic in zero field, become anisotropic under an applied field. The structure is determined by Small Angle Scattering (of Neutrons or X-rays), the collective long-time diffusion by Rayleigh Forced Scattering and the self short-time diffusion by Spin Echo of Neutrons.

EMLG-JMLG Annual Meeting 2010

Complex liquids

Modern trends in exploration,
understanding and application

Posters

September 5–9, 2010

Lviv, Ukraine

Ultrafast dynamics of lipids at the phospholipid - water interface

H. Abramczyk, P. Ciąćka and B. Brożek-Płuska

Technical University of Łódź, Institute of Applied Radiation Chemistry, Laboratory of Laser Molecular Spectroscopy, Wroblewskiego 15, 93-590 Łódź, Poland

It is well known that lipid molecules play a key role in activity of biological membranes and decide about the health-disease balance in living creatures. The interactions with water modify physical properties, both static and dynamical of the lipid bilayer. Moreover, the interactions lead to the modification of the diffusion barrier across the membrane to ions and oxygen. The modification by water may play an important role in the energy dissipation in lipids that is a key mechanism in maintaining the photostability of the biological tissue.

We report on energy dynamics of water at the water/lipid interface of Dipalmitoyl phosphatidylcholine (DPPC). Femtosecond infrared (IR) two-color and bleaching pump-probe experiments were used to investigate vibrational relaxation dynamics of the O-H stretching mode of water at the water/DPPC interface for a controlled humidity of the sample. The detailed vibrational dynamics of interfacial water and interactions with DPPC has been elucidated. We report also on the results of the spectral anisotropy as a function of the delay time that provides insight into mechanisms of energy transfer, mechanisms of hoping and reorientational relaxation at the binding sites.

1. F.S. Parker, *Applications of Infrared, Raman, and Resonanse Raman Spectroscopy in Biochemistry*, Plenum, New York, (1983).
2.J. Liquier, E. Taillander, In *Infrared Spectroscopy of Biomolecules*, H. H. Mantsch, D. Chapman, Eds., Wiley, New York, (1996).
3.A. Ghosh, M. Smits, M. Sovago, J. Bredenbeck, M. Muller, M. Bonn, Chem. Phys. **350**, 23-30 (2008).

The invesigation of concentration features of molecular water–alcohol solutions

N. Atamas, G.N Verbinskaya and L.V. Bulavin

Kyiv Taras Shevchenko University, 2 Glushkov Ave., 03128 Kyiv, Ukraine

A molecular level understanding of the local structure in water solution has been sought for long time, yet there no comprehensive model that can sufficiently describe a wide range of microscopic and macroscopic properties. Smell clusters of water molecules can be considered as prototypes for understanding the fundamental interaction that govern hydrogen bonds. In the present work, we report MC simulation results for water-ethanol and water-propyl mixtures in the isothermal and isobaric ensemble at T=300K and p=1.0 atm at various concentrations. Conducted calculations allowed us to obtain information on the structural characters of water in the two-component water-alcohol solution at different molar concentrations of alcohols. The analysis of the radial distribution functions for hydrogen bounding between alcohol molecules and water molecules was done. The changing of the form water clusters from tetramer to trimer with changing of the concentration of alcohol in solution was done. Results calculations of the indicated solutions structure, conducted by the method of Monte Carlo, are confronted with neutron experiment. It is indicated that minimums in concentration dependence of self-diffusion coefficient corresponds the certain local structures of investigational alcohol –water solution. Received results allowed to determine the solution local structures range of variation. The model approximation of describing of water–alcohol system for different concentrations was proposed.

Dielectric permittivity of the mixture of non-polar particles

Yu. Blazhyevskyi and M. Holovko

Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine

The dielectric permittivity ε of the multicomponent systems of particles with different polarization is calculated. General expressions defining ε via dielectric permittivities ε_i and concentrations n_i of the particular sorts are obtained. Two methods are used in the calculations. First, in the random phase approximation the dipole moments of particles induced by an external electric field are found. Second, it is shown that the induced dipole moments can be taken into account by introducing some additional degrees of freedom into the configurational integral. Specific calculations are made for the hard sphere model and for the Lennard-Jones liquid. The obtained results are compared to the known expressions of the phenomenological approach.

Static and transport properties at the base for development of an all-atom force field for ethylene glycol

M.N.D.S. Cordeiro and B. Szefczyk

REQUIMTE/University of Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal

Ethylene glycol (1,2-ethylenediol), the simplest diol, has a vast number of applications in technology, chemistry and chemical engineering. It is commonly used as an antifreeze agent and coolant; it is a precursor in production of poly(ethylene glycol), a polymer commonly used for biocompatibility purposes and nanoparticle stabilization. Recently, it has been also applied as a component of ionic liquids (ILs) [1]. In molecular modelling, glycol molecule is used as a template to develop force fields for more complex systems [2]. As a result, several force fields for glycol have been developed and published [3,4]. In this work, we focus our attention on force fields compatible with the all-atom OPLS force field [5], commonly used to simulate molecular liquids, including ILs. Unfortunately, most of the OPLS-AA-based force fields for glycol were developed to reproduce the microscopic structure of the liquid (e.g. equilibrium between trans and gauche conformers [4,6]) or to design force field for biological molecules, like sugar [2]. This came at the sacrifice of the ability to reproduce the physical properties of the liquid glycol itself. Also, for the glycol molecule, it has been proposed to use different scaling factors than in the original OPLS-AA force field [3,4] or even apply an extra scaling factor for the interaction between atoms separated by four bonds (1-5 interactions) [2]. Although this approach has been found to improve the quality of the force field, it affects the "userfriendliness", when the force field is used for mixtures. Namely, MD packages like GROMACS, usually allow defining only a single scaling factor for the whole system. This can be problematic if the goal of the study is to simulate complex system, like IL (e.g. composed of glycol and choline chloride [1]) or mixtures (e.g. with other alcohols [7]).

In this work, we attempt to optimize the force field for liquid glycol, with two main goals: (i) the physical properties of liquid glycol, like density, thermal expansion, compressibility, heat of vaporisation and surface tension should be reproduced as good as possible, (ii) the force field should be kept as simple as possible, without introducing "exotic" parameters and maintaining full compatibility with the OPLS-AA force field. Such a force field could be easily combined with other compounds.

1. Abbott A.P., Harris R.C., Ryder K.S., J. Phys. Chem. B, **111**, 4910-4913,(2007)
2. Kony D., Damm W., Stoll S., van Gunsteren W.F., J. Comp. Chem. **23**, 1416-1429 (2002)
3. Gubskaya A.V., Kusalik P.G., J. Phys. Chem. A **108**, 7151-7164 (2004)
4. de Oliveira O.V., Freitas L.C.G., J. Mol. Struct. (THEOCHEM) **728**, 179-187 (2005)
5. Jorgensen W.L., J. Phys. Chem. **90**, 1276-1284 (1986)
6. Saiz L., Padró J.A., Guàrdia E., J. Chem. Phys. **114**, 3187-3198 (2008)
7. Jerie K., Baranowski A., Przybylski J., Gliński J., J. Mol. Liquids **111**, 25-31 (2004)

Application of recursive sequences and diagram technique in the theory of associated liquids

V.A. Durov and A.P. Moscalets

Department of Chemistry, Moscow State University, Moscow, Russia

A new method based on recursive sequences (RS) is developed to calculate differential and integral characteristics of supramolecular organization, as well as dielectric properties of associated liquids in the framework of quasi-chemical model of non-ideal associated solution QC-NAS [1,2]. The RS-method is consistent with matrix-based technique [2] in detailed description of structure and properties of aggregates, and moreover can be extended to models of branched (for instance, tree-like) supramolecular structure of liquids.

Studying supramolecular structure of associated liquids and solutions basing on their physicochemical properties is of current importance for physical chemistry [1,2]. Information about the supramolecular organization of liquids using permittivity data results from Onsager - Kirkwood-Fröhlich equation [3]:

$$\frac{9k_BT(\varepsilon_s-\varepsilon_\infty)(2\varepsilon_s+\varepsilon_\infty)V_m}{4\pi N_A\varepsilon_s(\varepsilon_\infty+2)^2}=g^{dip}\mu_b^2, \tag{1}$$

where N_A - Avogadro's number, k_B - Boltzmann constant, T - absolute temperature, ε_∞ - deformation permittivity of the liquid, g^{dip} - Kirkwood dipole correlation factor. Generalization of Eqn. (1) for mixtures in work [4] is performed.

In the RS-method such sequences $\{G_n\}$ and $\{T_n\}$ are to be constructed that

$$\lim_{n\to\infty} G_n = c_{sum}, \quad \lim_{n\to\infty} T_n = g^{dip}, \tag{2}$$

for the terms of which recursive relations are performed:

$$G_{n+1} = f_1(G_n), \quad T_{n+1} = f_2(T_n), \tag{3}$$

in which f_1, f_2 - some of the functions defined explicitly while constructing the sequences $\{G_n\}$ and $\{T_n\}$. A passage to the limit $n\to\infty$ in formulas (3) taking into account relations (2) implies the algebraic equations

$$c_{sum} = f_1(c_{sum}), \quad g^{dip} = f_2(g^{dip}), \tag{4}$$

allowing the desired values c_{sum} and g^{dip} to be found. Construction of the RS will give us possible to make clearer with the use of proposed diagram technique [5].

1. Durov V.A., *Novel approaches to the structure and dynamics of liquids: experiments, theories, and simulations*; Samios J., Durov, V. A. Eds.; NATO Science Series. II. Mathematics, Physics, and Chemistry **133**, Kluwer: Dordrecht, p 17–40, (2004)
2. Durov V.A., *Kontsentrirovannye i nasyshchennye rastvory.* M.: Nauka, S. 170-254, (2002).(Durov V. A. *Concentrated and saturates solutions.* Monograph In Russian)
3. Fröhlich H. *Theory of dielectrics: dielectric constant and dielectric loss.* Clarendon: Oxford, 192 p., (1958).
4. Durov V.A., Russian J. Phys. Chem. **63**, No 6., P. 875 (1989).
5. Durov V.A., Moscalets A.P., Moscow University Chem. Bull. Accepted.

Ion association in aqueous alkali formate solutions

A. Eiberweiser,[a] M. Bončina,[b] H.M.A. Rahman,[a] M. Bešter-Rogač[b] and R. Buchner[a]

[a] *Institut für Physikalische und Theoretische Chemie, Universität Regensburg, Germany*
[b] *Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia*

The carboxylate group –COO- is the most common anionic residue of biomolecules, such as proteins and its hydration and interaction with other ions is often vital for the functioning of these molecules. Recent theoretical [1] and experimental [2] investigations, revealing different affinities for sodium and potassium ions with carboxylate, have fuelled ideas that the small difference in binding strength is a major reason for the different physiological behaviour of these two cations. However, a closer look at the literature reveals that quantitative data on carboxylate-metal ion interactions are scarce, possibly because of their weakness. In this contribution we study the association of formate ion, HCOO-, with the alkali cations Li+, Na+ and K+ at 25°C. Formate is the simplest model for the carboxylate moiety in biomolecules. In contrast to its higher homologues, like acetate, HCOO- possesses no hydrocarbon moiety and thus offers the possibility to study carboxylate-metal ion and carboxylate-water interactions without interference from hydrophobic effects. As techniques we use high-precision conductivity measurements of dilute (< 0.01 M) solutions in conjunction with dielectric relaxation spectroscopy covering the concentration range $0.05 \leqslant c/M \leqslant 1$. Whilst conductivity measurements yield accurate data for the association constants at infinite dilution, KA ○, dielectric spectroscopy allows direct determination of ion-pair concentrations, informs on the ion-pair species present and yields effective hydration numbers which can be compared to results from other methods.

1. B. Jagoda-Cwicklik, R. Vácha, M. Lund, M. Srebro and P. Jungwirth, J. Phys. Chem. B. **111**, 14077 (2007)
2. J.S. Uejio, C.P. Schwartz, A.M. Diffin, W.S. Drisdell, R.C. Cohen and R. Saykally, Proc. Nat. Acad. Sci. **105**, 6809 (2008)

Temperature and density effects on structural features of near- and supercritical diluted aqueous lithium chloride solutions

M. Fedotova

Institute of Solution Chemistry of Russian Academy of Sciences,
Academicheskya str., 1, 153045 Ivanovo, Russia

The microstructure of supercritical aqueous electrolyte solutions has received significant attention in recent years as a result of its interest in industrial applications as well as the importance of such fluids in many geochemical processes. However, a detailed microscopic explanation of the behavior of supercritical water-salt fluids at the molecular level is still lacking, although there have been many studies and considerable progress made recently. In particular, there are still structural features which remain unclear both for supercritical water and aqueous solutions. The difficulties arise from the multiplicity of the parameters involved (T, p and ρ) and their concomitant interdependence, which can lead to opposing effects.

We report the results of a study of the structural features of near– ($T = 573K, \rho_1 = 1.0\,g/cm^3, \rho_2 = 0.65\,g/cm^3$) and supercritical ($T = 1073K, \rho = 0.65\,g/cm^3$) 0.24 M LiCl(aq) solution. Structural characteristics have been calculated by the RISM integral equation method. The obtained data are compared to structural parameters at ambient conditions ($T = 298K, p = 0.1MPa$). As expected, it was found that on transition from ambient conditions into supercritical state the tetrahedral network of water is destroyed, ions are thermally dehydrated and ion association to contact ion pairs is promoted. In particular, the hydration numbers decrease by about 33.5% for Li^+ and 40.3% for Cl^-, whereas the fraction of contact ion pairs increases by a factor of 3.13. Solvent separated ion pairs are absent under sub- and supercritical temperatures.

We have analyzed the influence of various factors on the structural changes, namely, the temperature effect at constant fluid density ($\Delta T_1 = 298{-}573K, \rho = 1g/cm^3$ and $\Delta T_2 = 573{-}1073K, \rho = 0.74g/cm^3$) or/and the fluid density effect at constant temperature ($\Delta\rho = 1.0 - 0.74g/cm^3$, $T = 573K$). It was found that the impact of rising temperature and density on the observed decrease of the number of the H-bonded water molecules and on thermal dehydration of the ions is comparable

($\sim 11 - 17\%$). At the same time, in the range of 298–573 K ($\rho_{const} = 1 g/cm^3$) the temperature effect on ion association many times larger than in the range of 573–1073 K ($\rho_{const} = 0.74 g/cm^3$). However, the density effect ($1.0 - 0.74 g/cm^3, T_{const}$ =573 K) on the strengthening ion association is negligible at near-critical conditions (Δn_{LiCl}=5%). Thus, ion association is mainly affected by rising temperature. Moreover, this effect is largest in the subcritical region. As it has been established, the maximal effect on structural changes in LiCl(aq) solution comes from the combined influence of T and ρ.

This work was supported by the Russian Foundation for Basic Research (grant No. 09–03–97507–r_centre_a).

IR spectroscopic study of the local stucture of water rich phase in ternary water–scCO$_2$ –NaCl system

R. Oparin and M. Fedotova

Institute of Solution Chemistry of Russian Academy of Sciences,
Academicheskya str., 1, 153045 Ivanovo, Russia

Due to unique properties, the ternary system water–scCO$_2$–electrolyte, and in particular, water–scCO$_2$–NaCl, have great practical importance for various technologies such as hydrothermal processes. Therefore, their studies find a large interest. Moreover, water–scCO$_2$–NaCl mixture consists of the most distributed components in hydrothermal fluids and can be used as the standard model for fluid inclusion in the top layer of the Earth's crust.

The present report presents results from infrared (IR) spectroscopic study of the effect of isobaric heating ($T = 313 - 633K$ in steps of $\Delta T = 20K$, $p_{const} = 25MPa$) on hydrogen bonding. The water rich phase of the ternary water–scCO$_2$–NaCl system with various salt concentrations (0; 6; 15; 23 wt.%) were investigated. The partial density of water was estimated from near–IR spectra, whereas the investigation of thermal effects on the H–bond distribution was based on the analysis of mid–IR spectra.

It has been established that the temperature-induced decrease of the average number of H–bonds, $< n_{HB} >$, is reduced with increasing salt concentration. At vanishing salt concentration temperature increase leads to the disappearance of water molecules having more than three H-bonds and to the preferential formation of water dimers (molecules with a single H–bond). However, already for small addition of salt (only 6 wt. %) the water molecules with three H-bonds remain in the system over the entire temperature range. For the highest NaCl concentration (23 wt. %) water molecules with two H-bonds become the major species at temperatures above 613 K.

This work was supported by the Russian Foundation for Basic Research (grant No. 09–03–97507–r_centre_a).

On the calculation of structural and thermodynamic characteristics of ion hydration in the framework of RISM approach

M. Fedotova and S. Kruchinin

Institute of Solution Chemistry of Russian Academy of Sciences,
Academicheskya str., 1, 153045 Ivanovo, Russia

One of the widely used theoretical methods for the description of ion solvation is the Ornstein-Zernike integral equation method in the framework of RISM approach. However, the results of this method are not exact because of the involved assumptions and approximations leading thus only to a qualitative description of the properties for ion-molecular systems. In particular, the RISM results depend on the used potential model. It is well known that different models yield significantly different magnitudes for the pair correlation functions (PCFs). As a consequence, the derived thermodynamic properties differ from model to model and deviate from the experimental data. Obviously, the selection of proper interparticle potentials is critical choice. In this report the results of testing different potential models for calculations of the ion-water PCFs and the hydration free energy for monovalent ions at infinite dilution by the RISM approach are presented. The solute-solvent intermolecular interactions were described by a combination of Lennard-Jones (LJ) and Coulomb terms. LJ parameters were taken from data sets of Aqvist [1], Jorgensen [2], Cheatham [3], and Horinek [4]. The goal of this study is to determine the set of LJ parameters which is capable of providing the most accurate description of the solvation structure and thermodynamics of ions within the RISM theory. For the chosen sets we have also checked some expressions for the hydration free energy in the framework of the hypernetted chain closure [5]. These include also the assumption of Gaussian fluctuations (GF) for the solvent [6], the use of a repulsive bridge (RB) correction [7], the effect of the partial wave (PW) expansion [8], and the PW with semi-empirical corrections [9]. Comparison of the data obtained reveals a significant spread of results which is connected both to the choice of the scheme of calculation, and to the use of various LD sets. It was found that the results received with use of Cheatham's and Horinek's sets yield the smallest deviation from literature data. Additionally, the analysis of the hydration free energies showed that in the case of the cations the GF and the HNC+RB equations give best results whereas for the anions the GF and the standard HNC equations agree best with the experimental results.

1. Aqvist J., J.Phys.Chem. **94**, 8021 (1990).
2. Chandrasekhar J., Spellmeyer D.C., Jorgensen W.L., J.Am.Chem.Soc. **106**, 903 (1984); McDonald N.A., Duffy E.M., Jorgensen W.L., J.Am. Chem. Soc. **120**, 5104 (1998); Jensen K.P., Jorgensen W.L., J.Chem. Theory Comput. **2**, 1499 (2006).
3. Suk J., Cheatham Th. E., J.Phys.Chem.B. **112**, 9020 (2008).
4. Horinek D. et al, J.Chem.Phys. **130**, 124507 (2009).
5. Singer S.J., et al, Mol.Phys. **55**, 621 (1981).
6. Chandler D. et al, J.Chem.Phys. **81**, 1975 (1984).
7. Kovalenko A., Hirata F., J.Chem.Phys. **113**, 2793 (2000).
8. Ten-no S., J.Chem.Phys. **115**, 3724 (2001).
9. Chuev G.N., Fedorov M.V., et al, Chem.Phys.Lett. **448**, 198 (2007).

Structure of water and methanol-water mixture at high-temperatures and high-pressure by energy dispersive X-ray diffraction combined with EPSR modeling

K. Fujimura,[a] K. Uchi,[a] K. Yoshida,[a] Y. Katayama[b]
andT. Yamaguchi[a]

[a] *Department of Chemistry, Faculty of Science, Fukuoka University, 8-19-1 Nanakuma, Jonan-ku, 814-0180 Fukuoka, Japan*
[b] *SPring-8, Japan*

Supercritical water changes its density continuously from a gaseous to a liquid state with changing temperature and pressure, and thus the corresponding physicochemical properties, such as dielectric constant and ionic product, can be varied as a function of temperature and pressure. Owing to these unique properties supercritical water has been utilized as a unique solvent for decomposition of hazardous chlorinated organic compound and formation of metal oxide nano particles, etc. It is also interesting to note that addition of methanol facilitates such reactions effectively even under more moderate thermodynamic conditions. Such properties and roles of water and water-methanol mixture are relevant to hydrogen bonding in the solvents. In this study, we performed energy-dispersive X-ray diffraction (EDXD) measurement on water and water-methanol mixture at high-temperatures and high-pressures, and on the basis of the structure factors obtained Empirical Potential Structure Refinement (EPSR) simulations were run to extract all the partial pair correlation functions and the details of hydrogen bonding in the systems. Samples measured were pure water and 0.3 mole fraction methanol-water mixture. An energy-dispersive type of X-ray diffractometer consists of an rotating W cathode X-ray generator operated at 10 $\sim$ 200 mA and 50 keV, a Ge SSD, and a glassy carbon cell covered by a Be cell specially designed for X-ray measurements of high-temperature and high-pressure liquids. EDXD data were collected on both solvents under thermodynamic conditions of 298 K at 0.1 MPa, 473 K and 573 K at 30 MPa. In EPSR simulation, initial potentials used were SPC/E and OPLS-AA models for water and methanol, respectively. The simulations were run for the experimental structure factors over the scattering vector $Q = 0$ to 11 Å^{-1}, and the potentials were modified to obtain good agreement between the observed and simulated structure factors. It has been found that the pair correlation functions of hydrogen bonded pairs of ! water-water and methanol-water in the mixture changed dramatically with temperature, whereas those related with the hydrophobic methyl group of alcohol-alcohol and alcohol-water were little perturbed by elevating temperature. These findings suggest that the thermal effect strongly affects the hydrogen bonded interactions in the systems. We will show other features of hydrogen bonding, such as spatial density functions, distributions of clusters, and coordination numbers as a function of temperature.

Influence of confinement on solvation dynamics of ethanol in water by Raman spectroscopy and transient fluorescence spectroscopy

B. Gadomska and W. Gadomski

Laboratory of Physicochemistry of Dielectrics and Magnetics,
Department of Chemistry, University of Warsaw, ul. Żwirki i Wigury
101, 02-089 Warsaw, Poland

Herewith we present the results of our studies on the effect of confinement on the solvation dynamics of ethyl alcohol in aqueous solutions using Raman spectroscopy of the O-H stretching band. Basing on Gaussian-Lorenzian deconvolution of the O-H band Raman spectra we investigate the local structures created between water-water–, water-alcohol– and alcohol-alcohol– molecules, which are directly related to the solubility of the liquids. Comparison of the responses in bulk solutions and in solutions confined in the pores of the gelatin gel shows that for high ethanol concentrations solubility significantly increases with decrease of the pore sizes. On the other hand, using methods of transient fluorescence spectroscopy, we investigate the influence of the presence of alcohol on the process of gelation.

Volumetric properties of peptides from Voronoi tessellation analysis of hydration shells

V.P. Voloshin,[a] A.V. Anikeenko,[a] N.N. Medvedev,[a] M.N. Andrews,[b]
R. Winter,[b] and A. Geiger[b]

[a] *Institute of Chemical Kinetics and Combustion, SB RAS, Novosibirsk, Russia*
[b] *Physical Chemistry, Dortmund University of Technology, Germany*

The study of hydration, folding and interaction of proteins by volumetric measurements has been promoted by recent advances in the development of highly sensitive instrumentations. But the separation of the measured apparent volumes into contributions from the protein and the hydration water $V^{app} = V^{prot} + \Delta V^{water}$ is still challenging. A promising approach is the combination of such experiments with molecular simulations. But even with the detailed microscopic structural information from the simulations, a proper separation of the volumes is delicate. As a test case we present results of an extended Voronoi tessellation analysis of a Molecular Dynamics simulation study, treating an aqueous solution of the human islet amyloid polypeptide hIAPP, which consists of 37 amino acid residues. The simulations comprise a temperature range from 250 to 450 K. We find a small negative contribution ΔV^{water} of the hydrations water, and a positive thermal expansivity of the hydration water and the peptide. The latter is paralleled by a decreasing packing of the polypeptide, i.e. increasing intramolecular voids due to increasing thermal fluctuations. This is in contrast to the results of a recent study, where a radial distance approach has been used to define the hydration shell and a strong positive contribution ΔV^{water} has been detected. The used Voronoi tessellation techniques, like Voronoi-S-region constructions, and the application of Weiss-corrections to the volume distribution of the Voronoi cells, are presented in the poster.

Effects of cryoprotectants on the hydrophobic hydration of small apolar solutes in aqueous solutions

S. Heckhausen, J. Holzmann, D. Paschek and R. Ludwig

Physikalische und Theoretische Chemie, Universität Rostock,
Dr.-Lorenz-Weg 1, 18059 Rostock, Germany

Cryoprotectants are molecular compounds which prevent water from freezing in the subzero temperature range. Cryoprotective agents are used in medical and cryobiological applications where they protect biological tissue from freezing damage. Compounds like ethylene glycol, propylene glycol, glycerol, DMSO and certain sugars are known to act as cryoprotectants [1]. The cryoprotectants inhibit (re-)crystallization of the supercooled liquid and sometimes allow even vitrification of the solution. Although the effect on supercooled solutions has been known and exploited for quite some time, the molecular mechanisms behind are far from being fully understood. Molecular Dynamics (MD) simulations are a powerful tool to examine detailed changes in the aqueous solution structure, dynamics, and thermodynamics. Here we focus on the solvation of small apolar particles, such as methane and noble gas molecules, in aqueous cryoprotectant solutions. To quantify the temperature dependence, simulations are conducted over a broad temperature range, extending largely into the deeply supercooled region. We determine the hydrophobic hydration by calculating the solvation free energy of those particles. By employing temperature dependent data, we are also in the position to provide the higher order derivatives of the free energy, such as the solvation enthalpy, entropy and heat capacity. The solvation of apolar particles in cryoprotectant solutions is compared with the behavior observed recently for aqueous salt solutions [2].

1. J. Dashnau, N. Nucci, J. Vanderkooi, J. Phys. Chem. B **110**, 13670-13677 (2006).
2. J. Holzmann, R. Ludwig, A. Geiger, D. Paschek, ChemPhysChem **9**, 2722-2730 (2008).

Dynamics of water in aqueous salt solutions

J. Holzmann, D. Paschek and R. Ludwig

Physical Chemistry, University of Rostock, Dr.-Lorenz-Weg 1, D-18055 Rostock, Germany

One of the anomalies of water is the unusual dynamical behaviour which is observed in saline water. At moderate to high temperatures the self diffusion coefficient decreases by adding salt while in the supercooled region the addition of ions leads to an increase in the mobility of water [1]. Salts are often classified in kosmotropes and chaotropes in the way they interact with water [2]. Here we present MD simulations of different alkali halogenides (NaCl, CsCl, NaI and CsI) in water focussing on the dynamics of water. We show translational dynamic coefficients D, rotational dynamic reorientation times τ_2 as well as the overall dynamics expressed in $D{\cdot}\tau_2$ in a wide temperature range. We demonstrate that the influence of salts is dominated by the cation - especially in the supercooled region. The overall dynamics $D{\cdot}\tau_2$ is increased by caesium-salts and decreased by sodium-salts compared to water. We discuss the structural cause for this phenomenon.

1.J. Holzmann, R. Ludwig, D. Paschek and A. Geiger, Angew. Chem. Int. Ed. **46**, 8907 (2007).
2. Y . Marcus. Chem. Rev. **109**, 1346 (2009).

The structure of Ag^+, Ca^{2+} and Y^{3+} hydration in confinement in nanometer scale over the temperature range of 298 – 190 K

K. Ito,[a] H. Sugino,[a] K. Yoshida,[a] S. Kittaka[b] and T. Yamaguchi[b]

[a] *Department of Chemistry, Fukuoka University, 814-0180 Fukuoka, Japan*
[b] *Department of Chemistry, Okayama University of Science, 700-0005 Okayama, Japan*

Ion hydration in confinement in nanometer scale play a crucial role in various fields, such as biological systems like ion channel, catalysts in chemical synthesis, and formation of nano wires in nanotechnology. Thus, the structure and properties of ion hydration in confined geometry are highly needed. In this study, we have performed X-ray absorption fine structure (XAFS) measurements to investigate the structure of ion hydration in 1.5 M $AgNO_3$, and 1.0 M $Y(NO_3)_3$ aqueous solutions over the temperature range of 298 $\sim$ 190 K and in an 1.0 M $CaCl_2$ aqueous solution at 298 K in mesoporous silica MCM-41 C10 (pore diameter 21 Å), C14 (28 Å), C18 (37 Å) and cross-linked polymer gel Sephadex G-15. The corresponding bulk samples and Ag foil were also measured. The Ag and Y K-edge XAFS spectra were measured over the temperature range of 298 – 190 K, whereas the Ca K-edge spectra were measured at 298 K at the Photon Factory, KEK. X-ray diffraction (XRD) measurements on the corresponding $AgNO_3$ sample were also made in the same temperature range by using an Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). The differential scanning calorimetry (DSC) data showed that the $AgNO_3$ aqueous solution remain in the liquid state in C10 and G15 in the measured temperature range, whereas three exothermic peaks due to ice formation appeared at 221, 233, and 251 K in C14. The Ag K-edge Fourier Transforms of the 1.5 M $AgNO_3$ aqueous solution confined in C10 have shown the presence of aqua Ag^+as a predominant species throughout the temperature range. The Ag-H_2O distance were in the range of 2.34$\sim$2.38 Å as in bulk. The hydration number of Ag^+ was found to 4.1$\sim$4.6 at temperatures above 233 K and 2.8$\sim$3.6 below 223 K. This crossover in hydration number might be related to the structural transformation of high-density to low-density water at $\sim$223 K in C10. On the other hand, the corresponding Fourier transform for C14 clearly showed that new Ag-Ag interactions due to formation of metallic silver are evolved, accompanied by a drastic decrease in the Ag^+-H_2O peak with lowing temperature. Interestingly, such a reduction of $Ag^+$to Ag in C14 did not take place by radiating Mo$K\alpha$ X-rays to the aqueous sample in C14 at low temperatures. For Ag^+ hydration in G-15, there appeared a predominant aqua Ag^+ together with a small amount of metallic Ag. In the case of Y^{3+} hydration, the Y K-edge data showed the aqua Y^{3+} are formed in all the pores over the temperature range The Y^{3+}-H_2O distance and the hydration number were 2.38∼2.40 Å and 7.5∼8.2, respectively, independent of temperature, which is due probably to the strong electrostatic interactions between the trivalent Y^{3+} and water molecules. The Ca^{2+} K-edge data at 298 K have shown the presence of aqua Ca^{2+} are formed in all the pores. The Ca^{2+}-H_2O distance were 2.37∼2.43 Å, and the hydration number of Ca^{2+} appeared to decrease from 7.2 in C10 to 5.6 in C18 and 4.8 in G15 with an increase in pore volume.

Translational and rotational dynamics of methanol and nickel chloride – methanol solutions: quasi-elastic neutron scattering *vs* molecular dynamics simulations

O.N. Kalugin,[a] D. Duzenko,[a] K. Grivnak[a] and A.K. Adya[b]

[a] *Department of Inorganic Chemistry, V. N. Karazin Kharkiv National University, Svoboda sq., 4, 61077 Kharkiv, Ukraine*
[b] *Division of Biotechnology and Forensic Sciences, School of Contemporary Sciences, University of Abertay Dundee, Bell Street, DD1 1HG Dundee, United Kingdom*

The high-resolution quasi-elastic neutron scattering (QENS) technique has been applied to study the translational and rotational diffusion of methanol protons in pure methanol (CH_3OH and CD_3OH) and in 0.5 and 1.1 molal solutions of $NiCl_2$ in methanol in the temperature range 223 – 323 K. Molecular dynamics (MD) simulations, in conjunction with the present QENS results and our previously published structural results obtained by neutron diffraction isotopic substitution (NDIS) experiments, have been carried out in the NVT ensemble to explore the theoretical models of tarslational and rotational diffusion of methanol in the experimentally investigated systems.

Liquid-gas phase behavior of polydisperse dipolar hard-sphere fluid

Yu. Kalyuzhnyi,[a] S. Hlushak,[a] I. Protsykevytch[a] and P. Cummings[b]

[a] *Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine*
[b] *Vanderbilt University, Nashville, USA*

Liquid-gas phase diagram for the dipolar hard-sphere fluid was calculated theoretically more than thirty five years ago by Rushbrooke et al. [1]. According to these calculations the critical point is located at reduced temperature 0.279 and reduced density 0.159. Systematic computer simulation search for the liquid-gas phase coexistence was initiated only twenty years later [2,3]. These investigations were carried out at a temperatures well beyond predicted theoretically, however no evidence for the phase transition was found. Shortly after there appeared a number of the theoretical papers, in which the arguments were given as to why the existence of the liquid-gas phase transition has to be ruled out. It was suggested that due to the highly anisotropic character of the dipole-dipole interaction the formation of the chains in the 'nose-to-tail' arrangement suppresses the liquid-gas phase transition. However, recent computer simulation [4], carried out for the temperatures lower than those studied earlier, presented the evidence for the phase transition with the critical point located at T=0.15-0.16 and density 0.1.

We present and discuss the liquid-gas phase diagrams of the monodisperse and polydisperse versions of the dipolar hard-sphere fluid, calculated using thermodynamic perturbation theory for associative fluids with center-center type of interaction [5,6].

1. Rushbrooke G.S., Stell G., Hoye J.S., Mol.Phys. **26**, 1199 (1973).
2. Caillol J.-M., J.Chem.Phys. **98**, 9835 (1993).
3. van Leeuwen M.E., Smit B., Phys.Rev.Lett. **71**, 3991 (1993).
4. Camp P.J., Shelley J.C., Patey G.N., Phys.Rev.Lett. **84**, 115 (2000).
5. Y.V.Kalyuzhnyi, G.Stell. Mol.Phys. **78**, 1247 (1993).
6. Y.V.Kalyuzhnyi, I.A.Protsykevytch, P.T.Cummings, EPL **80**, 56002 (2007).

Phase behavior of a simple model of ferocolloidal dispersion

Yu. Kalyuzhnyi and I. Protsykevytch

Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine

We propose a simple model for ferocolloidal dispersion and study its phase behavior. The model consists of a two-component mixture of charged hard spheres with large hard spheres representing polyions and small hard spheres representing counterions. Hard-sphere size and charge ratios are chosen to be 1:10 for the size and from 1:0 up to 1:20 for the charge. In addition to the charge polyions bear magnetic point dipole moment. Theoretical description of the model at hand is carried out using thermodynamic perturbation theory for the central force (TPT-CF) associative potential, developed earlier [1,2,3]. Liquid-gas phase behavior is studied at different values of the charge on the polyion. In the limiting case of zero charge on the polyion concentration of the counterions is zero due to electroneutrality conditions and corresponding phase diagram coincide with the liquid-gas phase diagram for hard-sphere dipolar fluid. For the largest value of the charge ratio studied contribution of the dipole-dipole interaction is negligible and the phase diagram almost coincide with the liquid-gas phase diagram of corresponding charged hard spheres. Upon increasing of the charge ratio from 1:0 to 1:20 critical temperature and density show nonmonotonic behavior. At lower values of the charge on the polyions the critical temperature decreases and critical density slightly increases. Further increase of the charge causes critical temperature to increase and critical density to decrease. At the intermediate values of the charge crossover region, where dipolar regime in the phase behavior is switching to charge regime, has been detected. In this region phase diagram shows two critical points. Behavior of the critical point at lower values of the density is governed by the charge-charge interaction and behavior of the critical point at larger values of the density is governed by the dipole-dipole interaction.

Hydration structure of pyridine molecule studied by neutron diffraction with isotopic substitution method

Y. Kameda, Y. Amo, and A. Usuki

Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, 1-4-12 Kojirakawa, 990-8560 Yamagata, Japan

Neutron diffraction measurements were carried out on 10 mol% pyridine heavy water solutions in order to obtain direct information concerning hydration structure around both nitrogen and hydrogen atoms of the pyridine molecule.

Three sample solutions with different isotopic compositions of $^{14}N/^{15}N$ and H/D within the pyridine molecule, were prepared, namely, I (^{14}N,H-pyridine)0.1(D_2O)0.9, II (^{15}N,H-pyridine)0.1(D_2O)0.9, and III (^{14}N,D-pyridine)0.1(D_2O)0.9. Diffraction measurements were carried out at 298 K using the ISSP diffractometer 4G(GPTAS) installed at the JRR-3M research reactor (Tokai, Japan) with incident neutron wavelength of 1.093(3) Å. Scattered neutrons were collected over the angular range of $3 < 2\theta < 118$ deg. corresponding to $0.3 < Q < 9.8$ 1/Å. Preset time was 180 s for each data point. The first order difference functions [1,2], $\acute{N}(Q)$ and $\acute{H}(Q)$, were derived from the difference between the scattering cross section observed for sample solutions I and II, and III and I, respectively. The intermolecular difference function was obtained by subtracting intramolecular contribution calculated from known molecular structure of pyridine in the gas phase [3]. The least squares fitting analyses were adopted to the observed intermolecular difference functions to determine structure parameters for the nearest neighbor pyridine-D_2O interaction. Intermolecular distribution function GN inter(r) is characterized by a well defined first peak corresponding to the nearest neighbor hydrogen-bonded N(pyridine)… D(D_2O) interaction. The least squares fit of the observed intermolecular difference function revealed that 2.5 water molecules are hydrogen bonded to the N atom of the pyridine molecule with the intermolecular N…D distance of 1.95(1) Å.

Intermolecular distribution function around H atom of the pyridine molecule, GH inter(r) seems rather featureless. Structure parameters for the nearest neighbor H(pyridine)…D_2O interaction was determined by the least squares fitting analysis of intermolecular difference function $\acute{H}$ inter(Q). It is found that the first hydration shell of the H atom of the pyridine molecule involves on the average, 1.2 D_2O molecule with the intermolecular distance of 2.82(1) Å.

1. J.E. Enderby, Chem. Soc. Rev. **24**, 159 (1995).
2. G.W. Neilson, J.E. Enderby, J. Phys. Chem. **100**, 1317 (1996).
3. W. Pyckhout, N. Horemans, C, van Alsenoy, H.J. Geise, J. Mol. Struct. **156**, 315 (1987).

Molecular dynamics simulation of n–butanol from glacial state to supercritical conditions

M. Kiselev,[a] F. Affouard,[b] A. Idrissi[c] and D. Ivlev[a]

[a]*Institute of Solution Chemistry of Russian Academy of Sciences, Academicheskya str., 1, 153045 Ivanovo, Russia*

[b]*Laboratoire de Dynamique et Structure des Matériaux Moléculaires - UMR CNRS 8024 - UFR de Physique - BAT P5 - Université Lille 1, 59655 Villeneuve d'Ascq, France.*

[c]*Laboratoire de Spectroschimie Infrarouge et Raman (UMR CNRS A8516), Centre d'Etudes et de Recherches Lasers et Applications, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq Cedex, France*

Hydrogen bonding (HB) liquids belong to a special class of liquids: due to the strong directional hydrogen bonding, they tend to be locally more organized than ordinary van der Waals liquids. It is particularly well recognized from X–ray experiments that primary alcohols (1–ethanol, 1–propanol, 1–butanol) and substituted aromatics (metatoluidine, metacresol) exhibit a small–Q peak of the structure factor S(Q), the so–called prepeak, below the first sharp diffraction peak in the domain where supra-molecular collective effects are expected. The existence of this peak can thus be interpreted as the presence of some short range HB arrangements of nanometer scale. Both primary alcohols and substituted aromatics molecular liquids can also be supercooled and form a glass.

We present here an investigation of the structural properties of 1–butanol $C_4H_{10}O$ from MD simulations. The N–butanol is one of the interesting example of aliphatic alcohols regarding glass transition properties. This widely studied compound can be supercooled and form a glass at the temperature $T_g = 113K$ (19). It exhibits a slower single exponential Debye–type relaxation. A possibility of polyamorphism was suspected in 1–butanol with the existence of a so–called "glacial phase". The molecular dynamics simulations have been performed for liquid n-butanol in a wide interval of temperatures from 180 K to 700 K. The glacial phase has been found for low temperature region and transition state is found to be around of 220 K. The study of local structure using nearest neighbors distribution functions and hydrogen bonded clusters topology are supposed to show change of structure from ring like at high temperature to be multibranch one during the temperature decrease. There were no indications found for polyamorphism appearance in supercooled butanol.

Spinodal decomposition in nematic liquid crystals filled with nanoparticles.

A.V. Kleshchonok,[a] V.Yu. Reshetnyak[a] and V.A. Tatarenko[b]

[a] *Taras Shevchenko National University of Kyiv , Physics Faculty, 64, Volodymyrs'ka St., 01601 Kyiv, Ukraine*
[b] *G.V. Kurdyumov Institute for Metal Physics, Nat. Acad. Sci. of Ukraine, Kyiv, Ukraine*

In the last decade, much attention has been attracted to Filled Liquid Crystals – highly disperse suspension of impurity particles in nematic liquid carrier. In this report we study the spinodal decomposition of the rigid-sphere-like magnetic-impurity particles on the base of the host nematic liquid crystal. Both the indirect effective interaction between the impurity particles by means of nematic medium and the direct magnetic interaction are considered as being responsible for the formation of (modulated) structures. In the general case, the total interaction between the impurity particles includes several contributions - direct Van der Waals-type interaction (at short distances between the particles) as well as indirect interactions (through both the director-field distortions and the density inhomogeneities). The last one depends on temperature, density of nematic host medium and impurities' concentration. Such effective interaction controls the structure formation and properties of a system. Using continuum-mechanics and statistical-thermodynamics approaches, we analyze kinetics of the system and thermodynamic conditions for necessary the spinodal decomposition. This condition allows to estimate the temperature of the stability loss and to estimate period of the appearing structures. We have estimated diffusive scattering intensity, which gives an opportunity for energy parameters and impurity particle distribution calculation. These systems may find application in the development of integrated-optics devices to control the light-beam propagation (diffraction gratings of an optical range etc.)

Dipole glass state in hydrogen bonded ferro-antiferroelectric mixed compounds

M. Korynevskii[a,b] and V. Solovyan[a]

[a]*Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine*

[b]*Institute of Physics of the University of Szczecin, Wielkopolska 15, 70451 Szczecin, Poland*

The problem of microscopic description of low-temperature phases in hydrogen bonded ferroelectric-antiferroelectric mixed compounds is discussed. Experiment for solid mixtures of hydrogen bonded ferro- and antiferroelectric crystals, namely for RADA ($Rb_{1-n}(NH_4)_nH_2AsO_4$) [1,2] shows the existance at low temperatures (below 60K) both separated ferroelectric and antiferroelectric phases and a specific type of ordered state (with short range correlations), so called dipole glass phase. At sufficiently high temperature (about 100K) only precursors of dipole glass phase can be observed [3].

The suggested theoretical approach is based on the calculation and analysis of single and pair (nearest neighbours) correlation functions of investigated system. Using the self-consistent cluster approximation, these functions are obtained in the second order of replica expansion. Dipole glass order parameter is directly connected with the calculeted correlation functions. It has been theoretically proved that the ordered ferroelectric- and antiferroelectric phases exist only separately. Between percolation barriers ($0.2 < n < 0.5$) for both types of long-range ordering at temperatures below 60K the dipole glass state takes place.

Phase diagram and different thermodynamic characteristics (phase transition temperatures, order parameters, static dielectric susceptibility, heat capacity) for investigated system of RADA type were calculated and tested in a wide temperature and concentration regions [4]. For long ordered phases (ferroelectric and antiferroelectric) they behave in a usual way demonstrating (susceptibility and capacity) an unlimited divergence in a ferroelectric phase transition point. In the dipole glass phase the behaviour of the susceptibility and the capacity is close to their behaviour in a non-ordered medium, but with some peculiarities (jumps) caused by the internal structure of dipole glass phase. The fine characteristics of dipole glass phase has been analyzed and discussed.

1. S. Kim, S. Kwun, Phys. Rev. B **42**, 638 (1990).
2. Z. Trybuła, J. Kaszyński, H. Małuszyńska, Ferroelectrics **316**, 125 (2005).
3. Z. Trybuła, K. Kaszyńska, M.Trybuła, R.R. Levitski, Book of Abstracts of IX Polish-Ukrainian Meeting and XXIX International School on Ferroelectric Physics, Krakow, Poland 24, (2008).
4. M.A. Korynevskii, V.B. Solovyan, Physica B **405**, 2232 (2010).

Maier-Saupe nematogenic system near hard wall

I. Kravtsiv and M. Holovko

Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine

We consider Maier-Saupe nematogenic fluid of point particles confined by hard wall. By solving the spatially inhomogeneous Ornstein-Zernike equation, we obtain analytical expressions for the pair and singlet correlation functions. Based on the singlet correlation function we derive analytically the density profile and the order parameter profile. From the singlet correlation function we calculate and explore the adsorption coefficient and the order parameter excess.

Structural behaviour of associating polymers through dielectric properties using TDR

A.Ch. Kumbharkhane

School of Physical Sciences, Swami Ramanand Teerth Marathwada University, 431606 Nanded, India

Dielectric studies of small polar molecules and polymers in pure liquid state and in nonpolar solutions at microwave frequencies provide information on molecular configuration of a system. The values of complex permittivity for associating polymers have been determined in the frequency range 10 MHz to 30 GHz using Time domain reflectometry (TDR) method. Number of hydrogen bonds between polymer-polymer are estimated from the values of dielectric constant. The binding energies for polymer-polymer have also been estimated.

Generalized relations for partial conductivities in ionic liquids

V. Kuporov and I.M. Mryglod

Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine

More than 50 years ago the ratio of partial ionic conductivities in molten salts, known also as the "universal golden rule", has been obtained by Sundheim [1] from the analysis of available experimental data. This relation states that the ratio of the partial conductivities is equal to the inverse mass ratio of ions. Recently, several theoretical attempts [2] were made to derive this relation rigorously using the equations of motion, the Langevin equation as well as molecular dynamics simulation for a charge-symmetrical model of molten salts. Somewhat later similar approach has been used for pseudo-binary molten salt KClNaCl [3].

In this report it is shown that such relations for partial conductivities directly follow from general properties and rigorous expressions for the generalized (k, ω)-dependent mutual diffusion coefficients of a multicomponent fluid [4]. The generalized versions of "universal golden rule" are derived for ionic charge-asymmetric binary fluid and some partial cases of ternary and four-component ionic mixtures. It is shown that the "universal golden rule" is only one example of more general class of relations for its (k, ω)-dependent counterparts.

1. B.R. Sundheim, J. Phys. Chem. **60**, 1381, (1956).
2.T. Koishi, S. Kawase, S. Tamaki, J. Chem. Phys. **116**, 3018, (2002); T. Koishi, S. Tamaki, J. Chem. Phys. **121**, 333, (2004)
3. S. Matsunaga, T. Koishi and S. Tamaki, AIP Conference Proceedings, **982**, 399-402 (2008).
4.Mryglod I., Bryk T., Kuporov V. In: NATO Science Series II, Eds. D.Henderson, M.Holovko, A.Trokhymchuk, **206**, 109 (2005)

Second virial coefficients of prolate and oblate molecules interacting through nematogenic intermolecular potentials

S. Lago, F. Gámez and Á. Quintanal

Dpt. Sistemas Físicos, Químicos y Naturales, Univ. Pablo de Olavide, Ctra Utrera Km 1, 41013 Seville, Spain

Phase diagram of liquids composed by prolate molecules is well-known when the intermolecular interactions are modelled by different nematogenic (allowing for the appearance of a nematic mesophase) intermolecular potentials. Our results show how it is possible to map the existence domain of a new macroscopic phase (isotropic, nematic, smectic A, smectic B,...) to a single feature of the intermolecular potential. Very recently, we have given some steps to put the liquids formed by oblate molecules at the same foot than those formed by prolate ones1. However, we cannot yet in any case relate simulations or theory results to experiments on real substances because we are lacking of potential parameters corresponding to a determined substance. Here, we present results for second virial coefficients for prolate and oblate models obtained from different nematogenic intermolecular potentials (Gay-Berne, Kihara and Gay-Berne-Kihara2). This is the first step to obtain reliable values for real substances, particularly the depth of the potential well from Boyle's temperature, and we give some sets of intermolecular potential parameters for important molecules showing liquid crystal phases.

1. F. Gámez, S. Lago and P.J. Merkling, Chem.Phys.Lett. (in press)
2. A. Cuetos, B. Martinez-Haya, S. Lago and L.F. Rull, J. Chem. Phys. **122**, 024908(1-8) (2005).

Liquid crystal colloids

B. Lev

Bogolyubov Institute for Theoretical Physics NAS Ukraine,
Metrolohichna 14 b, 03650, Kyiv, Ukraine

The general description of the formation of a r structure in the system of interacting particles in liquid crystal is proposed. The analytical results for possible structures in the usual colloidal systems, systems of particles immersed in a liquid crystal have been presented. Theoretical investigation of colloidal system focused on thermodynamic treatment or on general arguments. The essential point which is neglected any at these arguments is that the colloidal particles are interacting via their direct forces and indirect interaction mediated by free energy of solvent phases. The presentation and develop method for system of interacting particle, several interesting feature have become evident. The method must describe to bservations on similar system with different nature of interaction between particles which formed systems. Based on general approach can estimate formation structure inliquid crystal colloids.

Light-induced effects in cholesteric mixtures containing photoactive nematics: challenges to molecular theories of helical twisting

L. Lisetski,[a] M. Serbina[a] and G. Chilaya[b]

[a] *Institute for Scintillation Materials, STC "Institute for Single Crystals", NAS of Ukraine, 60 Lenin Ave., 61001, Kharkiv, Ukraine*
[b] *Institute of Cybernetics, Tbilisi, Georgia*

Liquid crystal mixtures based on a photoactive nematic host and a photoinactive chiral component (ChC) are known for their unusual behavior under UV irradiation. For mixtures containing azo- and azoxy nematics, the literature data [1-5] on their selective reflection (SR) are analyzed, and our new experimental data are reported for mixtures of nematic ZhK-440 (alkyl- and alkoxy azoxybenzenes) and of cholesterol esters. The ChC concentration was varied within 5-40%, ensuring SR maximum in the visible range and different character of its temperature changes. At small ChC concentrations, UV-induced changes in the helical pitch p could be described using known theoretical models [6], with formation of non-mesogenic and non-chiral cis isomer [7] depressing the isotropic transition temperature roughly proportional to the cis isomer concentration and changing p corresponding to the sign of dp/dT in the initial mixture. However, at larger ChC concentrations p decreased under UV irradiation in all cases, regardless of the dp/dT sign. A theoretical explanation giving a consistent description of all available experimental data is offered, based on a development of our molecular models of helical twisting [6] involving notions of "pseudoscalar liquid crystals" [8]. Hindered rotation of cis-molecules with "up" and "down" directions of their short axes stabilized implies a possibility of the effective chirality of rotationally ordered cis-molecules (a generalization of the "closest packing" principle - a molecule introduced into the cholesteric mesophase tends to assume the orientation corresponding to the sense of the already formed cholesteric helix). Validity of our assumptions was checked by measurements of dielectric permittivity as function of frequency before and after UV irradiation. Characteristic inflections are normally observed at certain frequency corresponding to reorientation of anisometric molecules. The loss of rotation freedom by cis-molecules is reflected in a shift of this inflection towards lower frequencies.

Possibilities of practical applications are discussed, including creation of efficient tunable cholesteric dye lasers reversibly controlled by UV radiation.

1. C. Ruslim, K. Ichimura, J.Phys.Chem.B **104**, 6259 (2000).
2. A. Chanishvili, G. Chilaya e.a., Mol.Cryst.Liq.Cryst. **409**, 209 (2004).
3. G. Chilaya, A. Chanishvili, G. Petriashvili, R. Barberi, R. Bartolino, M.P. DeSanto, M.A. Matranga, P. Collings, Mol.Cryst.Liq.Cryst. **453**, 123 (2006).
4. G.S. Chilaya, Crystallography Reports **51**, S108 (2006).
5. S.V. Serak, N.V. Tabiryan, G. Chilaya e.a., Mol.Cryst.Liq.Cryst. **488**, 42 (2008).
6. G.S. Chilaya, L.N. Lisetski, Mol.Cryst.Liq.Cryst., **140**, 243 (1986).
7. D. Aronzon, E.P. Levy, P.J. Collings, G. Chilaya e.a., Liq.Cryst. **34**, 707 (2007).
8. Ya.B. Zel'dovich, ZhETF (Sov.Phys.-JETP) **67**, 2357 (1974)

Molecular dynamics simulations of the thermocapillary effect at model liquid-liquid interfaces

H. Maier,[a] Ph.A. Bopp[b] and M.J. Hampe[a]

[a] *Thermal Process Engineering, Technical University Darmstadt, Petersenstrasse 30, D-64287 Darmstadt, Germany*

[b] *Department of Chemistry, Université Bordeaux 1, 351 Cours de la Libération, FR-33405 Talence CEDEX, France; currently on sabbatical at Materials Chemistry, Ångström Laboratory, Uppsala University and Max Planck-Institut für Mathematik in den Naturwissenschaften, Leipzig*

Convections occur at spatially variable liquid-fluid interfaces. These convections can play an important role in the transport of particles across such interfaces, e.g. in the solvent extraction processes frequently used in chemical engineering. Model systems of two partially miscible liquids have been studied previously [1,2]. They consist of Argon-like Lennard-Jones particles under equilibrium conditions.

We focus here on similar systems which are additionally subject to a temperature gradient parallel to the interfaces. Vortices are observed along each interface; they always localize close to it and the flow is directed from the hot to the cold region. We observe that they have all the characteristics ascribed to thermocapillary convection, the well-known Marangoni effect [3-5].

1. J.B. Buhn, Ph.A. Bopp, and M.J. Hampe,*A Molecular Dynamics Study of a Liquid-Liquid-Interface: Structure and Dynamics*, Fluid Phase Equilibria, 224 (2004)
2. J.B. Buhn, Ph.A. Bopp, and M.B. Hampe,*Structural and dynamical properties of liquid-liquid interfaces: A systematic molecular dynamics study,* J. Mol. Liq. **125**, 187 (2006)
3. E.H. Weber, *Mikroskopische Beobachtungen sehr gesetzmäßiger Bewegungen, welche die Bildung von Niederschlägen harziger Körper aus Weingeist begleiten,* Berichte über die Verhandlungen der königlich sächsischen Gesellschaft der Wissenschaften, Mathematisch-Physische Classe (1854)
4. J. Thomson, *On certain curious motions observable at the surfaces of wine and other alcoholic liquors*, Phil. Mag. 10, (1855)
5. C. Marangoni, *Über die Ausbreitung eines Tropfens einer Flüssigkeit auf der Oberfläche einer anderen*, Annalen der Physik und Chemie **143**, (1871)

On the problem of a consistent description of kinetic and hydrodynamic processes in dense gases and liquids

B. Markiv, I.P. Omelyan and M.V. Tokarchuk

Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine

For a consistent description of kinetic and hydrodynamic processes in dense gases and liquids the generalized non-Markovian equations for the nonequilibrium one-particle distribution function and potential part of the averaged enthalpy density are obtained. The inner structure of the generalized transport kernels for these equations is established. It is shown that the collision integral of the kinetic equation has the Fokker-Planck form with the generalized friction coefficient in momentum space. It also contains contributions from the generalized diffusion coefficient and dissipative processes connected with the potential part of the enthalpy density.

Acoustic spectra in dissipative hemodynamics taking into account erythrocytes size and shape

V.T. Matskevych,[a] M.Y. Kovalevsky[b] and L.V. Logvinova[b]

[a] *National Science Center "Kharkiv Institute for Physics and Technologies", 1 Akademicheskaya str., 61108 Kharkiv, Ukraine*
[b] *Belgorod State University, 85 Pobedy str., 308015 Belgorod, Russia*

The phenomenological dynamic theory of blood considering the erythrocytes size and shape at macroscopical level is offered. Work is based on Hamiltonian approach which is characterized by the Hamiltonian as the function of the reduced description parameters (hydrodynamic parameters). The question of a choice of the reduced description parameters for the given condensed matter is caused by a number of factors. The part from them is connected with properties of Hamiltonian symmetry, that is shown by presence of the dynamic equations caused by differential conservation laws. The essential factor influencing structure of the reduced description parameters is the erythrocytes form. Blood represents suspension of plasma and erythrocytes. We consider plasma as the condensed matter with infinitesimal structural elements for which Navier-Stoks equations are fair. Presence of erythrocytes leads to essential difference of hydrodynamics of all condensed matter and demands updating of the dynamic theory as their sizes and shape already cannot be neglected. It is especially important to consider it at blood movement on blood vessels of the small sizes when the characteristic sizes of vessels are comparable with the characteristic sizes of erythrocytes. Therefore for the hydrodynamic description of blood, except densities of momentum, entropy and number of particles, the additional dynamic parameter - erythrocyte diameter, which is considered as disc-like structural element, is entered. Introduction of this hydrodynamic parameter is like introduction of additional hydrodynamic parameters in uniaxial and biaxial nematic liquid crystals considering conformational degrees of freedom. For a full set of the reduced description parameters the closed algebra of Poisson brackets is received. The thermodynamics of the studied condensed matter is constructed. On the basis of the approach developed by us the equations of ideal hemodynamics taking into account erythrocyte diameter are formulated. Flux densities of additive integrals of motion are presented in terms of thermodynamic potential. The acoustic spectrum of collective excitations is found and it is shown, that the account of the erythrocytes size and shape leads to increase in speed of a sound that is in the accordance with the experimental data received earlier. The conclusion of the equations of hemodynamics taking into account dissipation processes is given. It is found out, that the account of the erythrocytes size and shape leads to occurrence of two new kinetic coefficients of infiltration, besides coefficient of heat conductivity and two coefficients of viscosity. Acoustic spectra of collective excitations are found and the structure of factors of attenuation of sounds is found out.

Green functions and polarization features of acoustic waves in uniaxial and biaxial nematic liquid crystals

V.T. Matskevych,[a] M.Y. Kovalevsky[b] and L.V. Logvinova[b]

[a]*National Science Center "Kharkiv Institute for Physics and Technologies", 1 Akademicheskaya str., 61108 Kharkiv, Ukraine*
[b]*Belgorod State University, 85 Pobedy str., 308015 Belgorod, Russia*

In the report the results of investigation of uniaxial (with rod-like and disc-like molecules) and biaxial (with ellipsoidal and discoidal molecules) nematic liquid crystals are presented. The work is based on Hamiltonian approach which is characterized by establishment of the set of reduced description parameters, macroscopically full specifying investigated physical systems, Hamiltonian as the function of these parameters and obvious kind of Poisson brackets for the whole set of reduced description parameters. For the adequate description of nematic liquid crystals, besides densities of momentum, entropy and number of particles, additional dynamic parameters are introduced. They are the unit vector of spatial anisotropy (the director) and the conformational degree of freedom (rod length or disc diameter) in the case of uniaxial nematics and two unit vectors of spatial anisotropy and three conformational degrees of freedom (lengths of molecule axes and an angle between them) in the case of biaxial nematics. On the basis of the approach, developed by as, the nonlinear dynamic equations taking into account molecules size and shape are derived. The densities of flows of additive integrals of motion are presented in terms of thermodynamic potential. The acoustic spectra of collective excitations for investigated condensed matters are found out and it is shown, that taking into account molecules size and shape leads to the appearance of two sounds in uniaxial nematics and to the appearance of one up to three sounds in biaxial nematics already in adiabatic approximation. The polarization features of acoustic waves in considered liquid crystals are investigated. The nonlinear dynamic equations for the considered liquid crystals with regard to the anisotropy axes and conformational parameters in external alternating field are derived and the kind of sources in the dynamic equations corresponding to this field is determined. The analytic expressions for low-frequency asymptotics of Green functions are obtained. Asymptotics of Green functions in the region of small wave vectors and frequencies essentially depend on the character of spatial anisotropy of considered condensed matter.

Structure and thermodynamics of simple fluids under extreme conditions

R. Melnyk,[a] I. Nezbeda[b,c] and A. Trokhymchuk[a,d]

[a] *Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine*

[b] *Faculty of Science, J. E. Purkinje University, 400 96 Ústí nad Labem, Czech Republic*

[c] *E. Hála Laboratory of Thermodynamics, Institute of Chemical Process Fundamentals, Academy of Sciences, 165 02 Prague 6 – Suchdol, Czech Republic*

[d] *Department of Chemistry and Biochemistry, Brigham Young University Provo, UT 84602, USA*

Simple fluids, i.e., the fluids whose molecules interact via a spherically symmetric potential, $u(r)$, are most commonly modeled as Lennard-Jones (LJ) fluids. A huge number of simulation data on the equilibrium properties, both thermodynamic and structural, of the LJ fluids have therefore been generated over several last decades (Ref. [1] and references therein).

Although the LJ potential represents only a crude approximation to real intermolecular interactions, when applied to real fluids it performs reasonably well at subcritical and slightly supercritical conditions. However, for quite obvious reasons it fails at high temperatures/pressures: It has been well established that at very high pressures the repulsive interaction between the molecules is much softer than that given by the LJ potential and the models with softer repulsions such as the EXP6 potential, provide much more faithful description of the intermolecular interactions at these conditions [2].

In present work an augmented van der Waals (vdW) theory of the simple fluids modeled by the EXP6 potential is developed. The theory is based on a two Yukawas (2Y) representation for the reference system that includes complete repulsion of the EXP6 model, reproduces exactly the depth and position of the EXP6 potential minimum and includes the short-range part of the attraction. Using molecular simulations it is shown that vdW/2Y theory is able to estimate accurately both the thermodynamic and structural properties of the EXP6 fluids in the wide range of the temperature and pressure conditions that were considered.

1. J. Kolafa and I. Nezbeda, Fluid Phase Equil. **100**, 1 (1994)
2. M. Ross and F. H. Ree, J. Chem. Phys. **73**, 6146 (1980).

X-ray diffraction studies of liquid-solid composites.

S. Mudry, I. Shtablavyi, Yu. Kulyk and R. Serkiz

Ivan Franko Lviv National University, 8 Kyrylo and Mephodii str.,
79005 Lviv, Ukraine

Most known composite materials on the base of liquid matrix are ferrocolloidal suspensions which are already used during last three decades. Update growth interest to such materials is motivated by new areas of application and fundamental interest to them as nanocomposite systems. In order to understand the mechanism of structure and properties formation and their transformation with time and temperature the X-ray diffraction studies of Al(Cu, Ni) powder mixed with liquid In, Ga, and Bi have been carried out. Analysis of structure factors, obtained from experimental intensity curves shown that liquid matrix transforms their atomic distribution due to presence of solid nanoclusters.

Increase of solid cluster content promotes the crystallization process which results in formation of nanocomposite alloy with improved properties. Dependence of structure factor principal peak position on duration of alloying allowed us to clarify the diffusion mechanism at the solid cluster-liquid matrix interphase.

Selektive coatings via the method of sol-gel technology for solar collectors

R Musiy[a] and S. Khayrnasov[b]

[a] *Department Of Physical Chemistry of Combustible Minerals L.M. Lytvynenko Institute of Physical-Organic Chemistry and Coal Chemistry NAS of Ukraine, 3a Naukova Str., 79053 Lviv, Ukraine*

[b] *National Technical University of Ukraine "Kyiv Polytechnic Institute", Ukraine*

The demand for low cost, efficient and environmental friendly energy resources is increasing rapidly. At using the gelious system with the effective solar collectors the solar energy becomes free–cost, effective and safety for environment, does not give the discharges of CO_2 into atmosphere. Selectively absorbing materials need the high absorption into the solar range of spectrum together with low thermal radiating ability in near and far infrared range of spectrum. We are proposed to develop the own selective coating by new type from the available in our country materials. In proposed development it is planned to be used the carbon—silica composite obtained via sol—gel technology. It was developed some types of the spectral—selective coatings from the carbonic nanoparticles dispersed into dielectric matrix SiO_2 and NiO for the solar collectors. It was used the sol—gel method based on tetraethoxysilane, methyltrimethoxysilane and different organic and inorganic additives. The temperature, the concentration, the viscosity, the thickness and others parameters have been controlled. The coatings were washed ashore upon the aluminum and copper samples with the sizes 40x40 mm by "spin coating" method with following drying under different temperatures.

The main aim of our investigations was to determine the most effective type of the selective coating based on different variants of their obtaining. In order to carry out the investigations of different type of selective coatings more efficiently it was developed the measuring bench in NTUU "KPI" . The following samples have been used: the coatings obtained via the sol—gel method; the aluminum alloy AD31 with the coated black anode; the selective coating by SunSelect firm (Germany). This sample was obtained by the vacuum sputtering technology and has a wide much application abroad under the solar collector performance. The contact pickups (namely, devices MBA8 and TRM202 by

"OVEN" firm production, Russia) have been used for the measurement of the temperature on the experimental samples and for the environmental temperature measuring (tenv., 0C). The measurement of the solar heat flow density (E, W/m^2) has been done using the following devices: TRM202 by "OVEN" firm production (Russia) and CMP3 ("Kipp & Zonen" firm, Holland), which provide the general error of the measurements not more than 10 %.

On a basis of the experimental investigations it was developed the some types of selective coatings for the solar collectors prepared via the sol—gel method. It has been done their starting comparative investigations with the sample by "SunSElect" firm (Germany), which confirmed that some of our samples are not fived way before the German analogues.

The approach for large scale simulation on the solution confining flucutuation

M. Nakada[a] and K. Maruyama[b]

[a] *Graduate School of Science and Technology, Niigata University, 8050, Ikarashi 2-no-cho, Nishi-ku, 950-2181 Niigata, Japan*
[b] *Faculty of Science, Niigata University*

We are trying the large scale Monte Carlo simulation on 1-propanol aqueous solution confining large concentration-concentration fluctuation at mesoscopic level, which was observed by small angle neutron scattering measurements. In general, the simulation for such solution requires a large simulation cell, and efficient sampling algorithm. In order to overcome these problems, we constructed the quasi-lattice liquid model. As a trial, we attempted to this model for liquid SPC/E water. The simulated pair distribution function agreed with published data.

In further more, we formulated the isotropic molecule approximation. Due to this approximation we found that the correlation longer than 2nd peak of pair distribution function depended on the orientation correlation shorter than 1st peak.

When feasible, we will simulate on 1-propanol aqueous solutions with above algorithms in order to create the large concentration-concentration fluctuation structural model in the solutions.

Frequency dependence of velosity and absorption of longitudinal, shear and thermal waves in the electrolyte solutions

S. Odinaev,[a] D. Akdodov[b] and N. Sharifov[a]

[a] *Osimi M.S. Tajik Technical University, Rajabov's av.10., 734042 Dushanbe, Tajikistan*

[b] *Tajik National University,, Rudaki av. 17., 734025 Dushanbe, Tajikistan*

The measurements of distribution velocity and absorption coefficient of sound and thermal waves in electrolyte solutions provide an information on nonequilibrium structure, physical and chemical processes taking place in them. It is of interest the study of thermophysical parameters and transport coefficients of solutions in a wide interval of changes of thermodynamic functions of a state and frequency of external influence. In particular, the dynamic modules of elasticity, viscosity coefficients and thermal conductivity define the frequency dispersion of velocity and absorption of longitudinal, shear and thermal waves in liquids and electrolyte solutions. The restoration of equilibrium structure of solutions that is caused by interstructural units is realized at presence of internal relaxation processes, in particular, structural relaxation. These relaxations processes contribute to the transport coefficients as to the acoustic parameters of electrolyte solutions.

For the study of a nature of relaxations processes in electrolyte solutions it can be used both measurement of absorption and velocity of longitudinal and shear waves [1,2]. Measurements of absorption coefficient is most effective, as frequency dispersion of velocity of a sound is too small for the study of such relaxations effects, except of concentrated electrolyte solutions. According to [2] the absorption of a sound in electrolyte solutions usually is lower than in majority of organic liquids. Consequently, the measurement of absorption with sufficient accuracy at low frequencies in electrolyte solutions is much more difficult than in organic liquids. However, an investigation of relaxations processes, in particular structural and chemical relaxation in electrolyte solutions usually it is not required of absolute value of absorption coefficient but the surplus absorption of a solution with respect to the solvent. Therefore the theoretical investigations of acoustic properties of electrolyte solutions is of interest, due to the contribution of relaxations processes, in particular, structural relaxation, that are the purpose of the present work.

As initial equations we shall use the equations of the generalized hydrodynamics for electrolyte solutions that were obtained on a basis of kinetic equations for one- and two-particles distribution functions [3], that contain relaxation flows of impulse and heat. Lasts contain the contributions of translational and structural relaxations. These systems of the equations have the same view, as the macroscopic laws of preservation of mass, impulse and energy. However, the transport coefficients are in the system of equation of the generalized hydrodynamics are the functions of spatial and time scales, Fourier transformation of that results to frequency dependences of these coefficients and also velocity dispersion and absorption of longitudinal, shear and thermal waves in electrolyte solutions.

Solving the system of the equations of the generalized hydrodynamics with respect of a vector of displacement $\vec{u}(\nu, \vec{k})$ we shall receive dispersion ratio for the shear, longitudinal and thermal waves and also frequency-dependent expressions of velocity $c(v)$and absorption coefficient $\alpha(\nu)$ of these waves in electrolyte solutions. Asymptotical behaviors of velocity c and the absorption on length of a wave $\alpha\lambda$ at low frequencies is proportionally to $\nu^{3/2}$ and completely coincide with results of the theory nonlocal-diffusion [4]. At high frequencies these acoustic parameters remain constant with growth of frequency and coincide with results of the general relaxation theory [1].

The received system of the equations of the generalized hydrodynamics allow also to obtain the analytical expressions for velocity and coefficient of absorption of thermal waves of electrolyte solutions, that coincide with results of [5] received in the case of independent flows.

At an optimal choice of statistical model of a solution, potential of interactions and radial function of distribution, the numerical calculation of velocity and absorption of acoustic and thermal waves for water solution of NaCl are carried out in a wide range of frequency. The results were compared with the theoretical and experimental literary data and are in the satisfactory consent with them.

1. Mihailov I.G., Solovyov V.A., Syrnikov Y.P. Bases of molecular acoustics: “Nauka”, 1964, 514
2. Physical acoustics, v. 2., part A. edited by U.Mezona. M: "World", 1968, 487
3. Odinaev S., Dodarbekov A., Report of the Akad. Science of Republic Tajikistan, **42**, 9, 68 (1999).
4. Isaakovich M.A., Chaban I.A., JETPh, **50**, 5, 1343 (1966).
5. Odinaev S., Akdodov D., Report of the Akad. Science of Republic Tajikistan, **49**, 10, 915 (2006).

Investigation of frequency dispersion of the viscosity coefficients of simple liquids depending on the thermodynamic parameters of a state

S. Odinaev, A. Abdurasulov and Kh. Mirzoaminov

Osimi M.S. Tajik Technical University, Rajabov's av.10., 734042 Dushanbe, Tajikistan

The nonequilibrium processes and changes of structure of liquids are accompanied by presence of the dissipation phenomena in them. Last are described by means of transport coefficients and corresponding elasticity modules by taking into consideration the contributions of internal relaxations processes, in particular, structural relaxation. Most well experimentally investigated both static and dynamic transport coefficients of liquids , in particular, the diffusion D, shear viscosity η_s, thermal λ and electrical conductivity σ and also velocity c and absorption α of sound waves coefficients are. However coefficient of bulk viscosity η_v and modules of elasticity of liquids by direct experimental measurements cannot be determined. They are determined by an indirect methods with the help of measurement of other coefficients or physical parameters. For example, coefficient of bulk viscosity is determined by measurement of surplus absorption of sound waves in liquids [1-3]. Accuracy of definition of η_v in liquids due to errors in estimation of absorption of a sound α, density ρ, velocity of a sound c, thermal capacity's c_p and c_v, shear viscosity η_s and thermal conductivity λ it is not enough for acquisition of precise empirical laws and their comparison to the theory.

It is shown [2] that at frequency ν=5·10^6 Hz on a line of saturation at T≥140 K at Ar, T≥200 K at Kr and T≥270K at Xe there exists the dependence α/ν^2 from frequency ν, i.e. the frequency dispersion of absorption of a sound is caused by the contributions of kinetics coefficients of viscosity η_s and η_v, the investigation of that has the large interest. There also analyses was made and attempts of definition of interrelation between characteristic of relaxations time of bulk τ_v and shear $\tau_s$viscosity with a time constant for the equilibrium distributions in configurational τ_q and impulse τ_p parts of phase space. The high-frequency decompositions of autocorrelators of a flow of a impulse in Green – Kubo expressions for coefficients of viscosity give limiting values of bulk K_0, K_∞ and shear μ_∞ modules of elasticity by means of which the times τ_v and τ_s are determined. The times τ_q and τ_p in case of independent flows are determined as times of attenuation of autocorrelators of average force and velocity accordingly, in which the coefficient of internal friction β of a liquid is contained. Definition of β on dependence of parameters of the condition remains open till the present time. The purpose of the present work is the determination of coefficients β, η_s and η_v investigation in a wide interval of change of density ρ and temperature T and also of frequency dispersions $\eta_S(\nu)$, $\eta_V(\nu)$ at an optimal choice of the potential of intermolecular interaction $\Phi(|\vec{r}|)$ and radial function of distribution $g(|\vec{r}|)$.

On the basis of an optimal choice of two modified Lennard-Johns potentials , Bukingeime potential and radial distribution function [4] the coefficients of friction β, times τ, τ_0 and coefficient of shear viscosity η_s for liquid Ar in a wide interval of change ρ and T are calculated . The analysis of numerical calculations of shear viscosity η_s shows, that the most satisfactory consent of theoretical and experimental results were obtained with the help of modified potential of intermolecular interaction for real liquids offered by J.S. Rowlinson, where an attraction potential was taken almost twice less than the factor r^{-6} in Lennard-Johns potential. Accepting this model as a basis, the dynamic viscosity coefficients $\eta_s(\nu)$ and $\eta_v(\nu)$ in a wide interval of change ρ and T are investigated.

As initial coefficients we shall use the expressions for $\eta_s(\nu)$ and $\eta_v(\nu)$ received by us on th basis of kinetics equations for one- and two-partial distribution function in by use of spatial correlation of density in configuration space. At the realization of numerical calculations the ρ and T values are taken for the liquids Ar, Kr and Xe from [2,3] as in far and near to the triple point. The received results of theoretical calculations of $\eta_s(\nu)$, $\eta_v(\nu)$ and $\eta_v(\nu)/\eta_s(\nu)$ for liquid Ar, Kr and Xe are given as the tables and diagrams, and also compared with the existing theoretical and experimental literary data, which are in the quantitative consent. The good consent is observed at low T and high ρ of the simple liquids. The obtained theoretical results show that the regions of frequency dispersion of $\eta_s(\nu)$, $\eta_v(\nu)$ takes place $\nu \approx 10^6 \div 10^{12}$ Hz takes place, i.e. a wide range of frequencies is caused by the presence of the contribution of structural relaxation. According to the general relaxation theory this area equal approximately to 10^2 Hz and the law of attenuation of these coefficients is $\sim \nu^{-2}$ but in our case $\sim \nu^{-1}$ is. Hence, on the basis of this model it is possible to investigate viscoelasticity and acoustic properties of simple liquids in a wide interval of change of parameters of the state and near to the triple point.

1. Naugle D.G., Lunsford J.H., Singer J.R.-J.Chem. Phys. **45**,12, 4669 (1966).
2. Mikhaylenko S.A., Dudar B.G., Shmidt V.A., Physics of low temperatures, **1**, 2, 224 (1975)
3. Malbrunot P., Boyer F., Charles E., Phys. Rev. A, **27**, 3, 1523 (1993).
4. Odinaev S., Mirzoaminov Kh., Report of the Akad. Science of Republic Tajikistan, 52, 11 and 12 (2009).

Processed algorithms for multiple time scale molecular dynamics

I.P. Omelyan

Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine

The coexistence of dynamical processes with significantly different time scales is a characteristic feature of many systems in physics, chemistry, and biology. One of the most powerful approach to study such complicated systems is the method of molecular dynamics (MD). The increase of efficiency of MD algorithms remains an important problem in view of the restricted capabilities of even modern supercomputers. A lot of multiple time stepping (MTS) schemes have been derived over the past decades to speed up the MD calculations. However, due to the resonance instability, the size of the time step in the usual MTS integrators is limited by the highest frequency mode presented in the system. In the improved MTS versions the instability can be postponed to larger time steps by changing the original forces or adding friction and random terms to the equations of motion. But this implies departure from the true Hamiltonian dynamics within the microcanonical ensemble or means passage to canonical simulations at a constant temperature, where the total energy is no longer conserved.

In our investigation we propose a new idea for overcoming the instabilities of the MTS algorithms. It is based on the introduction of so-called virtual forces to compensate uncertainties caused by the approximate character of the numerical integration. This is aimed at the fulfilling of the energy constraint imposed on the equations of motion. The virtual forces are negligible small with respect to the original ones and contribute to the dynamics by the term which is considerably smaller than the local error of the initial MTS algorithm. Despite such a smallness they lead to an amazing stabilizing effect on the produced phase trajectory. It is shown that now the long-term stability of the microcanonical MD simulations can be reached at much larger time steps than those of the standard MTS schemes. Moreover, the accuracy of the total energy conservation can be increased noticeably by combining the proposed approach with the phase-space transformation technique. The high efficiency of the resulting algorithms obtained were confirmed in actual MD simulations of many-body systems within models of simple fluid and water.

1. I. P. Omelyan, J. Chem. Phys. **127**, 044102 (2007).
2. I. P. Omelyan, Phys. Rev. E **78**, 026702 (2008).
3.I. P. Omelyan, J. Chem. Phys. **131**, 104101 (2009).

Phase equilibria in size- and charge-asymmetric primitive models of ionic fluids

O.V. Patsahan and T.M. Patsahan

Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine

We study the phase diagrams of $z:1$ size-asymmetric primitive models (PMs) using a theory that exploits the method of collective variables. Based on the explicit expression for the relevant chemical potential (conjugate to the order parameter) which includes the correlation effects up to the third order we consider some particular cases of asymmetric PMs (1:1, 2:1 and 3:1 systems). Coexistence curves and critical parameters are calculated as functions of size ratio $\lambda = \sigma_+/\sigma_-$ Similar to simulations, our theory predicts the reduction of coexistence regions as well as a decrease of critical parameters T_c^* and ρ_c^* with an increase of size asymmetry.

A hard sphere fluid in one- and two- dimensional disordered porous media

T. Patsahan,[a] M. Holovko[a] and W. Dong[b]

[a] *Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine*
[b] *Laboratoire de Chimie, UMR 5182, CNRS, Ecole Normale Supérieure de Lyon, 46, Allée d'Italie, 69364 Lyon Cedex 07, France*

Despite the problem of fluids confined in disordered porous media has being studied extensively for the last two decades the first analytical results for such systems appeared very recently. Last year Holovko and Dong [1] proposed an extension of the scaled particle theory being able to describe a hard sphere fluid in hard sphere or overlapping hard sphere matrices. Later this approach has been improved and an excellent agreement with computer simulations has been reached [2]. Based on the recent achievements in this field a generalization of the given theory to the one- and two-dimensional cases is formulated. In the present study we verify this generalization making a comparison between the results found from analytical expressions [3] and those obtained from grand-canonical Monte Carlo simulations. For this purpose the chemical potential versus a fluid density is calculated in the matrices of different porosities and morphologies.

1. M. Holovko, W. Dong, J. Phys. Chem. B **113**, 6360; 16091 (2009).
2. T. Patsahan, M. Holovko, W. Dong, J. Chem. Phys. (2010) (submitted).
3. M. Holovko, W. Dong, V. Shmatolokha, Condens. Matter Phys. **13**, 23607 (2010).

Conformational vibrations of ion lattice in DNA solution

S.M Perepelytsya and S.N. Volkov

Bogolyubov Institute for Theoretical Physics, NAS of Ukraine,
Metrolohichna St. 14 b, 03680 Kyiv, Ukraine

The backbone of DNA double helix consists of the negatively charged phosphate groups that are neutralized by the counterions (the ions of alkaly metals). In solid state the counterions are tethered to the phosphate groups, but in water solutions they move around the double helix forming the ion-hydrate cloud. Under the high concentration of counterions in the solution the number of neutralized phosphate groups increases, and due to the regularity of the DNA backbone the structure of counterions with the phosphate groups should be also regular. In the present work the structure of counterions and phosphate groups is considered as an ion-phosphate lattice, resembling to the lattice of ion crystal. This lattice should be characterized by specific vibrations of counterions with respect to the phosphate groups (ion-phosphate vibrations). The goal of the presentation is to determine the conformational vibrations of DNA with different metal ions, to describe the specific modes of DNA ion-phosphate lattice, and to understand the role of counterions in the double helix structure formation. The conformational vibrations of DNA with counterions in different positions with respect to phosphate groups of the double helix have been studied within the framework of the developed phenomenological approach. Two cases of counterion localization have been considered: the neutralization of one phosphate group by one counterion (single-strand neutralization) and the neutralization of two phosphate groups of different strands of the double helix by one counterion (cross-strand neutralization). The calculated frequencies and amplitudes of vibrations for DNA with Na+, Cs+, and hydrated Mg2+ counterions have showed that Na+ counterions in single-stranded positions do not influence internal dynamics of the double helix, while Cs+ and Mg2+ counterions make move all structural elements of the nucleotide pair. The frequency of backbone vibrations drastically increases due to the influence of counterion in cross-stranded position. The calculated Raman spectra of DNA double helix with counterions is in the low-frequency range (¡200cm-1). The presence of Cs+ and Mg2+ in single-stranded position is characterized by the intensive modes of ion-phosphate vibrations. In the case of cross-strand neutralization the spectra of Na- and

Cs-DNA consist from the intensive mode of backbone vibrations, as well as of modes of H-bond stretching and intranucleoside vibrations, while in the spectra of Mg-DNA these modes form one united band. The developed approach allow to determine the position of counterions with respect to phosphate groups of DNA double helix by the manifestations of the ion-phosphate vibrations in DNA low-frequency spectra.

Optical Kerr effect measurements of methanol and acetone mixtures

K. Polok and W. Gadomski

Laboratory of Physicochemistry of Dielectrics and Magnetics,
Department of Chemistry, University of Warsaw, ul. Żwirki i Wigury
101, 02-089 Warsaw, Poland

In our work we extend the results from our previous work, where we have analyzed the long time reorientational response in Kerr signal for methanol, acetone and their mixtures. Here we present the full analysis of acetone Kerr signal with use of several techniques. Our methods include molecular dynamics simulations and calculations based on the molecular crystal structure. The presented data contains not only the time domain signal but also the low frequency Raman spectra that can be recovered from it. Additionally we present our attempt to apply those methods for mixtures containing methanol, acetone, ethanol and water. Our calculations were run in parallel with measurements in order to compare the theory with experimental results.

Helium - no molecular liquid but an interesting solvent

M. Probst and A. Mauracher

Innsbruck University, Technikerstrasse 25, 6020 Innsbruck, Austria

In this presentation we discuss various properties of molecular systems solvated in liquid He: (a) the solvation of molecular ions [1] and cluster ions [2] (b) molecules interacting with H_2O clusters [1] and discuss the differences caused by a temperature of practically 0K, compared to more usual conditions and solvents. Liquid He is a poor solvent but with recently developed [3] electrospray techniques practically all molecules or ions can be dissolved and also ionized.

1. S. Denifl, F. Zappa, I. Máhr, A. Mauracher, M. Probst, J. Urban, P. Mach, A. Bacher, D.K. Bohme, O. Echt, T.D. Märk, P. Scheier Angew. Chem. Int. Ed. **48**, 8940 (2009); J. Chem. Phys. **132**, 234307 (2010).
2. S. Jaksch, A. Mauracher, A. Bacher, S. Denifl, F. Ferreira da Silva, H. Schöbel, O. Echt, T.D. Märk, M. Probst, D.K. Bohme, and P. Scheier J. Chem. Phys. **129**, 224306 (2008).
3. J.P. Toennies, A.F. Vilesov, Angew. Chem. **116**, 2674 (2004); Angew. Chem. Int. Ed. **43**, 2622 (2004).

Solubility in water of chlorophenols and chloroanisoles as an example of hydrophilicity and hydrophobicity with practical consequences

D. Segura,[a] S. Lago,[a] S. López-Vidal,[b] L. Arce[c] and Á. Quintanal[a]
[a] *Dpt. Sistemas Físicos, Químicos y Naturales, Univ. Pablo de Olavide, Ctra Utrera Km 1, 41013 Seville, Spain*
[b] *Dpt.,Univ. San Pablo-CEU,Madrid, Spain*
[b] *Dpt. Química Analítica, Univ.Córdoba, Córdoba, Spain*

Chloroanisoles (CA) are important chemicals present in cork, the best traditional material to produce wine bottle stoppers. They are responsible for the mouldy or muddy taste of wine when their concentration overrates a threshold value (40ppb). A useful method to eliminate CAs (mainly 2,4,6-trichloroanisole and pentachloroanisole) from rough cork (the bark of a tree called Quercus suber) consists in washing the cork with boiling water. CAs are nearly apolar compounds and their solubility in water is quite limited but we have shown that the presence of these compounds in water at the very low concentrations of interest can be determined using gas chromatography with a mass spectrometer as detector (GC/MS) to analyze the cork washing waste water [1]. An added problem is that the cork always contains chlorophenols (CF) that are precursors of CAs in some circumstances. These compounds are polar and can also be removed from cork using boiling water. That is an important point from a practical point of view because CFs do not give bad taste to the wine but they can be transformed in CAs by the fungus Armillaria Mellea present in some trees. A possible solution to this problem comes from the analysis of the variation of solubility of CAs and CFs with temperature. This variation is markedly different for both types of compounds. In the case of CFs, solubility increases with temperature as in many other (hydrophilic) compounds. In the case of chloroanisoles solubility increases with temperature up to 65°C about and then decreases, a typical behaviour of a hydrophobic substance. Assuming that a simple proportionality can be established between the area of chromatographic peaks and Gibbs free energy, we present here results for relative enthalpies and entropies of both the families of compounds showing the differences between hydrophilic and hydrophobic compounds. These differences allow us to improve the method of extraction of chloroanisoles using hot water.

1. S. López-Vidal, L. Arce and S. Lago in "Food proteins and colloids of industrial interest," Eds.J.Girón-Calle et al, Universidad de Sevilla Press, ISBN:84-472-0884-2 (2005).

Self-assembly in liquid crystalline suspensions 5CB filled by aluminsilicate discs

Y. Shaydyuk, G. Puchkovska, A. Goncharuk and N. Lebovka

Institute of Physics of the National Academy of Sciences of Ukraine,
46, Nauki ave., 03039 Kyiv, Ukraine

The liquid crystals (LC) filled by nanoparticles with highly anisotropic shape (wires, tubes, rods, discs, or prisms) attracted great attention both from fundamental and practical points of view. These systems combine different unique anisotropic interactions from molecu-lar to micron-size scales. The nature of mesogenic transition (Onsager transition) for nanopar-ticles in anisotropic solvents is still unclear. The self-assembling in LC filled by nanoparticles often results in anisotropy of mechanical, electric and optical properties. Their mesophases can often be aligned by the action of an electric or magnetic field, so these materials are promising for manufacture of sensors and biosensors, shielding screens, memory and display nanode-vices.

This work studies the mesogen suspensions on the base of 5BC and lamellar alumino-silicates: montmorillonite (MMT) and its organophilic form (OMMT). MMT and OMMT are in the form of 1 nm thick disk-like particles. Usually they tend towards formation of nematic gels; however, their gelation mechanism has not been fully elucidated yet even in isotropic solvents. The viscosity, electrical conductivity and microstructure of nanodisc suspensions (0-5 % wt) in LC at different temperatures $(25 - 40^\circ\ )$ were investigated. The microscopic and electrical conductivity studies revealed noticeable differences in aggregation behavior of MMT and OMMT suspensions and noticeable exfoliation of OMMT nanoplates. The thixo-tropic behavior was observed in suspensions filled by both MMT and OMMT. The concentra-tion dependence in the isotropic phase followed the Einstein viscosity law. However, an anomalous viscous behavior was observed in nematic phase of suspension filled by OMMT. A model is proposed for description of the structure formation and anomalous viscosity beha-vior.

Dynamics of protic and aprotic ionic liquids: what distinguishes ethylammonium nitrate from imidazolium ils?

T. Sonnleitner,[a] J. Hunger,[a] A. Ortner,[b] M. Walther,[b] D. Turton,[c]
K. Wynne[c] and R. Buchner[a]

[a] *Universität Regensburg, Institut für Physikalische und Theoretische Chemie, Regensburg, Germany*
[a] *Albert-Ludwigs-Universität Freiburg, Freiburger Materialforschungszentrum, Freiburg, Germany.*
[a] *Strathclyde University, Dept. of Physics, SUPA, Glasgow, UK*

Studies of the dynamics of ionic liquids (ILs) have generally focused on aprotic ionic liquids, especially imidazolium salts[1]. A combined broad-band (200 MHz to 10 THz) study of the dielectric relaxation (DR) and the time-resolved optical Kerr effect (OKE) spectra revealed complex dynamical behaviour ranging from intermolecular vibrations and librations in the THz region via cation reorientation through large-angle jumps occurring at 5-10 GHz to a slow cooperative motion indicative of large aggregates which dominates the OKE response below 1 GHz[2].

For various practical reasons, protic ILs like the archetypal ethylammonium nitrate (EAN) have come into the focus of interest recently[3]. Knowledge of the dynamics of this class of ILs is very limited so far but expected to be complicated due to the additional possibility of fast proton transfer. In this contribution we present first results of a joint DR and OKE study of EAN in the 200 MHz to 10 THz region. In addition to these broad-band data recorded at 25°C, dielectric spectra covering 0.1-90 GHz were determined as a function of temperature in the range of $5-65$°C. From these data the activation energy for the relaxation dominating this spectral region was extracted. A possible assignment of the resolved modes will be presented and the results compared with those for imidazolium ILs.

1. H. Weingärtner, Angew. Chem. Int. Ed. **47**, 654 (2008).
2. D. Turton, J. Hunger, A. Stoppa, G. Hefter, A. Thoman, M. Walther, R. Buchner and K. Wynne, J. Am. Chem. Soc. **131**, 11140 (2009).
3. T.L. Greaves and C.J. Drummond, Chem. Rev. **108**, 208 (2008).

Miicrosolvation of the oh radidal in high temperature water - molecular dynamics study

J. Szala-Bilnik and D. Świątła-Wójcik

Institute of Applied Radiation Chemistry, Technical University of Łódź, Zeromskiego str.116, 90-924 Łódź, Poland

The pressurized high-temperature water is widely used to safely destroy hazardous materials in the wet oxidation and supercritical water oxidation (SCWO) technologies. Despite significant research activity, still very little is known about the behaviour of the main oxidants in the high-temperature water at the molecular level. Study of the microsolvation of oxidising agents is crucial for understanding their transport properties and reactivity and, consequently, for developing industrial applications. In this work the NVE molecular dynamics simulations have been performed to examine the effect of temperature on the hydration of the OH radical in water up to 673 K. Five thermodynamic states of water have been simulated in total. The water molecule and the radical were described by the flexible three- and two-site models, respectively. In each of the simulation runs the system was modelled by the periodically repeated cubic box comprising one OH radical per 400 water molecules. The solute-solvent radial distribution functions (RDFs) have been calculated and compared with the solvent-solvent RDFs obtained from the simulations of pure water at the corresponding thermodynamic conditions. This comparison revealed that the radical tends to occupy cavities in the hydrogen-bonded network of water. The hydration number, of ca. 14 at ambient conditions, decreases with increasing temperature. Being localised in the cavity usually forms one H-bond to the surrounding water molecules acting as the H-donor. The probability of formation H-acceptor bonds is lower but noticeably increases with temperature.

Structural and thermodynamic properties of discrete potential fluids in first-order mean spherical approximation

S. Hlushak,[a,b] A. Trokhymchuk[b,c] and S. Sokołowski[d]

[a] *Laboratoire PECSA, Université Pierre et Marie Curie-Paris6, 4 Place Jussieu, 75252 Paris Cedex 05, France*
[b] *Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine*
[c] *Department of Chemistry and Biochemistry, Brigham Young University Provo, UT 84602, USA*
[d] *Department for the Modelling of Physico-Chemical Processes, Maria Curie Sklodowska University, 20031 Lublin, Poland*

The first-order mean spherical approximation (FMSA) for square-well fluid is extended for attractive well widths up to two particle diameters ($2 < \lambda \leq 3$). Analytical expressions for direct correlation function are obtained. The developed theory represents non-trivial extension of the recent study due to Tang [Y.Tang, J. Chem. Phys. **127**, 164504 (2007)] where the width of square-well attraction was limited by one particle diameter ($1 < \lambda \leq 2$). Prediction of the FMSA theory is validated by direct comparison against Monte-Carlo simulation data, and to the parameters of the critical points of the square-well fluids with different ranges of attraction.

Linear combinations of the obtained direct correlation functions of square well fluids are then used to construct the first-order mean spherical approximations for square barrier, square well, as well as square well-barrier-well fluids. The structural properties of the fluids are compared with the results of hybrid mean spherical approximation [I. Guillen-Escamilla *et al.*, J.Phys.: Condens. Matter, **19**, 086224 (2007)] and with the results of computer simulations. The compressibility route to thermodynamics is then used to check whether the theory is able to predicts multiple fluid-fluid transitions for model fluids.

Statistical mechanical theory for model of water and hydration

T. Urbic[a] and K. Dill[b]

[a] *University of Ljubljana, Slovenia*
[b] *University of California, San Francisco, USA*

We develop a statistical mechanical model for the thermal and volumetric properties of water-like fluids. Each water interacts with neighboring waters through a van der Waals interaction and an orientation-dependent hydrogen-bonding interaction. This model, which is largely analytical, is a variant of the Truskett & Dill (TD) treatment of the "Mercedes-Benz" model. The present model gives better predictions than TD for hydrogen bond populations in liquid water by distinguishing strong cooperative hydrogen bonds from weaker ones. We find that the volumetric and thermal properties follow the same trends with temperature as real water and are in good general agreement with Monte Carlo simulations of MB water, including the density anomaly, the minimum in the isothermal compressibility, and the decreased number of hydrogen bonds for increasing temperature.

The monomer density profiles of real polymer chains in confined geometries

Z. Usatenko

Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine

The monomer density profiles of ideal polymer chains and real polymer chains with EVI in a good solvent between two parallel repulsive walls, one inert and one repulsive wall and for the case of wall and a mesoscopic particle of a big radius is obtained using the massive field theory approach in fixed space dimensions $d < 4$ up to one-loop order. Besides, the monomer density profiles and the density profiles of end points near the repulsive and inert wall is analyzed up to two-loop order. The obtained results are in qualitative agreement with previous theoretical investigations and with the results of Monte Carlo simulations.

The new force field model for imidazolium-based ionic liquids

I. Voroshylova, V.V. Chaban and O.N. Kalugin

V.N. Karazin Kharkiv National University, 4 Svoboda sq., 61077 Kharkiv, Ukraine

The new non-polarizable force field model (FFM) for imidazolium-based room-temperature ionic liquids (RTILs), 1-ethyl-3-methyl-imidazolium tetrafluoroborate and 1-butyl-3-methyl-imidazolium tetrafluoroborate, is developed. Based on the results of our density functional theory (DFT) calculations using the explicit ionic environment, we modified the electrostatic charges on the interacting sites of RTILs starting from the model originally derived by Liu et al. [Zh. Liu, Sh. Huang and W. Wang, J. Phys. Chem. B **108**, 12978-12989 (2004)]. The refined FFM allows us to reproduce well experimental heat of vaporizations, diffusion coefficients, ionic conductivity and shear viscosity of the RTIL under investigation. All these properties were hardly inconsistent with experimental values with an original model. The main advantage of the proposed procedure is its clearness, simplicity and the possibility to improve the functionality of the existing force field models by modifying exclusively electrostatic charges. Being successful with imidazolium-based RTILs, the proposed procedure can be applied for improvement/development of the FFMs for other classes of RTILs and some other condensed matter systems where polarization plays a key role.

Development of the QM/MM/RISM theory: Application to the intercalation of proflavine with solvated DNA

N. Yoshida, and F. Hirata

Institute for Molecular Science, 38, Nishigo-naka, Myodaiji, 4448585 Okazaki, Japan

A new approach for investigating solvent effects on the electronic structure of solvated macromolecules is proposed. The method is constructed by combining the quantum and molecular mechanics (QM/MM) methods with the reference interaction site model (RISM) theory. The system treated with the method is divided into three regions, quantum and molecular mechanical regions of solute, and the solvent region. The two solute regions are treated by the ordinary QM/MM method, while the solvent region is handled with the RISM theory. The method is applied to investigate the intercalation of proflavine to two types of decameric B-DNA, namely [deca(dG-dC)]2 and [deca(dA-dT)]2. Our results indicate that the affinity of intercalation of proflavine to the dG-dC base sequence is higher than that of the dA-dT DNA base sequence, which is consistent with the experimental results. The drastic change of solvation structure due to the intercalation makes large positive change in the solvation free energy which is attributed to the dehydration penalty of PR, the screening of electrostatic interaction between PR and DNA, and the hydrophobic interaction of elongated DNA chain.

Polymers in crowded environment: shape anisotropy

V. Blavatska,[a] C. von Ferber[b,c] and Yu. Holovatch[a]

[a] *Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine, 1 Svientsitskii Str., 79011 Lviv, Ukraine*
[b] *Theoretische Polymerphysik, Universität Freiburg, 79104 Freiburg, Germany*
[c] *Applied Mathematics Research Centre, Coventry University, Coventry, UK*

We study the size and shape characteristics of long flexible polymer macromolecules in an environment with structural obstacles. We consider the case of defects that are correlated at large distances x according to power law x^{-a} in d dimensions. Applying the field-theoretical renormalization group approach evaluated using a double $\varepsilon = 4 - d$, $\delta = 4 - a$ expansion, we estimate rotationally invariant universal quantities such as the size ratio $\langle R_e^2 \rangle / \langle R_G^2 \rangle$ and averaged asphericity ratio $\hat{A}_d$. Our results qualitatively indicate that compared with the pure case the long range correlation of the environment induces additional asymmetry in the polymer shape, increasing with δ.

Orientational correlations in molecular liquids containing tetrahedral molecules

S. Pothoczki,[a] L. Temleitner[a,b] and L. Pusztai[a]

[a] *Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, Budapest, POB 49, H-1525, Hungary*
[b] *Japan Synchrotron Radiation Research Institute (SPring-8/JASRI) 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan*

The structure of liquids containing tetrahedral molecules has been an evergreen topic in the area. A possible way of systematize the investigation of these liquids would be increasing the size of their molecules or distorting step-by-step the perfect symmetry of the ones with higher symmetry: this way, changes of the microscopic structure induced by the changing molecular shape could be monitored. Following this route, three molecular liquid families (XY_4[Ref.1-3], CXY_3[Ref.4,5] and CX_2Y_2 [Ref.6,7]) are compared here, from the point of view of orientational correlations.

This contribution reports detailed structural analyses of (neutron and X-ray) diffraction data, performed by Reverse Monte Carlo (RMC) [Ref.8] computer simulation that provided large structural models. These collections of particle coordinates ('configurations') are consistent with experimental data within their uncertainties. Later, structural parameters could be calculated from the configurations.

Despite several published studies of these systems, open questions, regarding especially orientational correlations, remain: What are the most frequent conformations of two molecules? Can we talk about ,,long range order"? Are they different from what is expected if only the density and the molecular structure would influence orientations?

In an attempt to tackle these issues, we have carried out very detailed analyses of the orientational correlations via the approach suggested by Rey [Ref.9]. From the correlation functions it is apparent that as the size of molecules increases or the symmetry of the molecule deteriorates, the range of correlations between their mutual orientations becomes shorter.

1. Sz. Pothoczki, L. Temleitner, P. Jóvári, S. Kohara, and L. Pusztai, *Nanometer range correlations between molecular orientations in liquids of molecules with perfect tetrahedral shape:* CCl_4, $SiCl_4$, $GeCl_4$ *and* $SnCl_4$, J. Chem. Phys. **130**, 064503 (2009).

2. L. Pusztai, Sz. Pothoczki, S. Kohara, *Orientational correlations in molecular liquid* SnI_4, J. Chem. Phys. **129**, 064509 (2008).
3. L. Temleitner and L. Pusztai, *Local order and orientational correlations in liquid and crystalline phases of carbon tetrabromide from neutron powder diffraction measurements*, Phys. Rev. B **81**, 134101 (2010).
4. Sz. Pothoczki, L. Pusztai, S. Kohara, *The structure of liquid iodomethane*, CH_3I/CD_3I, JPCM **19**, 335204 (2007).
5. Sz. Pothoczki, L. Temleitner, S. Kohara, P. Jóvári, and L. Pusztai, *The liquid structure of haloforms* $CHCl_3$ *and* $CHBr_3$, JPCM (in press) (2010).
6. Sz. Pothoczki, L. Temleitner, L. Pusztai, *Extended orientational correlation study for molecular liquids containing distorted tetrahedral molecules: application to methylene halides*, J. Chem. Phys. **132**, 164511 (2010).
7. Sz. Pothoczki, S. Kohara, L. Pusztai, *Partial radial distribution functions of methylene halide molecular liquids*, J. Mol.Liq. **153**, 112 (2010).
8. L. Pusztai and R. L. McGreevy, Mol. Phys. **90**, 533 (1997).
9. R. Rey, J. Chem. Phys. **126** 164506 (2007).

Aggregation Gibbs energy of liquids and liquid mixtures

V.A. Durov and I.Yu. Shilov

Department of Chemistry, Moscow State University, Moscow, Russia

A new thermodynamic function characterizing self-organization of liquid systems due to specific interactions like hydrogen bonds - aggregation Gibbs energy - is introduced. Aggregation Gibbs energy is defined as the difference between Gibbs energies of associated liquid system and that of hypothetical nonideal liquid system consisting of monomers, at the same temperature and pressure. General analytical expressions are obtained in the framework of quasichemical approach (QCNAS model) [1,2] for molar aggregation Gibbs energy of pure liquid and binary solution with account of contributions of specific and universal (dipole, dispersive) interactions.

An equation is obtained for aggregation Gibbs energy of pure liquid as a function of mean degree of chain-like aggregation in the framework of athermal solution model. In the same approximation an equation is obtained for aggregation Gibbs energy of binary solution of associating component in inert solvent as a function of composition and mean degree of chain-like aggregation of the pure liquid. The results of calculations of aggregation Gibbs energy of pure liquid and binary solution are presented.

This work was supported by the Russian Foundation for Basic Research, project N 10-03-01164 and by the Program of Ministry of Education and Science of the Russian Federation ”Development of scientific potential of higher education institutions (2009-2010)”, project N 2.1.1/3305.

1. V.A. Durov, Pure Appl. Chem. **76**, 1 (2004).
2. V.A. Durov, J. Mol. Liq. **118**, 101 (2005).

Dioxane-ethanol mixtures: supramolecular structure, thermodynamic and dielectric properties.

V.A. Durov, and I.Yu. Shilov and O.G. Tereshin

Department of Chemistry, Moscow State University, Moscow, Russia

The quasichemical models [1,2] provide a unified approach for correlating various macroscopic properties of H-bonded molecular liquids on the molecular basis and studying their supramolecular ordering, including the long range molecular correlations, which extend beyond the nearest coordination shells. We present an application of the quasichemical approach to the 1,4-dioxane + ethanol mixtures, a system with complex supramolecular structure due to hydrogen-bonding between like and unlike molecules.

The excess thermodynamic functions (Gibbs energy, enthalpy, and entropy) and the dielectric permittivity of dioxane-ethanol solutions have been analyzed and described in the whole range of compositions and in a wide temperature range in the framework of the quasichemical model of nonideal associated solution (QCNAS) [1,2]. It is shown that the model of supramolecular structure, taking into account chain-like and cyclic aggregation of alcohol molecules and complexation of alcohol aggregates with non-polar solvent [3], is able to reproduce the physicochemical properties of the mixtures with good accuracy. The equilibrium constants, enthalpies, and entropies of aggregation, and structural parameters of supramolecular aggregates have been determined. Distribution functions of aggregates over size and structure are reported and nanosize aggregates are revealed. Specific interactions are shown to give the main contribution to the positive deviations from the ideal solution behavior. Positive deviation of the dipole correlation factor from unity is due to predominantly parallel orientation of the dipoles in the ethanol aggregates and in the complexes with dioxane.

This work was supported by the Russian Foundation for Basic Research, project N 10-03-01164 and by the Program of Ministry of Education and Science of the Russian Federation "Development of scientific potential of higher education institutions (2009-2010)", project N 2.1.1/3305.

1. V.A. Durov, Pure Appl. Chem. **76**, 1 (2004).
2. V.A. Durov, J. Mol. Liq. **118**, 101 (2005).
3. V.A. Durov, I.Yu. Shilov, J. Mol. Liq. **92**, 165 (2001).

EMLG-JMLG Annual Meeting 2010

Complex liquids

Modern trends in exploration,
understanding and application

List of participants

September 5–9, 2010

Lviv, Ukraine

Abramczyk, H. abramczy@mitr.p.lodz.pl
Technical University of Łódź, Poland

Atamas atamasphys@mail.univ.kiev.ua
Taras Shevchenko National University of Kyiv, Ukraine

Blavatska, V. viktoria@icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Blazhyevskyi, Y. yura@icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Bopp, Ph. A. philippebopp@yahoo.com
Depart. of Chemistry, Université Bordeaux 1, Talence CEDEX, France

Borzsák, I. borzsak@iif.hu
Nyugat-magyarországi Egyetem, Szombathely, Hungary

Brodin, A. alex.brodin@gmail.com
National Techn. Univ. of Ukraine ”Kyiv Polytechnic Institute”, Ukraine

Bryk, T. bryk@icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Buchner R. richard.buchner@chemie.uni-regensburg.de
Inst. für Physik. und Theor. Chemie, Universität Regensburg, Germany

Bulavin, L. bulavin@univ.kiev.ua
Taras Shevchenko National University of Kyiv, Ukraine

Ciach, A. aciach@ichf.edu.pl
Institute of Physical Chemistry, PAS, Warsaw, Poland

Cordeiro, M.N.D.S. ncordeir@fc.up.pt
REQUIMTE/University of Porto, Portugal

Dietrich, S. dietrich@mf.mpg.de
Max Planck Institut for Metals Research, Stuttgart, and Institute
for Theoretical and Applied Physics, University of Stuttgart, Germany

Druchok, M. maksym@icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Dong, W. Wei.Dong@ens-lyon.fr
Lab. de Chimie, UMR 5182, CNRS, Ecole Norm. Supér. de Lyon, France

Durov, V. durov@phys.chem.msu.ru
Department of Chemistry, Moscow State University, Russia

Eiberweiser, A. andreas.eiberweiser@chemie.uni-regensburg.de
Inst. für Physik. und Theor. Chemie, Universität Regensburg, Germany

Fedotova, M. mvf@isuct.ru
Institute of Solution Chemistry, RAS, Ivanovo, Russia

Fujimura, K. fujisan_fukkun@yahoo.co.jp
Depart. of Chemistry, Faculty of Science, Fukuoka University, Japan

Gadomska, B. bogad@chem.uw.edu.pl
Department of Chemistry, University of Warsaw, Poland

Gadomski, W. gado@chem.uw.edu.pl
Department of Chemistry, University of Warsaw, Poland

Geiger, A alfons.geiger@udo.edu
Physikalische Chemie Technische Universität Dortmund, Germany

Giorgini, M.G. mariagrazia.giorgini@unibo.it
Dipart. di Chimica Fisica ed Inorganica, Universitá di Bologna, Italy

Hampe, M.
Thermal Process Engineering, Technical University Darmstadt, Germany

Heckhausen, S. silke.heckhausen@uni-rostock.de
Physikalische und Theoretische Chemie, Universität Rostock, Germany

Hirata, F. hirata@ims.ac.jp
Institute for Molecular Science, Okazaki, Japan

Holovko, M. holovko@icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Holzmann, J. hans-joerg.holzmann@uni-rostock.de
Physical Chemistry, University of Rostock, Germany

Idrissi, N. nacer.idrissi@univ-lille1.fr
Univ. des Sci. et Techn. de Lille, Villeneuve d'Ascq Cedex, France

Ignatyuk, V. ignat@icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Ilnytskyi, J. iln@icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Ito, K. ito_kanae@hotmail.com
Department of Chemistry, Fukuoka University, Fukuoka, Japan

Kalugin, O.N. onkalugin@gmail.com
V.N. Karazin Kharkiv National University, Ukraine

Kalyuzhnyi, Yu. yukal@icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Kameda, Y. kameda@sci.kj.yamagata-u.ac.jp
Department of Material and Biological Chemistry, Faculty of Science,
Yamagata University, Japan

Kerlé, D. daniela.kerle@uni-rostock.de
Physical Chemistry, University of Rostock, Germany

Kiselev, M. mgk@isc-ras.ru
Institute of Solution Chemistry, RAS, Ivanovo, Russia

Kleshchonok, A. V. avklesh@gmail.com
Taras Shevchenko National University of Kyiv, Ukraine

Klevets, I. ivank@icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Korynevskii, M. koryn@icmp.lviv.ua.
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Kovalenko, A. andriy.kovalenko@nrc-cnrc.gc.ca
National Institute for Nanotechnology, Edmonton, and Department
of Mechanical Engineering, University of Alberta, Edmonton, Canada

Kravtsiv, I. ivankr@icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Kumbharkhane, A.Ch. akumbharkhane@yahoo.co.in
Swami Ramanand Teerth Marathwada University, Nanded, India

Kuporov, V. slw@icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Lago, S. slagara@upo.es
Dpt. Sist. Físicos, Químicos y Naturales, Univ. Pablo de Olavide, Spain

Lavrentovich, O. olavrent@kent.edu
Liquid Crystal Institute, Kent State University, Kent, Ohio, USA

Lehn, J.M. lehn@isis.u-strasbg.fr
ISIS, Université de Strasbourg and Collège de France, Paris, France

Lev, B. blev@bitp.kiev.ua
Bogolyubov Inst. for Theor. Physics, NAS of Ukraine, Kyiv, Ukraine

Lisetski, L. lisetski@isma.kharkov.ua
Institute for Scintillation Materials, NAS of Ukraine, Kharkiv, Ukraine

Lozada-Cassou, M. marcelo@imp.mx
Mexican Petroleum Institute, Mexico City, Mexico

Ludwig, R. ralf.ludwig@uni-rostock.de
Physical Chemistry, University of Rostock, Germany

Maier, H. maier@tvt.tu-darmstadt.de
Thermal Process Engineering, Technical University Darmstadt, Germany

Markiv, B.B. markiv@icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Matskevych, V.T. matskevych@mail.ru
National Science Centre ”Kharkiv Inst. for Phys. and Technol.”, Ukraine

Matveev, O. matveyev@icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Mayer, V. mayer@orc.ru
Bureau CNRS de Moscou (Russie et Nouveaux Etats Independ.), France

Melnyk, R. romanr@icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Menchyshyn, O. menchyshyn@icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Minko, S. sminko@clarkson.edu
Depart. of Chem. & Biomolecular Sci., Clarkson Univ., Potsdam, NY, USA

Mryglod, I. M. mryglod@icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Mudry, S. mudry@physics.wups.lviv.ua
Ivan Franko National University of Lviv, Ukraine

Musiy, R. rostyslav_musiy@ukr.net
L.M. Lytvynenko Institute of Physical-Organic Chemistry and Coal Chemistry, NAS of Ukraine, Lviv, Ukraine

Nakada, M. f09j001a@mail.cc.niigata-u.ac.jp
Graduate School of Science and Technology, Niigata University, Japan

Nazarenko, V. vnazaren@iop.kiev.ua
Institute of Physics, NAS of Ukraine, Kyiv, Ukraine

Odinaev, S. odsb@tarena-tj.org
Osimi M.S. Tajik Technical University, Dushanbe, Tajikistan

Omelyan, I. P. omelyan@ph.icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Palinkas, G. palg@chemres.hu
Chemical Research Center, Budapest, Hungary

Paschek, D. dietmar.paschek@uni-rostock.de
Institut für Chemie der Universität Rostock, Germany

Patsahan, M. patsahan@icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Patsahan, O. oksana@icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Patsahan, T. tarpa@icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Perepelytsya, S. M. perepelytsya@bitp.kiev.ua
Bogolyubov Inst. for Theor. Physics, NAS of Ukraine, Kyiv, Ukraine

Perzynski, R.
Université Pierre et Marie Curie, France

Pizio, O. pizio@servidor.unam.mx
Instituto de Quimica, UNAM, Mexico City, Mexico

Polok K. gado@chem.uw.edu.pl
Department of Chemistry, University of Warsaw, Poland

Probst, M. michael.probst@uibk.ac.at
Innsbruck University, Austria

Pusztai, L. lpusztai@szfki.hu
Research Institute for Solid State Physics and Optics, HAS, Hungary

Ruocco, G. Giancarlo.Ruocco@roma1.infn.it
Dipartimento di Fisica, “Sapienza” Universitá di Roma, Italy

Schmidt, E. eliane.schmidt@gmx.de
University of Rostock, Germany

Schröer, W. schroer@uni-bremen.de
Department of Biology and Chemistry, University of Bremen, Germany

Segura, D. slagara@upo.es
Dpt.Sist. Físicos, Químicos y Naturales, Univ. Pablo de Olavide, Spain

Seitsonen, A.P. Ari.P.Seitsonen@iki.fi
Physikalisch-Chemisches Institute, University of Zurich, Switzerland

Sergiievskyi, V. sergiiev@mis.mpg.de
Max-Planck-Inst. for Mathematics in the Sciences, Leipzig, Germany

Shaydyuk, Y. evgs@bk.ru
Institute of Physics, NAS of Ukraine, Kyiv, Ukraine

Sokolić, F. sokolic@pmfst.hr
Department of Physics, Faculty of Science, University of Split, Croatia

Sonnleitner, T. thomas.sonnleitner@chemie.uni-regensburg.de
Inst. für Physik. und Theor. Chemie, Universität Regensburg, Germany

Szala-Bilnik, J. jszala@toya.net.pl
Institute of Applied Radiation Chemistry, Techn. Univ. of Łódź, Poland

Takamuku, T. takamut@cc.saga-u.ac.jp
Saga University, Japan

Terazima, M. mterazima@kuchem.kyoto-u.ac.jp
Kyoto University, Japan

Torii, H. torii@ed.shizuoka.ac.jp
Shizuoka University, Japan

Trokhymchuk, A. adt@icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Turq, P. pierre.turq@upmc.fr
Université Pierre et Marie Curie, France

Urbic, T. tomaz.urbic@fkkt.uni-lj.si
University of Ljubljana, Slovenia

Usatenko, Z. zz_usatenko@ph.icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Vlachy, V. vojko.vlachy@fkkt.uni-lj.si
University of Ljubljana, Slovenia

Voroshylova, I. V. voroshylova@gmail.com
V.N. Karazin Kharkiv National University, Ukraine

Yamaguchi, Toshio yamaguch@fukuoka-u.ac.jp
Faculty of Sci., and Adv. Materials Institute, Fukuoka University, Japan

Yamaguchi, Tsuyoshi tyama@nuce.nagoya-u.ac.jp
Nagoya University, Japan

Yoshida, N. noriwo@ims.ac.jp
Institute for Molecular Science, Okazaki, Japan

Yukhnovsky, I. yukhn@icmp.lviv.ua
Institute for Condensed Matter Physics, NAS of Ukraine, Lviv, Ukraine

Zagorodny, A. azagorodny@bitp.kiev.ua
Bogolyubov Inst. for Theor. Physics, NAS of Ukraine, Kyiv, Ukraine

Austria
Probst, M.

Canada
Kovalenko, A.

Croatia
Sokolić, F.

France
Bopp, Ph. A.
Dong, W.
Idrissi, N.
Lehn, J.M.
Mayer, V.
Perzynski, R.
Turq, P.

Germany
Buchner R.
Dietrich, S.
Eiberweiser, A.
Geiger, A.
Hampe, M.
Heckhausen, S.
Holzmann, J.
Kerlé, D.
Ludwig, R.
Maier, H.
Paschek, D.
Schmidt, E.
Schröer, W.
Sergiievskyi, V.
Sonnleitner, T.

Hungary
Borzsák, I.
Palinkas, G.
Pusztai, l.

India
Kumbharkhane, A.Ch.

Italy
Giorgini, M.G.
Ruocco, G.

Japan
Fujimura, K.
Hirata, F.
Ito, K.
Kameda, Y.
Nakada, M.
Takamuku, T.
Terazima, M.
Torii, H.
Yamaguchi, T.
Yamaguchi, Ts.
Yoshida, N.

Mexico
Lozada-Cassou, M.
Pizio, O.

Poland
Abramczyk, H.
Ciach, A.
Gadomska, B.
Gadomski, W.
Polok, K.
Szala-Bilnik, J.

Portugal
Cordeiro, M. N. D. S.

Russia
Durov, V.
Fedotova, M.
Kiselev, M.

Slovenia
Urbic, T.
Vlachy, V.

Spain
Lago, S.
Segura, D.

Switzerland
Seitsonen, A.P.

Tajikistan
Odinaev, S.

Ukraine
Atamas, N.
Blavatska, V.
Blazhyevskyi , Yu.
Brodin, A.
Bryk, T.
Bulavin, L.
Druchok, M.
Holovko, M.
Ignatyuk, V.
Ilnytskyi, J.
Kalugin, O.N.
Kalyuzhnyi, Yu.
Kleshchonok, A. V.
Klevets, I.
Korynevskii, M.
Kravtsiv, I.
Kuporov, V.

Lev, B.
Lisetski, L.
Markiv, B.B.
Matskevych, V. T.
Matveev, O.
Melnyk, R.
Menchyshyn, O.
Mryglod, I. M.
Mudry, S.
Musiy, R.
Nazarenko, V.
Omelyan, I. P.
Patsahan, M.
Patsahan, O.
Patsahan, T.
Perepelytsya, S. M.
Shaydyuk, Y.
Trokhymchuk, A.
Usatenko, Z.
Voroshylova, I. V.
Yukhnovsky, I.
Zagorodny, A.

USA
Lavrentovich, O.
Minko, S.

Author Index

Contents