



Lomonosov Moscow State University

MSU Nanotechnology Education and Research Center

PCAM European Doctorate



Computer simulation of advanced materials

International Summer School

<http://nano.msu.ru/en/csam2012>

Lomonosov Moscow State University

Moscow, Russia

16 – 21 July 2012

Partners and sponsors



Lecturers and organizers

Scientific committee

Khokhlov A., *MSU, Russia*

(Chair)

Brivio G.P., *University of Milano-Bicocca, Italy*

Chertovich A., *MSU, Russia*

Potapkin B., *KintechLab, Russia*

Shaytan K., *MSU, Russia*

Suetin N., *Intel, Russia*

Voevodin V., *MSU, Russia*

Local organization

Alexander Chertovich

chertov@polly.phys.msu.ru

Olga Bogomolova

obogomol@gmail.com

Anna Kochurova

akochurova@rector.msu.ru

Olga Shamardina

Lecturers

Brivio G.P., *University of Milano-Bicocca, Italy*

Colombo L., *University of Cagliari, Italy*

Elliott J., *University of Cambridge, United Kingdom*

Khokhlov A., *MSU, Russia*

Knizhnik A., *Kurchatov Institute, Russia*

Korz A., *T-platforms ltd, Russia*

Morozov I., *JIHT, Russia*

Mueller M., *University of Gottingen, Germany*

Nelson J., *Imperial College, United Kingdom*

Nemukhin A., *MSU, Russia*

Norman G., *JIHT, Russia*

Potapkin B., *Kintech Lab, Russia*

Shaytan A., *MSU, Russia*

Tamm M., *MSU, Russia*

Tarek M., *CNRS, France*

VandeVondele J., *ETH Zurich, Switzerland*

Agenda

July 16

16-00 – 17-30	Registration
18-00 – 20-00	<i>Welcome-party</i>

July 17, "fundamental background"

9-30 – 10-45	Atom and molecular structure, quantum level of matter <i>(Alexander Nemukhin, MSU)</i>
10-50 – 11-10	<i>Coffee-break</i>
11-10– 12-25	Matter structure: gases, liquids, condensed (crystal and amorphous) <i>(Alexei Khokhlov, MSU)</i>
12-30 – 14-00	<i>Lunch</i>
14-00 – 15-15	Thermodynamics and statistical physics, phase transitions, field-driven and particle-driven description <i>(Mikhail Tamm, MSU)</i>
15-20 – 15-40	<i>Coffee-break</i>
15-40	practical seminar
17-30	<i>MSU campus excursion, free time</i>

July 18, "simulation methodology"

9-30 – 10-45	Ab-initio & DFT <i>(Gian Paolo Brivio, Milano-Bicocca, Italy)</i>
10-50 – 11-10	<i>Coffee-break</i>
11-10– 12-25	MD <i>(Alexey Shaytan, MSU)</i>
12-30 – 14-00	<i>Lunch</i>
14-00 – 15-15	Mesosopic and Monte Carlo Simulations <i>(Marcus Müller, Gottingen, Germany)</i>
15-20 – 15-40	<i>Coffee-break</i>
15-40	practical seminar

July 19, "hardware+software"

9-30 – 10-45	Supercomputer architecture <i>(Anton Korzh, T-platforms ltd)</i>
10-50 – 11-10	<i>Coffee-break</i>
11-10– 12-25	Atomistic simulations on supercomputers using open source codes <i>(Igor Morozov, JIHT)</i>
12-30 – 14-00	<i>Lunch</i>
14-00 – 15-15	Predictive Modeling of Advance Materials and Material Processing Based on Multiscale Simulation Paradigms <i>(Boris Potapkin, Kintech lab)</i>
15-20 – 15-40	<i>Coffee-break</i>
15-40	practical seminar

July 20, "simulations in material science: examples"

9-30 – 10-15	Composite materials: mechanical properties (<i>Luciano Colombo, University of Cagliari, Italy</i>)
10-20 – 10-40	<i>Coffee-break</i>
10-40 – 11-25	Materials in extreme states: from warm dense matter to laser induced surface nanostructuring (<i>Genry Norman, JIHT</i>)
11-30 – 11-40	<i>Break</i>
11-40 – 12-25	Materials for solar cell applications (<i>Andrei Knizhnik, Kurchatov Institute</i>)
12-30 – 14-00	<i>Lunch</i>
14-00 – 14-45	student talks
14-45 – 15-05	<i>Coffee-break</i>
15-05 – 15-50	student talks
15-50 – 16-00	<i>Break</i>
16-00 – 17-30	poster session
18-00 – 21-00	<i>School dinner</i>

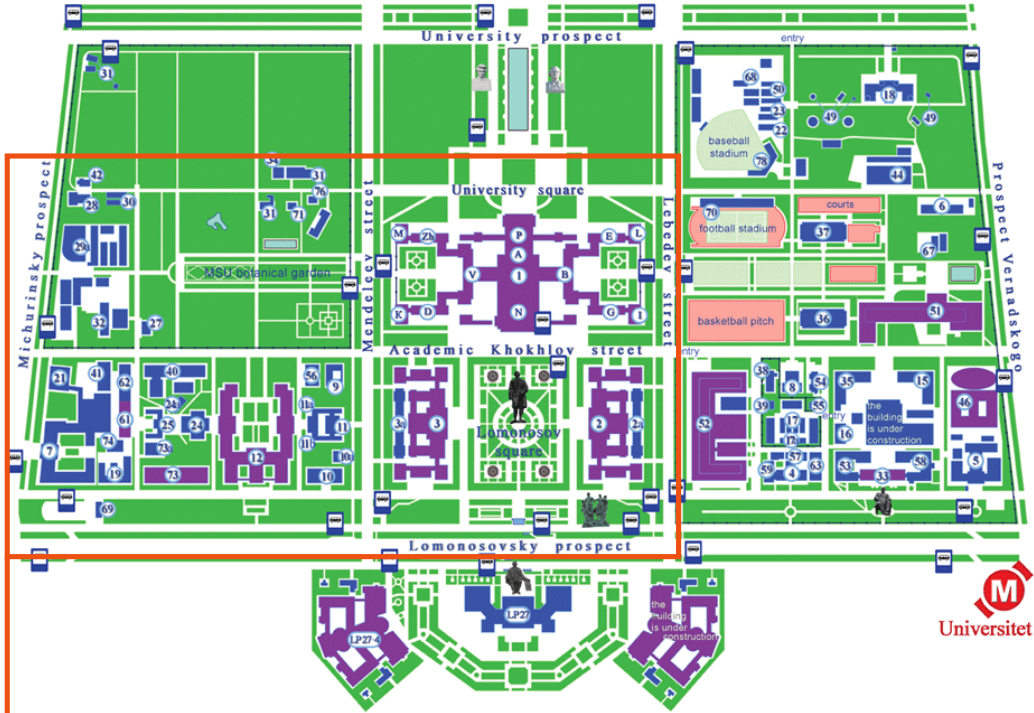
July 21, "simulation of complex systems: examples"

10-30 – 11-15	Multiscale modelling in materials science (<i>James Elliott, University of Cambridge, UK</i>)
11-20 – 11-40	<i>Coffee-break</i>
11-40 – 12-25	Large-scale quantum molecular dynamics (<i>Joost VandeVondele, ETH Zurich, Switzerland</i>)
12-30 – 14-00	<i>Lunch</i>
14-00 – 14-45	Organic Solar cells: from material design to system efficiency (<i>Jenny Nelson, Imperial College, UK</i>)
14-50 – 15-10	<i>Coffee-break</i>
15-10 – 15-55	Cell membranes: structure and transport properties (<i>Mounir Tarek, Nancy University, France</i>)
16-00 – 16-10	<i>Break</i>
16-10 – 17-30	poster session

**Lectures will be held at lecture hall 1624,
MSU main building, section A, 16-th floor**

Lunches will be served at canteen #4, MSU main building, section A, 2-d floor

MSU Campus Scheme



Main building: lecture hall and lunches

Lectures: lecture hall 1624, section A, 16-th floor

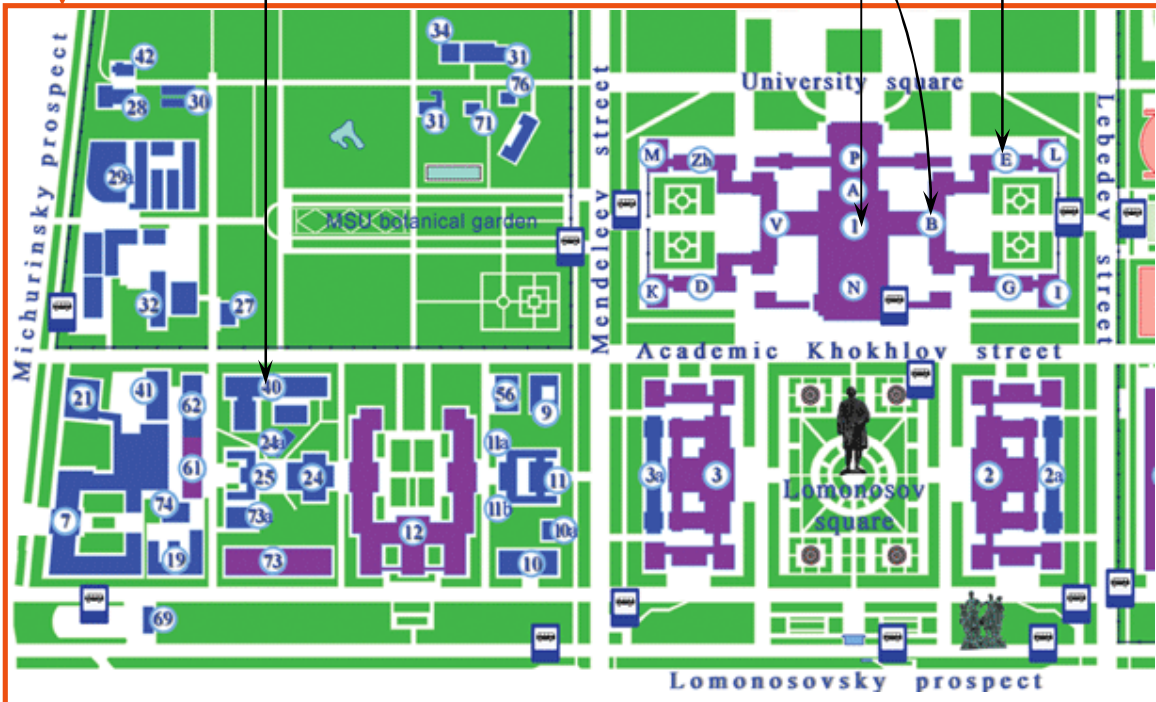
Lunches: canteen #4, section A, 2-d floor

MSU Guest house (same building)

Section B (reception)

Section E (living area)

Welcome Party and School Dinner place



Abstracts of poster presentations

P1

The mathematical description of the polymer films forming process out of solutions

Al Joda H.N.A.¹, Pyshnograï G.V. ²

¹Altai State Technical University

²Altai State Teacher- Training Academy

A number of advantages appears when using mathematical modeling at the design stage and production of polymeric materials. These advantages include the ability to manage the quality of polymer products, and address a number of optimization problems of production. The basis for this approach is a mathematical model, which should be fairly simple and yet reflect all the features of the process under investigation. Consider these statements and take the manufacturing process of the polymer film as an example.

Industrial production of polymer films mainly employs the method of extruding a polymer melt. This method is suitable for molding polymeric materials which are not subject to melting during thermal degradation. Polymer melt is extruded through an extruder, then after the release the obtained film falls on the cooling drum. As a result of the film moving from the extruder to the drum it cools and changes its width and thickness. Thus, the film stretches unevenly, which leads to "the effect of the neck." Since these processes occur simultaneously, for their mathematical modeling one should find a joint solution of equations for velocity, stress and heat transfer.

For polymers, melting temperature of which exceeds the temperature of their thermal decomposition to produce films, the so-called method of watering the polymer solution is employed. This method consists of three main stages: preparing the forming polymer solution of certain concentration, watering it through a die on a polished surface (endless belt or a drum), removing the solvent (by evaporation or by using a precipitation bath). For stress relief, and improving physical and mechanical properties of films produced during the molding process either heat treatment is used or single or biaxial orientation.

Solvent and melt technologies for polymer film production have common basic formation stages as well as their peculiarities. In particular, regardless of the method to obtain a liquid-solid film structure during the transition the non-uniform change in the geometric dimensions of the sample happens, which leads eventually to the emergence of "the effect of the neck." In both cases, the molding process is accompanied by relaxation and phase transitions. Upon receiving the films melt by solidification of the liquid film structure caused by the processes of heat transfer and mortar - by the mass transfer. The process of obtaining a film out of the polymer solution is inherently more complicated, because the system is two-component. At the same time while forming, the polymer concentration is increased, leading to a sharp increase in viscosity of the polymer system. Thus, the development of mathematical models of processes of forming polymer films, peculiarities inherent to each method of preparation should be taken into account.

In this work a mathematical model of the process to obtain a film out of the polymer solution is written in one-dimensional approximation, which allows one to find the ratio of concentration of the solvent, geometric dimensions, the speed of film formation and the distance to the exit out of the spinneret. Comparing the resulting model with the model of forming a film out of the polymer melt has revealed similarities and differences between the processes of solidification and evaporation of the solvent.

P2

Molecular cluster approach and study of point surface Ti^{3+} defect centers on nanoscaled TiO_2

Andreev A.S.; Chizhov Y.V.

V.A. Fock Institute of Physics, St. Petersburg State University, St. Petersburg, Russia

andreev.photonics.spbu@gmail.com

The properties of point intrinsic defect states on TiO_2 surface such as Ti^{3+} ions attract a great attention since they determine advantages of titania in various technological applications, especially in heterogeneous photocatalysis. The quantum chemistry methods are of key importance to make clear the nature of such species and pathways of their formation. At present the most widely used computational approaches in these studies are the slab calculations, the supercell calculations and calculations of free molecular nanoclusters. Among them the molecular cluster approach seems most prospective, but the validity range of this method still is not clear.

The goal of present work is to check the applicability of molecular cluster approach to modeling of point surface Ti^{3+} defect species on nanoscaled TiO_2 . The key point of present study is a connection between size and morphology of model systems and properties of these defect sites. Specifically, the formation of Ti^{3+} centers via interaction with the atomic hydrogen and characterization of these defect species with O_2 adsorption were investigated by DFT calculations. Two isolated molecular clusters with different size and crystallinity degree – the fully amorphous Ti_8O_{16} and “rutile-like” $\text{Ti}_{15}\text{O}_{30}$ – were used as model nanoparticles.

As a whole calculations show the similar results for both model clusters. Specifically, the atomic hydrogen reacts with surface oxygen atoms with negligible activation energy and forms stable OH groups. This is accompanied by reduction of Ti^{4+} -ions to Ti^{3+} with the appearance of singly-occupied $3d$ -levels near the middle of the clusters’ “band gap”. These Ti^{3+} sites actively interact with molecular oxygen. As a result, O_2 forms the stable adsorbed molecular O_2^- species by taking extra electrons from Ti^{3+} ions and the Ti $3d$ -levels in the clusters’ “band gap” disappear.

The results obtained for both model clusters are in agreement with the known experimental regularities of H plasma reduction of TiO_2 and interaction of reduced TiO_2 with oxygen. This means that: 1) the molecular cluster approach may be reasonably used for describing point surfaces defect centers on nanoscaled TiO_2 ; 2) the studied processes are non-sensitive to both the size and crystallinity degree of the model systems.

The present work was supported by Russian Foundation of Basic Research (Grant 10-03-00638-a) and St. Petersburg State University (Grant 11.37.25.2011).

P3

Computer simulation of laser sintering of metallic powders

Ankudinov V.E., Gordeev G. A., Krivilyov M. D., Rodionov V. I.

Udmurt State University, Universitetskaya str, 1/Izhevsk, Russia

vladimir@ankudinov.org

The laser sintering of submicron metal powders has been studied in connection with unsteady heat transfer in a porous powder layer under conditions of rapid phase transformations. The multi-scale theoretical approach was used during the simulation. The heating and cooling rates and depth of the sintered layer are estimated by the micro-scale model after analysis of geometrical characteristics of the metallic powder. Macro-scale computer analysis based on micro-scale modeling data revealed that the control parameters of the process are the scanning velocity and the permeability coefficient which depend on porosity and morphology of the powder layer. Effects of the laser annealing power, frequency of laser impulses and beam radius have a smaller effect on the depth of the sintering layer.

The relation between generalized thermal properties of powder and porosity was found non-linear. In fact, at the porosity higher than approximately 70%, the mechanism of heat transfer drastically changes and an approximation of continuum becomes incorrect. Full compaction of powder is depressed which degrades quality of the sintered layer. Its preliminary mechanical compressing via particle's ordering improves sintering and hence adherence of the coating to the substrate. A complex hierarchical structure of the sintered layer and heat transport at the scale of single particles (fig. 1) are discussed to suggest optimal processing modes of laser sintering.

Acknowledgement:

This research work was supported by the Ministry of High Education under the contract No. 2.1.2/13524.

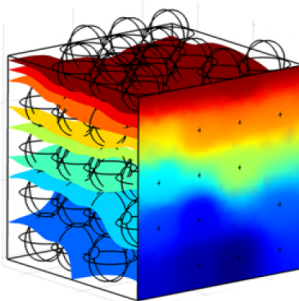
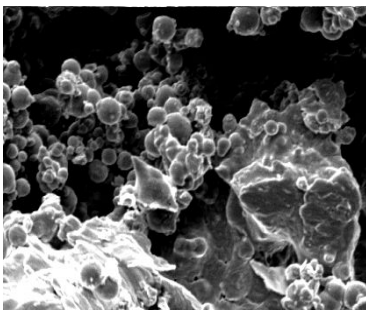


Fig.1: (left) SEM of the sintered layer reveals a hierarchical type of morphology. (right) Modeling of heat transport in a porous powder layer showed high inhomogeneity of the temperature field in a mixture of particles of different sizes.

P4

Quantum-chemical simulation and AFM study of poly(diphenylenephthalide) supramolecular structures

Baybulova G.Sh., Galiev A.F., Zhdanov E.R., Kornilov V.N., Lachinov A.N., Kalimullina L.R.

Bashkir State Pedagogical University named after M. Akmulla, Ufa

E-mail: 102galiya102@rambler.ru

Submicron thin films of nonconjugated polyarylenephthalides have unique electronic properties. For example, electronic transition from a dielectric state to a highly conducting one, under the influence of various physical and chemical factors, etc. These properties have a pronounced dimensional character. It is obvious that the emergence of new properties should be attributed not only to the electronic structure of these compounds, but also with the organization of polymer films at the molecular and supramolecular levels of organization. However, this relationship has so far been little studied. Therefore, the purpose of this study was to analyze the quantum-chemical characteristics of the intramolecular organization of the polymer molecules and to establish its connection with the results of atomic force microscopy (AFM) study of the submicron poly(diphenylenephthalide) (PDP) thin films.

We have been modeled and analyzed the fragments of the polymer macromolecules PDP, consisting of nine structural units. It was found that the energetically most favorable configurations of the macromolecules are linear syndiotactic and isotactic helix.

To search revealed the presence of structural formations were performed by AFM studies. The results showed that the macromolecules in the surface layers of polymer films preferably have a linear syndiotactic configuration, three-dimensional globular structure of the layers is determined by the helical isotactic configuration. In addition, the investigation results of the thickness influence of polymer films on the three-dimensional ratio and surface of supramolecular structures are presented.

Computer Simulation of Atomic Oxygen Impact on Polymer Composites

Chirskaya N.P.¹, Novikov L.S.², Voronina E.N.²

¹ *Lomonosov Moscow State University, Faculty of Physics*

² *Lomonosov Moscow State University, Skobeltsyn Institute of Nuclear Physics*

E-mail: novikov@sinp.msu.ru

Composites based on polymer matrices with embedded various nanostructures served as fillers are considered as very promising materials for the next generation spacecraft. In low-Earth orbits (LEO) one of the main factors that cause the damage of the spacecraft surface materials is atomic oxygen (AO) of the Earth's upper atmosphere which leads to the erosion and mass losses of materials [1]. High relative kinetic energy of oxygen atoms (~5 eV) due to the spacecraft orbital velocity enhances their reactivity and opens additional pathways of their reaction with near-surface layers of materials. The mechanisms of the hyperthermal oxygen atom impact on polymers and especially on nanostructures are currently not well understood, and the computer simulation may become an efficient mean for their investigation.

In this paper the structural damage of carbon and boron nitride nanostructures induced by oxygen atom adsorption was studied with the density functional theory (DFT) and self-consistent charge density functional tight-binding (SCC DFTB) methods. It was shown that AO impact on carbon and boron nitride nanotubes (CNT and BNNT, respectively) grew weaker with their diameter increasing, and the distinction between unzipping mechanisms for CNT and BNNT was demonstrated (Fig. 1). With SCC DFTB method the simulation of physical-chemical processes happened in nanostructures and polymers under the hyperthermal AO impact was carried out.

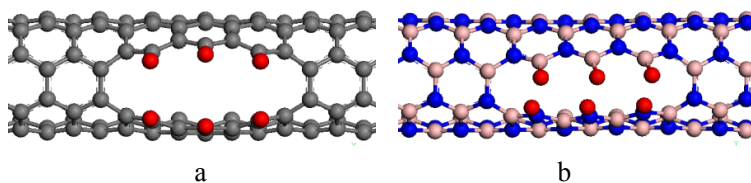


Fig. 1. CNT (a) and BNNT (b) unzipping

The erosion of polymer composites with spherical fillers of different diameter was simulated with Monte–Carlo method. It was shown that embedding nanosized particles into polymer matrices enabled to significantly improve their durability to AO impact, and the erosion intensity was reduced as filler size decreased. The simulation results are in good agreement with experimental data obtained [2].

References

1. Voronina E.N., Novikov L.S., Chernik V.N., Chirskaya N.P., et al. // *Inorganic Materials: Applied Research*, 2012, Vol. 3, No. 2, pp. 95–101.
2. Vernigorov K.B., Alent'ev A.Yu., Muzafarov A.M., Novikov L.S, Chernik V.N. // *Journal of Surface Investigation: X-ray, synchrotron and neutron techniques*, 2011, vol. 5, No. 2, pp. 263-268.

P6

Modeling of dependences «composition – biological activity» and «structure – dynamics of biochemical processes» for analogs of biological objects

Chzhu O.P., Shubenkova E.G.

Russia, Omsk, Omsk State Technical University

Creation of new preparations demands considerable financial and temporary expenses, and besides carrying out a some experiments according to biological properties. The vast majority of experimentally received biological structures don't show expected activity that reduces efficiency of their practical application. The solution of this problem is possible, if at first the structure and structure elements influencing manifestation of biochemical activity and pharmacodynamics of cellular processes are revealed, and also modeling and forecast is carried out and the most effective functional analogs of biological objects are offered. Therefore researches on the basis of a theoretical assessment of dependences «composition – biological activity» and «structure – dynamics of biochemical processes» and modeling of concrete biological structures are actual.

Among known analogs of biological structures the greatest interest for modeling of biochemical processes from the point of view of simplicity of receiving, possibility of a variation of biochemical properties depending on structure, and also existence of functional and structural similarity of particles of a disperse phase with a live cage a multiple nanoemulsion is represented [1]. Nanoemulsions are highly effective transport system, because they have big surface square and superficial energy.

Nanoemulsions find application in medicine, pharmacology. Application of nanoemulsions allows: to prolong action, to increase efficiency and to lower side effects, having reduced a dose of therapeutic preparations, to reduce negative reaction, to transfer insoluble substances to solution.

The approach which will allow to describe and carry out formally modeling of a wide range of analogs of biological structures is at the moment developed, to wit: metabolic ways of assimilation of biologically active substances, membrane transport, pharmacokinetics, and dynamics of biochemical processes, creation of mathematical models of biological systems and numerical modeling of their dynamics.

In this work the special attention is given to identification and modeling of dependences «composition – biological activity» and «structure – dynamics of biochemical processes» for multiple nanoemulsions.

There are very many various ways of optimization of designing and pharmacodynamics by means of different nomograms, various graphic methods and application of more modern methods. In especially difficult cases it is recommended to prefer methods based on use of modern computer programs (HTS-metoda (High Through-put Screening), to QSAR (Quantitative Structure Activity Relationship), CAD (Computer Assisted Design)) [2]. Besides, authors develop the mathematical model describing process of diffusion of liposomalny emulsions in skin. The model basis on the parabolic equations with private derivatives, reflecting processes of concentration diffusion for an one-dimensional case [3].

1. Zaitzev S.Y. Supramolekulyarnye's hares nanodimensional systems on limit of the section of phases: Concepts and prospects for bionanotechnologies. – M: Publishing group URSS, 2010. - 208 pages of ISBN 978-5-9710-0276-5
2. Shilov G. N., Homenko A.I., Yevstigneyev V. V. Bases of development of new medicines//«Medical news», 2009. – No. 2.
3. Tomashevich M. S. Mathematical modeling in the course of creation of aplikatsionny medicines with use of substances of a biotechnological origin. – Art. of Cand.Tech.Sci., 2006. – Moscow. – 164 p.

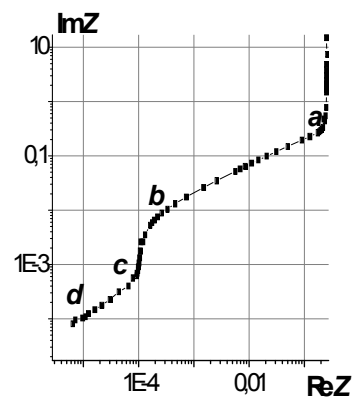
A computer modeling on sub-nanometer scale of ionic transport on ideally polarized heterojunctions of solid electrolyte/electronic conductor

Despotuli A.L., Andreeva A.V.

*Institute of Microelectronics Technology and High Purity Materials RAS,
142432 Chernogolovka Moscow Region, Russia*

The aim of the work is a search of new approaches for a modeling, on a sub-nanometer scale, the processes of fast ionic transport (FIT) on ideally polarized coherent heterojunctions of a solid electrolyte (SE)/electronic conductor (EC). A structure-dynamic model (S-DM) is proposed in which the atomic structure of the SE/EC interface determines the features of FIT by the distribution of depths of potential wells in the SE. The S-DM treats from uniform basis both fast and slow processes in a double electric layer (DEL) as the movement of mobile ions in potential relief of different depth. A method of hidden variables for a finding the SE/EC response to dynamic external influence is proposed. Certain combinations of the hidden variables correspond to experimental data characterizing the DEL-processes (phase shift between external current and potential of the DEL crystallographic plane, Z impedance of the SE/EC heterojunction, etc.). A mathematical apparatus is developed and calculations of space-time, frequency, concentration and temperature dependences of charge distribution in thin spatial structure of the DEL are executed. It allows the mechanisms of ionic transport processes, going in the SE/EC region, to be investigated in detail.

The behavior of $\text{Re}Z$ and $\text{Im}Z$ relative components of the impedance of the model SE/EC heterojunction (thickness $\approx 2\text{nm}$) with potential wells of 0.7, 0.5 and 0.3 eV depths. The temperature is 300K; the frequency range is 0.01 Hz – 10 kHz. The a - b and c - d sections of the graph correspond to analogues of the Warburg impedance and are determined by the frequency changing of fractions of mobile ions, which take part in translation movement in the DEL without noticeable delay.



P8

The modeling of dimers on a stepped surface (L = 3): metod of Monte Carlo.

Evseeva S.I., Stishenko P.V.

Omsk State Technical University

evseevasve@rambler.ru

Stepped surfaces are widely distributed in nature. Adsorption, desorption and reaction on such surfaces have interesting peculiarities. In this paper, we examined the stepped surface model of dimers with a step width (L) equal to 3. The adsorption model allowed transverse and planar placement of molecules. To take into account own size of the molecules and its chemical structure

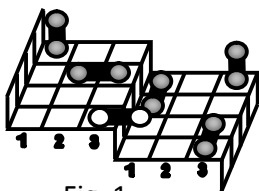


Fig. 1

we have involved infinitely strong repulsive interactions between nearest-neighbor particles. It was assumed that adsorbed dimer cannot be located on two different terraces simultaneously. The model is illustrated in Fig. 1, dimer with white spheres designates prohibited location. Our aim was to determine the critical values of the chemical potential at different

temperatures and, based on previously conducted analysis of the ground-state model, construct phase diagrams. For calculation of the critical values of the chemical potential, we have introduced the order parameter and examined the timetable for its susceptibility, for this we have plotted the susceptibility dependency graphs. To calculate the susceptibility, we used the following expression:

$$\chi = \langle \varphi^2 \rangle - \langle \varphi \rangle^2, \text{ where } \varphi = \frac{\sum_{i=1}^m \theta_i^{\max}}{m} - \frac{\sum_{i=m+1}^n \theta_i}{n-m}, [1]$$

where n,m - number of sublattices, \square -average cover of sublattices.

The order parameter value was calculated with a classical Metropolis algorithm:

- 1). Generate random initial configuration.
- 2). Pick a random surface process (adsorption, desorption or diffusion). Apply or decline the picked process according to before-mentioned probabilities.
- 3). If stop conditions (chemical potential will be out of range) are satisfied, then terminate simulation, otherwise – go to step 2.

Having susceptibility peaks we have constructed phase diagrams for the our models. Surface coverage remains unchanged in a range of chemical potential values corresponding to some of the surface patterns (between the peaks of the susceptibility) and changes rapidly when chemical potential overcomes an interphase threshold. The difference between the potential areas of the existence of coverage phases changes depending on the temperature.

[1] V.F. Fefelov, V.A. Gorbunov, A.V. Myshlyavtsev, M.D. Myshlyavtseva. Model of homonuclear dimer adsorption in terms of two possible molecule orientations with respect to surface: Square lattice //Physical Review E/ -2010/ - v.82, №4.-p.041602.

Atomistic modeling of epoxy-based oligomers with nonlinear-optical chromophores in each unit: conformational search and molecular dynamics

Fominykh O.D., Balakina M.Yu.

A.E. Arbuzov Institute of Organic and Physical Chemistry of Kazan Scientific Centre, RAS

e-mail: fominykh@iopc.ru

During two last decades the increasing interest in polymer materials exhibiting quadratic nonlinear optical (NLO) response to the applied electric field is stimulated by their possible applications in photonics and optoelectronics. Polymer NLO materials possess a number of essential advantages compared to their inorganic analogues traditionally used in the devices for modulation, transmission and storage of light signals. First of all polymer NLO materials have small value of dielectric constant and high values of electric susceptibilities, they can be easily fabricated and processed, and they appear to be compatible with a wide range of materials, what is important for the device fabrication. NLO response of polymer originates from NLO chromophores, incorporated in the polymer matrix. NLO chromophores possess high dipole moment and first hyperpolarizability. Polymer materials with quadratic NLO activity should have noncentrosymmetric structure. This is achieved by orientation of incorporated NLO chromophores in the applied electric field.

Molecular modeling is of great importance for the development of polymer materials with quadratic NLO response, since it can help in planning polymer synthesis, develop temperature-time poling protocol due to the study of local mobility of chromophore groups and of the bearing chain.

Atomistic modeling of epoxy-based oligomers (dimers) containing azo-chromophore fragments in each unit was performed: conformational space was determined by Monte-Carlo method, and peculiarities of torsion profiles were obtained for the angles of interest at different temperatures using MMFF94s and OPLS2005 force fields in solvent (chloroform, dielectric permittivity $\epsilon=4.8$). The modeling was performed using MacroModel program package (Schrodinger) [1]. The study allowed us to establish the temperature of chromophore groups motion (130°C), what should be chosen for performing the poling procedure. The behavior of the oligomer chain, containing 10 units, in the applied electric field was studied by Amorphous cell program of Materials Studio package (Accelrys) [2]. Some material characteristics (dielectric constant, molecular density, refraction index) were determined by Synthia program [2].

[1]. MacroModel, version 9.8, Schrodinger, LLC, New York, 2010.

[2]. Materials Studio 6.0, Accelrys.

P10

Effect of salts on carbon nanotube dispersions in an organic solvent

Frolov A.I.¹, Arif R.N.², Romanova A.O.³, Rozhin A. G.², Fedorov M.V.³

¹*Institute of solution chemistry RAS, Ivanovo, Russia;* ²*School of Engineering & Applied Science, Aston University, Aston Triangle, Birmingham, UK;* ³*Strathclyde University, Glasgow, UK*

aif@isc-ras.ru

In this study we discuss effects of inorganic salt ions on carbon nanotube (CNT) dispersions in a non-aqueous solvent - N-methyl-2-pyrrolidone. By fully-atomistic molecular dynamics simulation we show how the microscopic ion-surface interactions affect the stability of CNT dispersions. Our simulations reveal that an increase of the salt concentration should decrease the stability of the CNT dispersions (salting out effect) [1]. Direct experiments confirm the simulation results: for example, addition of salt into the N-methyl-2-pyrrolidone (NMP) dispersions of CNTs leads to precipitation of CNTs [1,2]. As a result, one can stimulate the bundle formation in the CNT dispersions and regulate the concentration of nanotubes in the dispersions by changing salt concentration.

[1] **Frolov**, Arif, Kolar, Romanova, Fedorov, Rozhin, *Chem. Sci.* **2012**, 3, 541-548

[2] Fedorov, Arif, **Frolov**, Kolar, Romanova, Rozhin, *Phys. Chem. Chem. Phys.* **2011**,13, 12399-12402

P11

Computational study of Polyethylene Oxide confined in Graphite Oxide

García-Yoldi I., Álvarez F., Colmenero de Leon J.

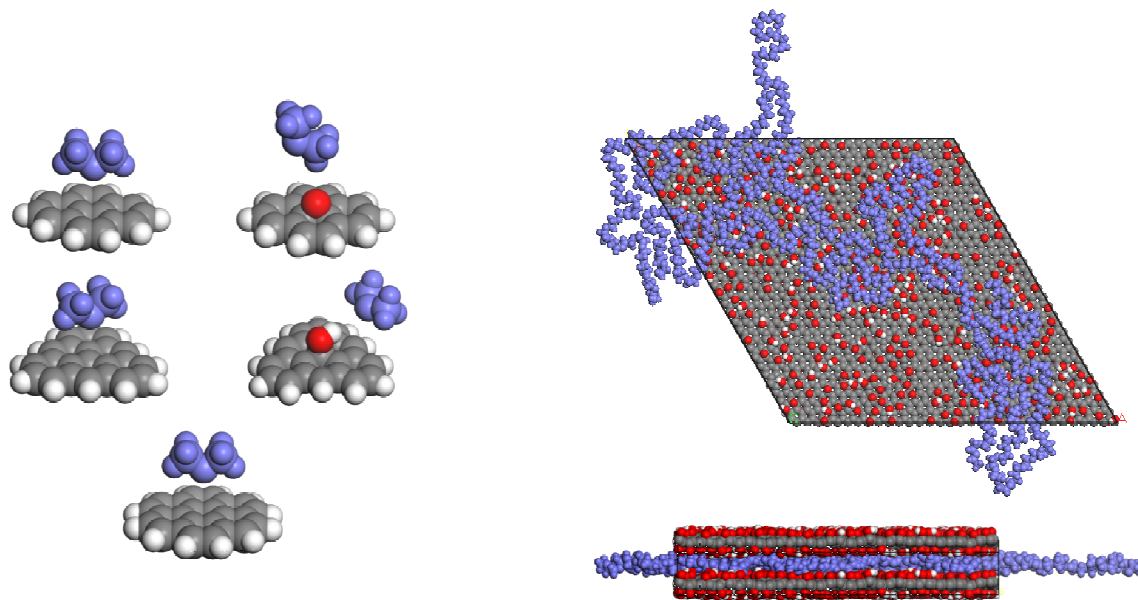
Polymers and Soft Matter Group, Centro de Física de Materiales (CFM-CSIC/UPV/EHU)

inigo_garcia@ehu.es

The study of the effect of confinement on the structural and dynamical properties of polymers is an area of active experimental and computational investigation, these properties can be very different from those in the bulk. The current work is a computational study of the Polyethylene Oxide (PEO) polymer confined in Graphite Oxide (GO) through a multi-scale modeling approach.

At first, the main interactions between polymer and substrate have been simulated at *ab-initio* level by means of 5 simplified PEO-GO models (left figure). The potential energy surfaces has been built and the different minima has been optimized using different DFT methods (B3LYP, MPWB1K, M05, M05-2X, M06, M06-2X, M06-HF and M06-L) and the MP2 reference method. The M05-2X method presents the better correspondence with the reference method.

The next step is to study the dynamics properties of a PEO-GO model by means of Molecular Dynamics simulations; the COMPASS forcefield has been used because it can properly described the PEO...GO interactions. A PEO system of 5 polymer chains (43 units) has been confined in a GO substrate (right figure) according to previous experimental data. The dynamic properties have been compared with those of the bulk polymer.



P12

Influence of the cooperative movement on critical temperature for order-disorder transition in the Ising model

Halagan K., Polanowski P.

Department of Molecular Physics, Lodz University of Technology, 90-924 Lodz, Poland

krzysztof.halagan@edu.p.lodz.pl

The Ising model was published in 1925 [1] by Ernst Ising as an attempt to describe phase transition in magnetic materials. Nowadays the model is treated as a mathematical structure that can be used to represent a variety of different physical phenomena, including phase transitions. In frame of classical Ising model physical system can be regarded as a regular lattice with molecules placed in lattice sites and interacting only on a short range i.e. only with nearest-neighbors. Ising model can be used to model binary mixtures and alloys - lattice is occupied by two types of molecules, which can change their position leading to stochastic self-diffusion. Total number of molecules of every species is conserved and rapid quench below critical temperature usually leads to order-disorder phase transition by nucleation and growth or spinodal decomposition. This kind of model is called model B [2] or COP (conserved order parameter). Several different types of dynamics has been proposed, like direct exchange (also called Kawasaki dynamics) [3] or vacancy model [4] (single vacancy model is the most promising when simulation must reflect no defected system). All of them gave perfect agreement with theoretical value of critical temperature [5] when impurities, long range interactions and external field where excluded. We propose the use of Dynamic Lattice Liquid (DLL) [6] model where particle movement is highly correlated. In this case critical temperature is slightly different from theoretical value. Simple explanation is given to that fact.

[1] E. Ising, *Z. Physik* **31**, 253 (1925).

[2] P. C. Hohenberg and B. I. Halperin, *Rev. Mod. Phys.* **49**, 435 (1977).

[3] K. Kawasaki, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, London, 1972), Vol. 2.

[4] K. Yaldram and K. Binder, *Acta Metall. Mater.* **39**, 707 (1991).

[5] L. Onsager, *Phys. Rev.* **65**, 117 (1944).

[6] T. Pakula and J. Teichmann, *Mater. Res. Soc. Symp. Proc.* **455**, 211 (1997); P. Polanowski and Z. Koza, *Phys. Rev. E* **74**, 036103 (2006).

P13

Mobility of paramagnetic probe in xanthan-based polyurethane systems with various OH/urethane group balance

Hubina A.V., Kozak N.V.

*Institute of Macromolecular Chemistry NAS of Ukraine
Kyiv-02160, Kharkivske shaussee, 48*

zurako@ukr.net

Paramagnetic probe TEMPO was introduced into polyglucanurethanes with calculated amount substituted hydroxyl groups 40, 60, 80 and 100% (PGU40, PGU60, PGU80 та PGU100, respectively) [1]. EPR spectra of TEMPO in various polymer environment were registered under при 25°C, 50°C, 75°C, 100°C та 125°C.

Under heating constriction of components of TEMPO spectrum is observed and also its isotropy increases as a result of polymer chains movements with temperature rise and unification of correlation time values from probe in different areas [2].

Correlation time $\tau \times 10^{-9}$ depending on polymer matrix content and temperature

PGU	Temperature, °C				
	25	50	75	100	125
40%	37	26	16	10	5
60%	25	23	7	9	7
80%	51	17	5	4	5
100%	33	10	6	6	5

It was shown that correlation time decreases with temperature rising. Higher temperatures cause less influence of hydroxyl/urethane balance on correlation time values while lower temperatures (25 °C) hydroxyl/urethane balance affects correlation time values notably.

References

[1] Interaction of polyglucanurethane networks with aqueous solutions of transition metals salts /Kozak N.V., Hubina A.V., Klepko V.V., Vasilkevich O.A., Slisenko V.I.// Interuniversity digest „Polymer physical chemistry», 2010, Vol.1

[2] Vasserman A. M., Kovarsky A. L. Spin marks and probes in polymer physical chemistry. M.: Nauka. – 1986. – 244 p.

P14

Regarding the crystallization process for iron carbon alloys with the participation of fullerenes

Ishbulatova R.I., Popova S.V.

Ufa State Petroleum Technological University

svetpv2007@yandex.ru

Iron alloys are spread in industry most widely. Main of them – steels and cast irons – present alloys of iron with carbon. In practice metal alloys are used with carbon content of no more than 5%. As known, quantitative content of carbon and its form play the decisive role in the development of properties of steels. Pure iron is soft, but should a little carbon be added, its strength and hardness increase. Traditionally it is deemed that carbon in the structure of iron carbon alloys exists in four forms: as a solid carbon solution in α -, γ -, and δ - iron; as carbides; as free carbon (flaked, tabulate, spherical graphite) and annealing carbon (amorphous carbon); as gas CO and CO₂ or, possibly, hydrocarbons, for example, CH₄.

However over the last years it has been ascertained, that carbon in Fe-C alloys (apart from its presence in the form of “traditional” phases) can acquire states which do not meet classical definition of phases. And considerable and in some cases even major part of carbon can be found in Fe-C alloys in these very states: in micro unevenness of alloy (close to the state of amorphous carbon); as Cottrell clouds; as segregations on dislocation clusters. The author [1] first detected fullerenes C₆₀ и C₇₀ in the structure of iron carbon alloys. Fullerenes develop in steels during crystallization and in the process of phase transitions. Endohedral fullerenes (complexes of iron with carbon) were also detected later in the structure of iron carbon alloys exposed to chemical-heat treatment (carbonization) [2].

A hypothesis has been advanced disclosing the mechanism of fullerenes development during crystallization. A group of scientists from Cambridge University observed (in situ) with the help of modified synchrotron radiation as silver surface “captured” a fullerene molecule. This phenomenon is explained by the development of covalent bonds between the surface of silver atoms and a fullerene molecule. Later this effect was also observed during interaction of fullerenes developing in the course of carbonization from the petroleum tar medium with the surface of steel [2].

At this point due to the lack of information regarding the nature of phases in the structure of iron carbon alloys and assumed participation of fullerenes in crystallization process it is deemed necessary to conduct theoretical research of this problem.

References

1. Закирничная М.М., Кузеев И.Р. Результаты исследования науглероженного слоя труб печей пиролиза/ III Международный конгресс и выставка «Защита-98», С.57-58, Закирничная М.М. Образование фуллеренов в углеродистых сталях и чугунах при кристаллизации и термических воздействиях. – Уфа: Гилем, 2002. – С. 180.
2. Попова С.В. Формирование металлофуллеренового слоя в ходе химико-термической обработки углеродистой стали/ Автореферат Дисс. на сосисание уч. степени канд. техн. наук. – 2010. – 25 с.

P15

The principle of calculation technique selection for electronic structure of phthalide derivatives

Kalimullina L.R.¹, Lachinov A.N.¹, Asfandiarov N.L.¹, Zhdanov E.R.², Baybulova G.Sh.²

1 Institute of Molecular and Crystal Physics USC RAS

2 Bashkir State Pedagogical University

KalimullinaLR@yandex.ru

The purpose of this work was to investigate the influence of an excess charge on electronic and geometrical structure, and to estimate theoretically ionization potential (IP) and electron affinity (EA) of some arylene-phthalides derivatives.

A lot of new electronic effects were discovered in thin films of polyarylene-phthalides. Its are related to transition from a dielectric state to a highly conducting one. Obviously, that the existence of such effects associated with changes in electronic structure of molecules of these polymers. Therefore, to explain the nature of the observed effects is extremely important to attract the methods of quantum-chemical modeling. The main method of research used the method of density functional theory UB3LYP/6-31 + G (d) level.

The report presents the results of geometry optimization and calculated the energy characteristics of model molecular systems. In particular, the total energy of the molecules and their negative and positive ions in the molecular ion and the optimized geometries, energies of upper occupied and lower unoccupied molecular orbitals, the vertical and adiabatic electron affinity and ionization potential for each of the system.

There are several approaches for the theoretical evaluation of the IP and EA. The first approach involves the use of Koopmans theorem approximation. For a quantitative agreement with experiment, the results of the calculation are scaling procedure $EA = a\varepsilon + b$, where a and b are constants. The second approach is a theoretical estimate IP and EA follows from the definition of the ionization potential and electron affinity.

We have carried out theoretical evaluation of ionization potentials and electron affinity energies of several model compounds under both approaches. The analysis results showed that these parameters are significantly different from each other. It is therefore proposed to determine a more accurate approach, the estimates of magnitude adiabatic electron affinity used as parameters of a statistical model that describes the process of an additional electron auto detachment of negative ions of the molecules.

P16

Long stripe transfer matrix simulation of viscoelastic properties of polymer filled with perfectly aligned platelets

Khudobin R.V., Timan S.A.

Semenov Institute of Chemical Physics RAS

rvhudobin@gmail.com

Dynamic mechanical testing (DMTA) has indicated an increase in heat-resistance of polymer-clay nanocomposites at a low weight fraction of clay. Specifically, the relative storage modulus of the polypropylene (PP) filled with 7 wt% of montmorillonite grows in a wide range of temperatures. A substantial decrease of the matrix storage modulus with increase of the temperature and, on the other hand, conservation of the platelets rigidity raises the reinforcing efficiency and may be one explanation of this effect.

In principle, self-consistent analytic approaches of composite mechanics are applicable for predicting hardening of polymer reinforced by rigid particles of highly asymmetric shape. Their solutions guarantee the shape of the inclusion is preserved: only its orientation and dimensions are changed. However, one intuitively expects a significant bending of strongly oblong or oblate ellipsoidal inclusions randomly placed in elastic medium. Hence, the effective moduli of such disordered heterogeneous materials predicted by self-consistent methods are inevitably overestimated.

The main objective of this work is to evaluate the influence of bending of rigid asymmetric inclusions on the reinforcing efficiency and the heat-resistance of polymer matrix composites.

The temperature dependences of the dynamic moduli of the polymer composites containing randomly located and perfectly aligned elastic inclusions were calculated on the basis of the solution of continuum mechanics boundary value problems by the finite element method (FEM). The first difficulty in our numerical simulation follows from the asymmetric shape of the inclusions, which requires a fine FE-mesh. The second one arises from the irregular structure of the heterogeneous system under consideration. A representative volume element (RVE) has to be large enough compared to the largest dimension of the inclusion to obtain an accurate statistical representation of viscoelastic properties of the disordered matrix composite. To overcome these problems, boundary value problems for the RVE in the shape of a long stripe (of length \gg width) were solved exactly by the transfer matrix method. Therefore, if the stripe is made long enough, all realizations of the statistical ensemble are included in a single calculation, and no averaging is necessary.

Our results compared with Halpin-Tsai equations show that bending deformations of inclusions, caused by non uniform mechanical fields, lower the stiffness of polymer composites. The effect is even stronger for higher concentrations and aspect ratios. Raising the temperature may either increase or decrease the degree of this effect, because of the competition of different factors which must be taken into account.

The temperature dependencies based on the FEM are close to those got from the experiments for pure PP (without any compatibilizer) and differ qualitatively from experimental data for PP with comatibilizers. Taking this into consideration, we can come up with a hypothesis that adding compatibilizer causes some changes in polymer morphology not taken into account in computer simulations.

P17

Revealing Non-Adiabatic Effects on Bi(111)

**Kraus P. (1), Tamtögl A. (1), Mayrhofer-Reinhartshuber M. (1), Campi D. (2),
Benedek G. (2), Ernst W.E. (1)**

*(1) Institute of Experimental Physics, Graz University of Technology, Graz, Austria
(2) Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Milano, Italy*

patrick.kraus@tugraz.at

The (111) surface of the semimetal bismuth exhibits unusual electronic and vibrational behavior. Due to its large spin-orbit coupling the bands for different spin orientations are not degenerate and give rise to a very good conductivity along the surfaces [1], while the bulk stays a very poor conductor. Additionally, those unique properties of bismuth cause an unexpectedly high corrugation of the surface electron density, perfectly suited for Helium Atom Scattering experiments. Those experiments reveal a practically non-reconstructed surface layer with a sixfold symmetry [2]. Additionally to the measured scattering features, small variations in the noise as well as strong fluctuations in the specular intensity give rise to a detailed description of the He-Bi(111) interaction potential. This potential supports bound states, which furthermore can lead to elastic and inelastic surface resonances. Especially the latter can explain the rather unusual data obtained in time-of-flight measurements.

Therefore, an extensive analysis of the inelastic scattering data was performed. Using a detailed model of the bismuth crystal and comparison to the simulation of the phonon dispersion on the antimony (111) surface [3], several non-adiabatic effects were revealed that are not accessible via ordinary DFPT simulations [4].

- [1] Yu. M. Koroteev et. al., PRL 93, (2004) 4
- [2] A. Tamtögl et. al., JPCM 22, (2010) 304019
- [3] D. Campi, G. Benedek, personal correspondence
- [4] J. Kröger, Rep. Prog. Phys 69, (2006) 899–969

P18

Nanostructured polyurethanes with immobilized *in situ* metal chelates

Lobko Eu.V., Kozak N.V., Klepko V.V.

*Institute of Macromolecular Chemistry, National Academy of Sciences of Ukraine
48 Kharkivske Shose, 02160, Kyiv, Ukraine.*

E-mail: lobko_zhenia@i.ua

Immobilization *in situ* chelate compounds of transition and rare-earth metal in linear and cross-linked polyurethanes results in nanoscale structuring of forming polymer. And it is accompanied of polymer matrix enrichment by the nanosize heteroligand macro complexes of metal formed simultaneously with organic nanosize structures characteristic for metal-free polymer. Nanostructuring of formed in this way polyurethane favours creation of a new hierarchy in structural organization of the polymer as compared with metal free system as well as changes in dynamic, relaxation, optical, dielectric, surface etc. properties of the modified polyurethane.

Metal containing polyurethanes were characterized using IR, UV-Vis, EPS, WAXS, SAXS, DRS, the optical microscopy and luminescent analyze.

Analysis of structural heterogeneity of metal-modified polymer indicates existence of two types of nanosize heterogeneities in the bulk of polyurethane. One of them is inherent to segmented PU and another is generated in the presence of transition metal chelate compound.

The essential increasing of luminescence intensity of the rare-earth metal in the polyurethane environmental is a way for creation of new optically active materials. The intensity of PU-Eu luminescence depends both on the europium chelate compound content and polymer topology.

The results obtained indicate significant influence of structural organization of the modified polyurethane on its properties. The effect is caused by complex formation between metal chelate compound and functional groups of the forming polymer. The analysis of dynamic of low molecular probes and complex formation in the nanostructured polyurethane gives experimental evidence of existence of additional coordination bond network in metal-contained polyurethanes.

P19

Ab initio studying of topological insulator under the stress

Lysogorskiy Y., Kijamov A., Nedopekin O., Tayurskii D.

Institute of Physics, Kazan Federal university, Kazan, Russia

A topological insulator is an unusual state of quantum matter which, while being an insulator in the bulk, has topologically protected electronic states at the surface. These states could be probably used in different applications, such as spintronics and quantum computing. However, in transport measurements, it has proven difficult to disentangle the surface contribution from the bulk conductivity, which is substantial even in the lowest carrier density samples. To distinguish surface and bulk contributions into transport properties an external pressure could be applied.

In the present work we have performed ab initio calculations of topological insulators under the strain. Calculations have been performed by means of DFT approach with taking into account the spin-orbit interaction, which is realized in the VASP code. It was found that hydrostatic pressure tends to increase electronic density of states in the bulk, whereas it did not modify sufficiently the surface states.

Thus, the results of ab initio calculations could complement the experimental investigations of high pressure transport properties in topological insulators samples and the experimentally detected growth of carrier density could be related to the bulk transport properties.

Biologically-active Nanocomposites with Self-Healing Effect

Mirsakiyeva A., Iskakov R., Yu V.

*Kazakh-British Technical University,
59 Tole bi, Almaty, Kazakhstan, 050000*

e-mail: aminam2011@inbox.ru

During the last decade self-healing materials were implemented by world-leading companies such as Nissan who is synthesizing special paints for automobiles and iPhones which could heal microdamages.

The aim of research was to create self-healing coatings which could provide some pharmaceutical properties. Experiments were based on microencapsulation process: the reagent was encapsulated to mechanically unstable polymer. There were used two types of reagent – linseed oil as healing agent and several biologically-active substances as pharmaceutical agents. The reaction type is polycondensation.

Method of research:

1. Creation of mixture of organic phase with reagent (self-healing or pharmaceutical) and water phase with shell polymer;
2. Synthesis of two types of microparticle by rotation and heating of mixture;
3. Washing of microparticles with ethanol solution;
4. Synthesis of coating polymer;
5. Analysis of created coating to self-healing and pharmaceutical effects.

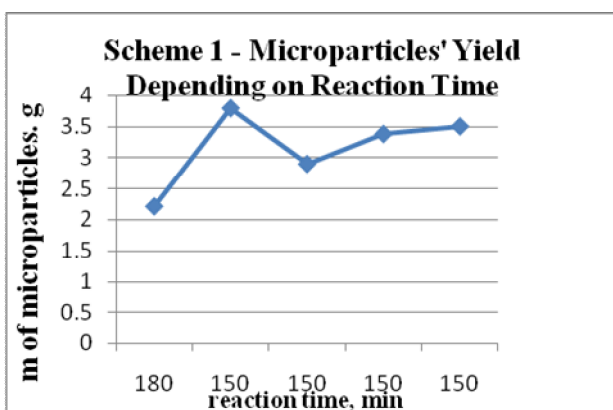


Fig 1 – Microparticles containing self-healing agent

Created microparticles (Fig. 1) have almost ideal spherical shape with low porosity. Analysis of microparticles showed that optimal sizes of microcapsules are 30-50 microns. The quality of microparticles depends on temperature (about 45-50°C), rotation (average) and reaction time. The minimum time of synthesis – 150 min (Scheme 1). Created capsules were tested for realize and showed high level of capsulation of reagent.

Useful links:

- [1] «Self healing in polymers and polymer composites. Concepts, realization and outlook: A review» by Y.C. Yuan, T. Yin, M.Z.Rong, M.Q.Zhang // Zhongshan University, Guangzhou 510275, P. R. China, 2008.
- [2] NATO SfP 982837 project “Nature-Like Self-Regenerating polymer Coatings for the Protection of Space Devices”, Final Report, by Alain Perichaud (Marseille, France), Rinat M. Iskakov (Almaty, Kazakhstan), August 2011.

P21

Molecular dynamics simulations of plastic thermostable nanocomposites

Nazarychev V.M.¹, Larin S.V.¹, Gurtovenko A.A.^{1,2}, Lukasheva N.V.¹, Yakimansky A.V.¹,
Lyulin S.V.^{1,2}

¹ Institute of Macromolecular Compounds RAS, Bolshoi pr., 31, St.Petersburg, 199004, Russia

² Department of Physics, Saint Petersburg State University, Petrodvorets, Ulyanovskaya Str., 46, St.Petersburg, 199504, Russia

nazarychev@imc.macro.ru

Typical equilibration times (t_{eq}) of atomistic computer simulations of melts of heat-resistant polymers are usually in the range 1-10 ns and in most cases no longer than 100ns; t_{eq} is determined by the relaxation time of the squared radius of gyration R_g^2 for a single chain. Such a definition of t_{eq} can be inexact and can lead to incorrect calculation of glass transition temperature T_g .

In present study we considered three types of plastic polyimide (PI) matrices on the base of dianhydride 1,3-bis-(3',4,-dicarboxyphenoxy)-benzene and one of three diamines: 4,4'-bis-(4''-aminephenoxy)-diphenyl sulfone, 4,4'-bis-(4''-aminephenoxy)-diphenyl, and 4,4'-bis-(aminephenoxy)-diphenyl oxide. Computer simulations were carried with the help of the GROMACS package. Partial charges were calculated by different methods with the use of semi-empiric and *ab initio* quantum-mechanic simulations. For all calculated types of partial charges we observed that typical times of the single chain diffusion at 600K on a distance comparable with R_g are around 100 μ s. To decrease t_{eq} of PI melts we simulated equilibration of neutral PI melt. Typical times associated with diffusion of a single polymer chain on a distance R_g in a neutral melt was decreased to \sim 500ns, i.e. t_{eq} was considerably reduced. After turning on partial charges in polyimide melts all local reorganizations of a structure were characterized by the times as short as \sim 10 ns. The 1 μ s-long simulations performed showed that the degree of equilibration of neutral samples of the studied PIs influenced considerably the corresponding values of T_g . After adding a short single-walled carbon nanotube (SWCNT) in the neutral melt of the investigated PIs we observed an increase of t_{eq} . We also witnessed re-orientation of benzene rings of the PI along the SWCNT surface which agrees well with known experimental data.

This work was carried out under financial support of RFBR grant № 11-03-00944-a and in the framework of the state contract № 16.523.12.3001 with Ministry of Science and Education of Russian Federation. Computer simulations were carried out on the computer cluster of IMS RAS and supercomputers "SKIF-Chebyshev" and "Lomonosov" of Moscow State University.

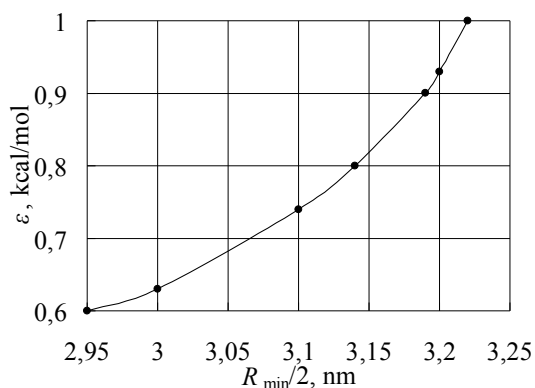
Molecular dynamics study of reverse micelle: the single-atom model of a solvent

Nevidimov A.V.

Institute of Problems of Chemical Physics RAS, Chernogolovka

nevidimovsasha@yandex.ru

The reverse micelles are nanoreactors that spontaneously form in “water-in-oil” systems at presence of surfactant molecules, and that are widely used for synthesis of nanoparticles with uniform shape, size, and composition. In addition to experimental approaches, computer simulation techniques are employed to investigate their structure. The most useful technique is a molecular dynamics simulation. It is necessary to use a simulation time scale up to tens or hundreds of nanoseconds [1]. However there is a difficult – huge number of atoms ($>10^5$) when detailed full-atomic models are used to describe water, surfactant, and solvent molecules. In this work a single-atom model for solvent is suggested and parameters for this model are found. Use of this model along with full-atomic models for water and surfactant provides detailed information about reverse micelles and reduces simulation cost by factor of ten [1].



All simulations were carried out by NAMD 2.8 program [2] at JSCC [3]. 64 processors were used for each simulation. Two simulated boxes contained 17^3 hexane molecules. In one box, molecules were described on detailed level; in another box, they were specified on simplified level. Parameters of simplified model ($R_{\min}/2$ and ϵ) were varied in order to reproduce density of detailed hexane (NPT ensemble, figure).

After that two reverse micelles were prepared: one with detailed hexane (131 255 atoms), another with simplified one (12 360 atoms). Properties of both micelles were studied.

This work was supported by the Russian Foundation of Basic Research, project no.10-03-00726a, and Federal Targeted Program, Scientific and research-educational cadres of innovative Russia on 2009-2013 years, project P673.

1. Nevidimov A.V., Razumov V.F. *Molecular Physics*, 2009, **107**, 2169.
2. Phillips J.C. *Computational Chemistry*, 2005, **26**, 1781.
3. Joint Supercomputer Center of RAS <http://www.jscs.ru/hard/mvs100k.shtml>

Electronic and optical properties of hafnia polymorphs

Perevalov T.V., Gritsenko V.A.

*Institute of Semiconductor Physics, Siberian Branch of Russian Academy of Sciences,
13, Lavrentieva Ave, 630090, Novosibirsk, Russia,*

E-mail: timson@isp.nsc.ru

Hafnia (HfO_2) is a wide band gap material, with a high dielectric constant, which has wide applications in optical and protective coating technology. HfO_2 is the most promising candidate to replace SiO_2 as gate oxide in metal-oxide semiconductor devices. These applications require knowledge of its electronic and optical properties. Oxygen vacancies are dominating intrinsic defects in the bulk of many high-k oxides including HfO_2 and are also thought to be presented in high concentrations in thin films [1]. However, in spite of numerous experimental studies, the role of oxygen vacancies in HfO_2 is still circumstantial. For instance, the measured defect energy levels differ considerably among the various experiments [2].

We used pseudopotential approach within spin-polarized generalized gradient approximation (GGA) of density functional theory (DFT) and hybrid DFT using the Quantum-ESPRESSO code. We calculated the oxygen vacancy in c-, t- and m- HfO_2 using 81, 108 and 96 atom supercells, respectively. An O atom was removed and the atomic positions were relaxed in GGA.

The fully relaxed structures and band gaps of c-, t- and m- HfO_2 agree very well with experimental data. From the band structure, the carrier effective masses and the complex dielectric function are obtained. In c- and t- HfO_2 both - light and heavy electrons and holes are presented, whereas m- HfO_2 shows only heavy charge carriers. The electron effective masses are shown to be several times heavier than the electron tunneling effective mass in amorphous HfO_2 [3].

After calculating of the Born effective charge tensors and the force-constant matrices, the lattice dielectric permittivity tensors for the c-, t- and m- HfO_2 are computed by decomposing the tensors into the contributions from individual infrared-active phonon modes. The calculated dielectric constants vary widely from phase to phase. The t- HfO_2 has the highest dielectric constants relative to other phases.

The neutral vacancies create one gap state which is doubly occupied. This level lies above the valence band edge at 1.8 eV in simple DFT and at 3.15 eV in hybrid DFT calculations. The second localized vacancy state is also found in the density of states at 6 eV, essentially at the conduction band edge.

It was obtained that electron and hole capture on oxygen vacancy is energetically favorable process. The energy gain for electron capture is 0.1 eV, 0.2 eV, 0.1 eV, whereas energy gain for hole capture is 2.7 eV, 2.7 eV, 2.6 eV for c-, t- and m- HfO_2 respectively. Thus oxygen vacancy can play role of charge localization center.

The calculated ELS spectrum (i.e. $-\text{Im}1/\epsilon$) of m- HfO_2 supercell with oxygen vacancy shows a wide absorption peak at 2.5-4.0 eV, which is attributed to an oxygen vacancy. This result is compared with experimental absorption peak that exists in the range 4.5-5.0 eV in absorption spectra $(\alpha h\nu)^{1/2}$ for polycrystalline HfO_2 [6]. The discrepancy is required the following investigations.

- [1] J. Robertson, Rep. Prog. Phys. Vol. 69 (2006) 327–396
- [2] F. Rochette et al, Microelec. Eng. 86 (2009) 1897-1900
- [3] H.T. Takeuchi et al, Appl. Phys. Lett. 83 (2003) 788-780
- [4] S.-G. Lim et al, J. Appl. Phys. 91 (2002) 4500-4505
- [5] M. Baloget al, Thin Solid Films. 41 (1977) 247-259
- [6] H. Takeuchiet al, J. Vac. Sci. Technol. A 22 (2004) 1337

Pressure induced ferroelastic phase transition in LiLuF₄ compound

Petrova A.*¹, Nedopekin O.¹, Tayurskii D.¹

¹*Institute of Physics, Kazan Federal University, Kazan, Russia*

*A.Petrova: npetrova131@gmail.com

A great progress has been done in the last years in the study of the pressure-effects on the structural and mechanical properties of scheelite compounds $MLiF_4$, where M stands for lanthanides^[1]. The interest to the LiLuF₄ compound was invoked by the fact that this material possesses the own electrical dipole moment in some temperature range. When a stress is applied the present material undergoes to the ferroelastic transition^[2], but the nature of this phase transition is still under the question. The study of LiLuF₄ behavior is very important for understanding the evolution of ferroelasticity under the pressure. We performed *ab-initio* calculations by means of DFT^[3,4] (density functional theory) with using VASP 5.2^[5] (Vienna Ab-Initio Simulation Package) program package, the part of the MedeA@interface². We have analyzed the structure parameters of LiLuF₄ for two possible crystal symmetries I4₁/a and C12/c1 versus the pressure. The structure with C12/c1 symmetry transforms to the structure with I4₁/a symmetry at pressure near 10.5 GPa. The change of symmetry can be associated with displacement of a certain type of atoms in the crystal lattice, or with a change in the crystal order in the material.

To specify the point of phase transition we have analyzed the order parameter. The scheelite to fergusonite phase transition can be classified, in conventional terms^[6], as a proper ferroelastic transformation. In such transition, the second-rank strain tensor components play the role of a primary order parameter. We can use such kind of order parameter because the fergusonite structural model (space group C12/c1) was derived from the model of scheelite type (space group I4₁/a^[7]) on the basis of supergroup–subgroup relationships. We have found a sharp change of the behavior of order parameter at 10.5 GPa.

To understand the nature of phase transition we have investigated the behavior of the unit-cell volumes of LiLuF₄ for two symmetries until 20 GPa. These volumes are practically the same and change smoothly with pressure increasing up to 10.5 GPa. As we know the energy and the volume of the unit cell at the second-order phase transition should not be changed sharply. The second order phase transitions are accompanied by changes in the symmetry of the crystal lattice. Other phase transitions are not observed until 20 GPa.

Thus, in this work we present a density functional theory (DFT) analysis of ferroelastic phase transition for LiLuF₄ scheelite (I4₁/a, $Z = 4$) structure under the pressure. The ferroelastic phase transition from the tetragonal structure of LiLuF₄ to fergusonite structure (C12/c1, $Z = 4$) was found near 10.5 GPa. Based on the experimental paper^[2] we have determined the nature of ferroelastic phase transition. A good agreement with experimental results has been obtained.

1. B. Minisini, P. Bonnaud, Q. A. Wang, F. Tsobnang, Computational Materials Science **42**, 156–160 (2008).
2. A. Grzechnik, K. Friese, V. Dmitriev, H.-V. Weber, J.-Y. Gesland, W. A. Crichton, J. Phys.: Condens. Matter **17**, 763–770 (2005).
3. P. Hohenberg, W. Kohn, Phys. Rev. B **136**, 864 (1964).
4. W. Kohn, L.J. Sham, Phys. Rev. A **140**, 1133 (1965).
5. G. Kresse, J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
6. S. Tsunekawa, T. Kamiyama, K. Sasaki, H. Asano, F. Fukuda, Acta Crystallogr. A **49**, 595 (1993).
7. E. Garcia, R. Ryan, Acta Crystallogr. C **49**, 2053 (1993).

²Materials Design, S.A.R.L.

Ab initio and semi-empirical studies of Cr atoms on superfluid He nanodroplets

Pototschnig J.V., Ratschek M., Koch M., Ernst W.E.

Institute of Experimental Physics, Graz University of Technology, Graz, Austria

E-Mail: jpototschnig@student.tugraz.at, markus.koch@tugraz.at

He nanodroplets (HeN) are a promising tool to synthesize nanostructures at 0.4 K in a quantum matrix environment. Particles can be spectroscopically investigated in situ and have recently been deposited on surfaces [1]. Dopants (atoms or molecules on HeN) can either reside on the surface or inside the HeN, which is crucial for the formation of nanostructures and for the amount of spectroscopic perturbation. The location can be determined theoretically by DFT calculations or the Ancilotto parameter [2], both requiring the dopant-He pair potential. DFT calculations directly show the He density of a doped HeN based on the Orsay-Trento functional [3].

We are especially interested in Cr as a dopant because of its outstanding magnetic properties. Cr has a septet groundstate and a weak van der Waals interaction with He. Cr lies in the threshold region between inside- and surface-residing atoms on HeN. Both methods DFT calculations and the Ancilotto parameter are sensible to alterations of the Cr-He pair potential curve. We studied the Cr-He pair potential with various post SCF methods and basis sets^a using Molpro [4]. Based on restricted open shell SCF calculations including relativistic Douglas-Kroll corrections, we applied CCSD(T), CI, and multireference perturbation theory (RS). We applied counterpoise correction for the basis set superposition error and extrapolated to the basis set limit. Based on the obtained pair potentials, we calculated the Ancilotto parameter and show first results of our DFT calculations. Our recent theoretical studies indicate that Cr resides inside HeN.

Our group also investigates the Cr-HeN complex experimentally by means of mass and laser spectroscopy. The location of Cr on HeN has not yet been determined experimentally.

We are interested in the formation of Cr clusters on HeN experimentally and theoretically. The magnetic properties of Cr clusters are the key aspects of ongoing and future research.

[1] E. Loginov, L. F. Gomez, A. F. Vilesov, J. Phys. Chem. A 115, 7199 (2011)

[2] F. Ancilotto, P. B. Lerner, and M. W. Cole, J. Low Temp. Phys. 101, 1123 (1995)

[3] F. Dalfovo, A. Lastrì, L. Pricauptenko, S. Stringari, and J. Treiner, Phys. Rev. B 52, 1193 (1995)

[4] MOLPRO, version 2010.1, a package of ab initio programs, H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, and others, see <http://www.molpro.net>.

^aCr: aug-cc-pwCVNZ-DK; He: aug-cc-pVNZ-DK (for N = T, Q, 5) (EMSL Basis Set Exchange)

P26

Charge transfer engineering via selective doping of oxides: Cr-doped MgO versus Mo-doped CaO

Prada S., Giordano L., Pacchioni G.

Dipartimento di Scienza dei Materiali, Università degli Studi di Milano-Bicocca, Italy

stefano.prada@unimib.it

The optimization of the structure and electronic properties of oxide supported metal catalyst in order to augment their conversion and selectivity is a goal in catalysis research. In particular, it is of special interest the ability to control their size, shape, crystallinity and charge state. Different approaches are possible to manipulate the properties of metal supported particles, introducing anchoring sites or adjusting metal-support interactions. The control of metal-support interactions is possible by selecting the proper combination of materials or by modifying the substrate by means of doping, a powerful and versatile approach to tailor the fundamental properties of oxide materials; this technique is based on the ability of the dopants to exchange electrons with the host oxide lattice or with adsorbates bound to the surface. The charge of the adsorbed clusters is strongly related to their shape and activity, for example it is well known that Au nano-particles adopt compact 3D shape when neutral, but form 2D islands when charged. In this poster, by means of theoretical DFT calculations, compared with STM experimental data, two model-systems for doped oxide materials are presented that have iso-structural and iso-electronic properties but behave completely different: Mo doped CaO and Cr doped MgO. STM analysis shows that while Au grows in 3D cluster over pristine thin films of CaO, monolayer 2D islands are formed over Mo:CaO thin films. On the contrary no change in shape is found for Au over Cr:MgO where all the particles remain 3D, meaning that Cr does not transfer charge to the adsorbed gold like Mo does. In a non-defective system when the dopants replace one cation in the oxide lattice they take a +2 charge. In contrast to the experiment DFT calculations show that both Mo^{2+} and Cr^{2+} are able to transfer one electron to the adsorbed atom, predicting that the 3D to 2D change would take place in both systems. In real system, however, electron traps are present that can drain charge from the impurity, resulting in a further oxidation of the dopant atoms. To account for the presence of intrinsic charge traps in MgO and CaO films, we have calculated the Au binding behavior and charge state for cases in which the dopants have already lost one electron to trap sites. While Mo^{3+} is still able to donate one electron to the adsorbed Au, Cr^{3+} is not, according to the experimental evidence. The different behavior of Mo and Cr is ascribable to the relative positions of the d-level of the dopants and the half filled 6s level of the Au; while the 6s levels fall below the t_{2g} levels of Mo in the 3+ state, they are located above the t_{2g} level of Cr^{3+} . Also the host matrix plays a role in the charge transfer process, in fact according to the crystal field theory the larger lattice parameter of CaO pushes the Mo^{3+} levels to higher energy enforcing the energy gain involved in the charge transfer to the adsorbed metal atom.

An activation of C≡C bond in gold-containing systems: DFT study

Ratmanova N.K., Mukhamedzyanova D.F., Pichugina D.A., Kuz'menko N.E.

M.V. Lomonosov Moscow State University, Moscow, Russia

e-mail: n.ratmanova@gmail.com

Gold nanoparticles supported on metal oxides are active and selective catalysts in the conversion of alkynes. An activation of C≡C bond is a key step in hydrogenation, oxidation and isomerization reactions. The investigation of adsorptive sites of gold nanoparticles and the evaluation of support influence on these sites are necessary for the design of new highly efficient catalysts.

In the present work the results of simulation of the simplest alkyne C₂H₂ adsorption onto neutral and charged cluster Au₁₂ (2D and 3D isomers), as well as onto the MgO(100) surface are described. The calculations were performed using the density functional theory (DFT/PBE) in the programs “Priroda 08” and “CASTEP 5.5”. Relativistic effects were taken into account using a scalar-relativistic approach. MgO(100) was investigated using a plane wave basis set and ultrasoft pseudopotentials under periodic boundary conditions.

The adsorption of C₂H₂ onto Au₁₂ cluster is accompanied by the formation of complexes where hydrocarbon bonded with the low-coordinated atoms of the cluster. The C₂H₂ adsorbs onto 2D isomer with the formation of π-complex (Q_{ads} = 75 kJ/mol), while the adsorption onto 3D isomer results in the bridge-type complex formation and a strong change of the carbon atoms hybridization from sp to sp³ (Q_{ads} = 139 kJ/mol). The molecular orbital analysis of the complexes indicates the interaction to occur via a donor-acceptor mechanism involving the HOMO of the hydrocarbon and the LUMO of the gold cluster. The preferable adsorption of C₂H₂ onto 3D over 2D cluster was found out based on the calculated adsorption heats, which is important for the design of the catalysts. The adsorption of hydrocarbons onto Au₁₂⁺ (Q_{ads} = 113 and 172 kJ/mol for 2D and 3D isomers respectively) and Au₁₂⁻ (Q_{ads} = 96 and 132 kJ/mol for 2D and 3D isomers respectively) clusters is accompanied by an increase in adsorption heats due to effective overlap between frontier orbitals of hydrocarbon and a cluster. It was shown that charge effect is more apparent than structural effect on adsorption. The dissociative adsorption of C₂H₂ onto the cluster is characterized with the high activation barriers (E_a = 127 and 125 kJ/mol for 2D and 3D isomers respectively). The C₂H₂ adsorbs on the MgO(100) surface physically in such way that the C≡C bond is coordinated above Mg²⁺ centers and hydrogen atoms are coordinated above O²⁻ centers.

This work was funded by grant of the President of the Russian Federation for state support of young Russian Ph.D. scientists (MK-107.2011.3) and RFBR (10-03-00999). The calculations were performed using supercomputer SKIF MSU “Chebyshev”.

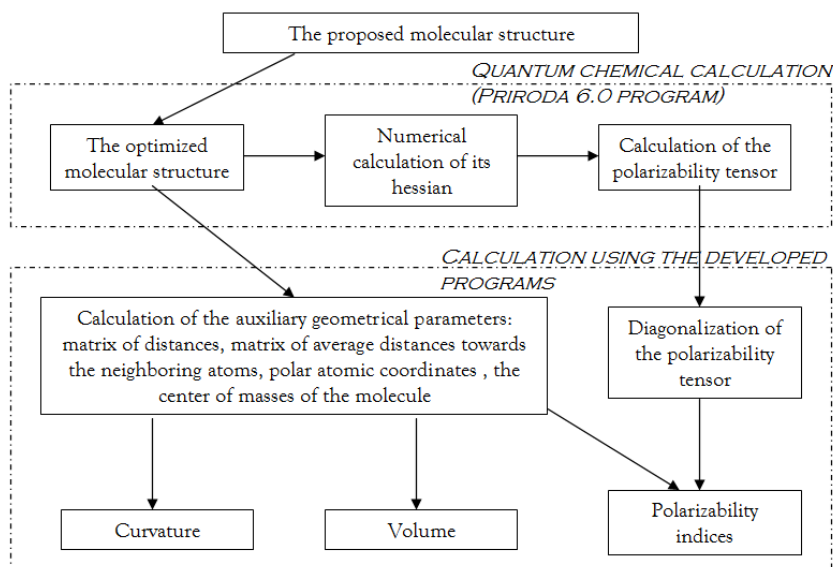
Molecular simulation on fullerene derivatives: algorithms and programs for calculation of their curvature, polarizability and volume

Sabirov D.Sh., Saitgalina A.D., Garipova R.R., Tukhbatullina A.A., Bulgakov R.G.

Institute of Petrochemistry and Catalysis of Russian Academy of Sciences

diozno@mail.ru

Currently, the reactivity and physicochemical properties (e.g., polarizability) only of C_{60} and C_{70} fullerenes have been measured experimentally, while these properties of their derivatives and higher fullerenes are studied mainly by quantum chemical methods. Previously, we have worked out several algorithms for calculation reactivity indices (local curvature, polarizability index, and volume) and mean polarizabilities of fullerenes and their derivatives. The use of the listed properties for theoretical studies of fullerenes reactivity leads to the results that are in good agreement with the experimental data. However, it is hard to apply these algorithms to larger systems (bulky fullerenes, nanotubes) that contain hundred atoms. So, we have developed the programs for the analysis of the structure of fullerenes and their derivatives and calculation of their reactivity indices based on the results of quantum chemical calculations in Priroda 6.0 program:



The use of our programs allowed us to study reactivities of higher (C_n , $n > 70$) and bulky fullerenes (C_{540}) towards molecules and radicals [1], to obtain the dependence of the polarizability of fullerene derivatives $C_{60}X_n$ on the number of X added [2], to analyze nanocones reactivity [3].

[1] a) D.Sh. Sabirov, R.G. Bulgakov, S.L. Khursan, U.M. Dzhemilev, Dokl. Phys. Chem. **425** (2009) 54; b) D.Sh. Sabirov, R.G. Bulgakov, Comput. Theor. Chem. **963** (2011) 185.

[2] a) D.Sh. Sabirov, R.G. Bulgakov, Chem. Phys. Lett. **506** (2011) 52; b) D.Sh. Sabirov, R.G. Bulgakov, Chem. Phys. Lett. **523** (2012) 92.

[3] D.Sh. Sabirov, R.G. Bulgakov, S.L. Khursan, ARKIVOC part 8 (2011) 200.

Computational investigation on water-poly(vinyl metylether) interactions

Saramak J., Kozanecki M.

*Department of Molecular Physics, Faculty of Chemistry, Lodz University of Technology,
Zeromskiego 116, 90-924 Lodz, Poland*

Gels are important in everyday life. More and more ideas for hydrogels goes for daily use, such as contact lenses, semi-permeable membranes, a drugs delivery and treatment systems. The gels sensitive to stimuli are particularly interesting. They exhibit a thermo-responsive phase transition commonly associated with the lower critical solution temperature - leading to a sudden change of physical properties. This transition results from the changes in water-polymer interactions. Poly(vinylmetylether) PVME is a well know representative of stimuli responsive gels and it was chosen as a model system because of its simple chemical structure.

Flowering of computational chemistry allowed to count ever large systems consisting of hundreds atoms. The aim of our study was to investigate the effects of thermal induced shrink of PVME in water. It is clear that the water-polymer interactions play a crucial role in such transition. Both the hydrogel and the aqueous solutions of linear PVME have been already well characterized by various experimental techniques but up to now it has not yet clearly stated the possibility of PVME:H₂O 1:2 complex formation, as it was proposed in literature [1]. In this work the PVME: H₂O 1:1, 1:2, etc. systems, with different chain lengths (from dimer to pentamer) were investigated. Water-PVME relationships were examined using computational chemistry using MP2 and DFT methods and based functional 6-31G (d, p). MP2 method was chosen because it gives good results for the hydrogen bonds and frequencies in water systems, DFT method was used because it is faster and it allow to study bigger systems comparing to MP2 method. In presented work the thermodynamic functions and energy of intermolecular interactions between PVME and water will be discussed, as well as a structure of hydration layer formed around the PVME chein. All obtained results will be supported by experimental results of IR and Raman spectroscopy as well as differential scanning calorimetry.

[1] E. Loozen, K. Van Durme, E. Nies, B. Van Mele, H. Berghmans, *Polymer*, Volume 47, Issue 20, 20 September 2006, Pages 7034-7042

P30

Size dependence of drift mobility in thin organic layers: Monte- Carlo and analytic modeling.

Sukharev V.M., Sannikova N.A., Nikitenko V.R., Strikhanov M.N.

National Reserch Nuclear University “MEPhI”, Moscow, Russia

Hopping transport of charge carriers in thin (< 100 nm) organic layers, which are suitable for organic light- emitting diodes and solar sells, is modeled in the framework of Gaussian disorder model. Monte-Carlo simulations yield considerable decrease of drift mobility with thickness of the layer in good agreement with the developed analytic model. Temperature dependence of drift mobility varieties considerably from that is typical for thick (> 1000 nm) layers. Quasi- equilibrium initial distribution is considered in order to omit effects of dispersive transport.

P31

A DFT study on the mechanism of silver-catalyzed propylene epoxidation.

Snyga Yu.G., Beletskaya A.V., Pichugina D.A., Kuz'menko N.E.

M.V. Lomonosov Moscow State University, Russia

e-mail: julia.g.snyga@gmail.com

Propylene oxide is one of the most important commodity materials produced by the chemical industry. Propylene oxide is used to produce propylene glycols ethers and propylene carbonate. Current commercial technologies for producing propylene oxide either use chlorine to promote the oxidation of propylene. These technologies are less efficient than direct oxidation of propylene because they generally generate significant amounts of other products, some of which are environmentally unfriendly. Fundamental research has shown that nanostructured silver catalysts may provide a route to such a direct oxidation process that is more environmentally friendly than currently used catalytic chemistries. However, the usage of silver catalysts in the reaction with propylene has been limited by low conversion and low selectivity towards propylene oxide and a detailed understanding of the mechanism is yet to be established.

The main aim of this study was to investigate the influence of the structure of the active center of the tetrahedral Ag₂₀ cluster on the mechanism of the epoxidation reaction. Calculations was performed in the framework of DFT/PBE approach with relativistic all electron basis set.

Modeling of Ag₂₀O complexes have revealed that oxygen atom is coordinated on the top and edge atoms of Ag₂₀. Ag₂₀O with oxygen on the top of Ag₂₀ is 26 kJ higher in energy than complex containing oxygen atom on the edge of a cluster. Oxygen atom leads to deformation of the initial Ag₂₀ clusters.

Epoxidation reaction on both the top and edge of the cluster goes through the formation of a five-membered oxametallacycle consisting of two silver atoms and a –O-C-C- fragment and four-membered oxametallacycle including a single silver atom and –O-C- fragment correspondingly. At the end of catalytic cycle Ag₂₀ cluster restores tetrahedral structure.

These results are necessary to improve the efficiency of the catalyst in the selective oxidation of propylene to propylene oxide.

Calculations have been performed using 'Lomonosov' and 'Chebyshev' supercomputer of Moscow State University.

This work has been financially supported by grants of Russian Federation President MK-158.2010.3, MK-107.2011.3 and grant for Leading scientific groups of Russian Federation NSh-6512.2010.3.

Methods for modeling the processes of structure formation during the heat treatment of samples from high-temperature nickel alloys.

Svetushkov N.N.

Moscow Aviation Institute (National Research University)

e-mail: svt.n.n@mail.ru

An important task in the manufacture of parts in the aviation industry (details propulsion systems) is a rational choice of modes of heat treatment, which on one hand would provide the desired hardness of the work surface, and the other would not lead to the formation of high thermal and residual stresses. As is known, the best performance characteristics for samples from a material having a finely dispersed structure that promotes wear resistance and heat resistance, which is provided by the most intense mode of cooling during heat treatment.

The most common methods of mathematical modeling of ongoing physical and chemical processes (eutectoid transformation) are based on the solution of unsteady heat conduction equations for the media, thermal parameters which depend on temperature. If we turn to a more complex model that takes into account the kinetics of the process - the probability of nucleation of a new phase and their rate of growth, the presence of a complex boundary region, almost makes it impossible to formulate the problem in the differential formulation (difficult to put conditions on amending the border, consisting of nuclei of different sizes and to compute the finite element method, which must be rebuilt at each step time).

The author proposes an approach, which is an extension of earlier results [1,2], in which the description of the processes of heat transfer by means of integral equations. In this case, the conditions at the interface (continuity of heat fluxes) are satisfied automatically, and therefore consideration of the boundary geometry does not represent significant challenges - it affects only the shape of the kernel of the integral operator.

Literature:

1. Svetushkov N. Geometric integral methods in simulation of thermal processes. // 4th International Conference on Thermal Process Modeling and Computer Simulation. Shanghai, CHINA. 28 May-3 June 2010, P. 60-61.
2. Светушков Н.Н. Моделирование процессов поверхностной закалки геометрически сложных изделий // Технология металлов. 2010. № 3. С. 23-29.

New shape controlled nano-fillers for rubber reinforcement

Tadiello L.¹, Wahba L.¹, D'Arienzo M.¹, Scotti R.¹, Morazzoni F.¹

1 INSTM, Department of Materials Science, University of Milano-Bicocca, Via R. Cozzi 53, 20125 Milano, Italy

luciano.tadiello@unimib.it

The reinforcement of elastomeric materials by using inorganic fillers is still an open challenge both from the industrial and fundamental point of view. Fillers may have effect on processability, stiffness, strength, ultimate strain, fracture toughness, energy dissipation, friction and wear. These effects depend on type, quantity and dispersion of the filler and on filler-filler and filler-rubber matrix interactions. It is expected that both the particle size and, though less studied, the particle shape of the fillers are able to modulate the two types of interactions. In particular, at the same filler amount the reduction of the particle size would increase the filler-matrix interface area. Moreover, nanosized particles with anisotropic shaped particles could extend the filler-rubber interface with respect to isotropic shape which produce a convenient extent of clustering (filler-filler interaction). By keeping constant the filler size, the number of filler-filler interactions increases with the filler amount. On the other hand, the filler-rubber interaction is strongly dependent on the chemical structure of both filler and polymer matrix and the introduction of suitable functionalities on the two components could properly enhance this interaction.

Based on previous considerations, aim of the present work was the synthesis of isotropic/anisotropic shape controlled silica nanofillers for the production of rubber composites, thus optimizing the performances of the final product. The goal was to investigate the relationship between the structure and the properties of the composites and the influence of the shape and size of the filler on the filler-filler and filler-rubber interactions, which are related to the optimization of composite performances. The synthesis of silica filler was performed by sol-gel procedure, using a surfactant (CTAB) as scaffold agent to drive the particle growth into different shapes. Silica nanowires, nanorods and nanospheres were obtained, all exhibiting mesoporosity, which were supposed to show different mechanical behavior of their rubber compounds. The different shaped nanofillers were also functionalized by grafting proper silanes coupling agent in order to compatibilize the filler particles with the rubber matrix through chemically reactive groups, capable of modulating the filler-rubber interactions. The obtained nanoparticles were mechanically blended with rubber and the filler structure and its dispersion into the matrix were studied by morphological analysis (SEM,TEM). The mechanical behavior of the compounds was determined through dynamic-mechanical analysis and the outcome of these tests was correlated to the fillers and compound morphology.

Interactions Between Nanoscale Crystalline Components In Hybrid Inorganic-Organic Biomaterials From Calcium Phosphates And Bacterial Cellulose.

Tolmachev D.A., Lukasheva N.V.

Institute of macromolecular compounds RAS

dm_tolmach@pochta.ru

Hybrid inorganic-organic composites are the most promising materials for implants which intended to replace bone. Properties of these materials should be similar to properties of bone. Studies in recent years [1] showed that the composites perspective for creation of bone grafts can be obtained by mixing aqueous suspensions of pre-synthesized components: calcium phosphates (CP), which are analogues of the mineral component of natural bone and chemically pure bacterial cellulose (BC) having mechanical characteristics comparable with those of collagen (organic component of natural bone). The properties of the composite materials directly depend on the binding strength of organic and mineral phases, that in turn depends on the intermolecular interactions at the phase boundaries. The aim of the present research was to find out the interactions which are responsible for the adhesion of CP nanocrystals and BC nanofibers, as well as the dependency of these interactions on morphology and chemical structure of CP crystallites.

Two crystalline structures of CP (hydroxyapatite and whitlockite) of two morphologies (plate-shape and rod-shape) were considered. Structural data about cellulose I β was used to create model of BC. The calculations of the structures of inter-facial regions were performed by potential energy minimization.

It is shown that the adsorption of CP nanocrystals on BC fibers is profitable in energy and their interaction has an attractive character. The main contribution to the binding of CP and BC make electrostatic interactions. The magnitude of the CP-BC interfacial energy depends on the structure and morphology of CP crystals, It turned out that rod-shaped crystals of whitlockite are most strongly adsorbed on the organic matrix. These crystals are recommended to use for the preparation of the most mechanically stable CP-BC composites.

References

1. Baklagina, Yu. G.; Lukasheva, N. V.; Khripunov, A. K.; Klechkovskaya, V. V.; Arkharova, N. A.; Romanov, D. P.; Tolmachev D. A. Interaction between Nanosized Crystalline Components of a Composite Based on *Acetobacter Xylinum* Cellulose and Calcium Phosphates *Polymer Science, A*, **2010**, 52, (4), 419–429.

Computational Modeling the Synthetic Polymer Selective Interactions with the HIV-1 Entry Nanomediators

Tsvetkov V.B.^{1,2}, Veselovskiy A.V.², Karaseva E.N.^{1,3}, Serbin A.V.^{1,3}

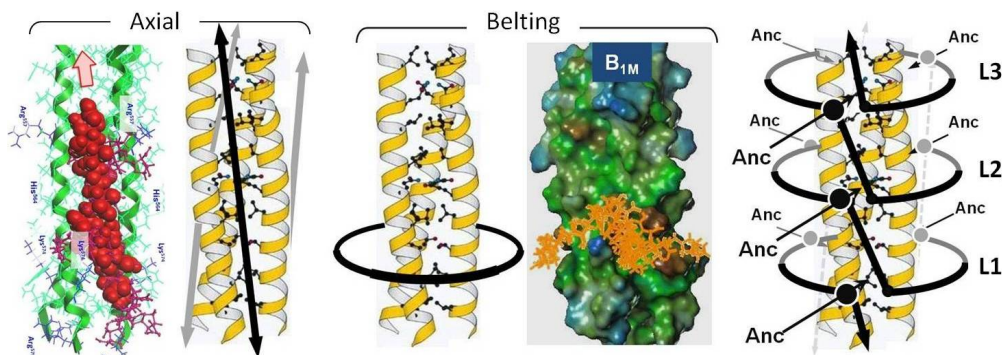
¹ A.V. Topchiev Institute of Petrochemical Synthesis, RAS, Moscow, Russia

² Orekhovich Institute of Biomedical Chemistry, RAMS, Moscow, Russia

³ Biomodulators & Drugs RC, Health RDF, Moscow, Russia

v.b.tsvetkov@gmail.com

Nano-scale tri-helical complexes of envelope proteins of many viruses (HIV-1, influenza, MMLV, SV5, Ebola viruses) play a crucial role in the viral entry into human cell, at the fusion steps. To protect the cells against the viral intervention, nano-selective "counter-intervention" molecular agents are required. Low-molecular drugs can't be high effective tools for this task because of their small size in comparison with viral fusion mediators as a nano-scale targets for antiviral therapy. But specially designed synthetic polymers molecules are capable to provide a recognition and blockage of such targets. Experimentally this possibility has been studied in series of biocompatible copolymers of maleic acid with alternative polycarboxylic chain modified by controlled combinations of side groups predicted as potential vectors to the viral targets. More than 170 compounds have been synthesized and evaluated *in vitro*, possessing, in particular, effectiveness of HIV-1 entry inhibitors, most probably, at the fusion step [Macromol Symp 2010, 296:466-77]. To investigate molecular mechanisms of expected nano-selectivity to the HIV-1 fusogenic envelope glycoprotein gp41 ectodomain tri-helical (HR1)₃ core (2.5 × 5.1 nm), the docking and molecular dynamics (MD) techniques have been applied for computational modeling the synthetic-viral polymers interactions. This simulation clarifies several alternative mechanisms of the viral target binding (axial, belting, and combined: see the fig.) and explains the *in vitro*



experimental facts of enhanced blocking efficiency as well as the HIV-1 drug resistance prevention in course of the polymeric inhibitors, in contrast with small molecular analogs. The polymeric agents are capable to multi-point occupation of all the L1-L3 levels of the target, while the small molecules can stable bind on the L1 level of hydrophobic pockets only.

P36

New insight into thrombin forms

Zalevsky A.¹, Zavyalova E.², Reshetnikov R.¹, Golovin A.¹

¹*Faculty of Biengineering and Bioinformatics, Moscow State University*

²*Department of Chemistry, Moscow State University*

aozalevsky@gmail.com

Thrombosis (localized blood clot formation) is a leading cause of mortality associated with arterial diseases. Anticoagulants are used for both the prevention and treatment of thrombosis. However, current drugs that dominate the market (warfarin and heparins) have numerous side effects such as excessive bleeding, osteoporosis and even death. Therefore, there is increasing interest in new agents with improved safety profile.

The key enzyme of the blood coagulation cascade is thrombin, serine protease that exists in two forms: active (“fast”) and inactive (“slow”). Conversion between the two forms is mediated by binding of sodium ion, which activates the enzyme. Despite numerous efforts, the structural difference between the forms has not been known yet.

Molecular dynamics simulations were used to investigate thrombin interactions with some novel inhibitors (15TBA - thrombin binding DNA aptamer, 25TOG - thrombin binding RNA aptamer and, hirugen - synthetic dodecapeptide). With the combination of MD results and experimental techniques (steady-state kinetics of the reaction of chromogenic substrate S2238 cleavage) we have found that the two forms differ in oxidized/reduced states of the enzyme's disulfide bridges. The chemical balance between the states depends on flexibility of one particular loop of thrombin.

Modifications of inhibitors like 15TBA in order to improve interactions with the loop and enhance affinity to thrombin will lead to the development of the next generation anticoagulants with high specificity, efficiency and minimized side effects.

Rationalization of stabilization of palladium nanoparticles in imidazolium-based ionic liquids using DFT combined with vibrational spectroscopy

Zvereva E.E.¹, Katsyuba S.A.¹, Yan N.², Yuan X.^{2,3}, Kou K.³, Dyson P.J.²

¹*A.E.Arbusov Institute of Organic and Physical Chemistry, Kazan Scientific Centre of the Russian Academy of Sciences,*

²*Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL),*

³*College of Chemistry and Molecular Engineering, PKU Green Chemistry Centre.*

helva@iopc.ru, skatsyuba@yahoo.com

A combined DFT-vibrational spectroscopy approach was used to determine the interactions between cations and anions comprising imidazolium-based ionic liquids (ILs) and Pd nanoparticles (NPs) immersed in these ILs. The IR spectra and their assignment with quantum chemical computations suggest that both the anions and cations interact with the Pd-NP surface in the IL. Palladium clusters Pd_n (n = 2-13), used to model the NPs, interact more strongly with the anions than with the cations, which suggests an important role of the anions in Pd-NP formation and stabilization in ILs. Indeed, the size of Pd NPs prepared from decomposition of Pd(OAc)₂ in a series of ILs comprising 1-(2'-hydroxyethyl)-3-methylimidazolium cation and various anions follows the trend: “the stronger the interaction between a Pd₅ cluster and the anions, the smaller the NPs”. The energy of the interaction of the IL components with the palladium clusters is smaller than the energy of addition of a Pd atom to the cluster, which suggests kinetic stabilization of Pd-NPs rather than thermodynamic stabilization.

Acknowledgement: Financial supports from the Switzerland-Russia and Sino-Swiss Science & Technology Cooperation Programs, and the Swiss National Science Foundation are gratefully acknowledged.

Table of contents

Partners and sponsors	2
Lecturers and organizers	3
Agenda	4
MSU campus scheme	6
Abstracts of poster presentations	7
P1. The mathematical description of the polymer films forming process out of solutions.....	8
P2. Molecular cluster approach and study of point surface Ti^{3+} defect centers on nanoscaled TiO_2	9
P3. Computer simulation of laser sintering of metallic powders.....	10
P4. Quantum-chemical simulation and AFM study of poly(diphenylenephthalide) supramolecular structures.....	11
P5. Computer Simulation of Atomic Oxygen Impact on Polymer Composites.....	12
P6. Modeling of dependences «composition – biological activity» and «structure – dynamics of biochemical processes» for analogs of biological objects.....	13
P7. A computer modeling on sub-nanometer scale of ionic transport on ideally polarized heterojunctions of solid electrolyte/electronic conductor.....	14
P8. The modeling of dimers on a stepped surface ($L = 3$): metod of Monte Carlo.....	15
P9. Atomistic modeling of epoxy-based oligomers with nonlinear-optical chromophores in each unit: conformational search and molecular dynamics.....	16
P10. Effect of salts on carbon nanotube dispersions in an organic solvent.....	17
P11. Computational study of Polyethylene Oxide confined in Graphite Oxide.....	18
P12. Influence of the cooperative movement on critical temperature for order-disorder transition in the Ising model.....	19
P13. Mobility of paramagnetic probe in xanthan-based polyurethane systems with various OH/urethane group balance.....	20
P14. Regarding the crystallization process for iron carbon alloys with the participation of fullerenes.....	21
P15. The principle of calculation technique selection for electronic structure of phtalide derivatives.....	22
P16. Long stripe transfer matrix simulation of viscoelastic properties of polymer filled with perfectly aligned platelets.....	23
P17. Revealing Non-Adiabatic Effects on Bi(111).....	24
P18. Nanostructured polyurethanes with immobilized <i>in situ</i> metal chelates.....	25
P19. Ab initio studying of topological insulator under the stress.....	26
P20. Biologically-active Nanocomposites with Self-Healing Effect.....	27

P21. Molecular dynamics simulations of plastic thermostable nanocomposites.....	28
P22. Molecular dynamics study of reverse micelle: the single-atom model of a solvent.....	29
P23. Electronic and optical properties of hafnia polymorphs	30
P24. Pressure induced ferroelastic phase transition in LiLuF ₄ compound.....	31
P25. Ab initio and semi-empirical studies of Cr atoms on superfluid He nanodroplets.....	32
P26. Charge transfer engineering via selective doping of oxides: Cr-doped MgO versus Mo-doped CaO.....	33
P27. An activation of C≡C bond in gold-containing systems: DFT study.....	34
P28. Molecular simulation on fullerene derivatives: algorithms and programs for calculation of their curvature, polarizability and volume.....	35
P29. Computational investigation on water-poly(vinyl metylether) interactions.....	36
P30. Size dependence of drift mobility in thin organic layers: Monte- Carlo and analytic modeling.	37
P31. A DFT study on the mechanism of silver-catalyzed propylene epoxidation	38
P32. Methods for modeling the processes of structure formation during the heat treatment of samples from high-temperature nickel alloys.	39
P33. New shape controlled nano-fillers for rubber reinforcement	40
P34. Interactions Between Nanoscale Crystalline Components In Hybrid Inorganic- Organic Biomaterials From Calcium Phosphates And Bacterial Cellulose.	41
P35. Computational Modeling the Synthetic Polymer Selective Interactions with the HIV-1 Entry Nanomediators.....	42
P36. New insight into thrombin forms.....	43
P37. Rationalization of stabilization of palladium nanoparticles in imidazolium-based ionic liquids using DFT combined with vibrational spectroscopy	44
Table of contents	45
Index	47

Index

Al Joda H.N.A.....	8	Karaseva E.N.....	42	Pyshnograi G.V.....	8
Álvarez F.....	18	Katsyuba S.A.....	44	Ratmanova N.K.....	34
Andreev A.S.....	9	Khudobin R.V.....	23	Ratschek M.....	32
Andreeva A.V.....	14	Kijamov A.....	26	Reshetnikov R.....	43
Ankudinov V.E.....	10	Klepko V.V.....	25	Rodionov V. I.....	10
Arif R.N.....	17	Koch M.....	32	Romanova A.O.....	17
Asfandiarov N.L.....	22	Kornilov V.N.....	11	Rozhin A. G.....	17
Balakina M.Yu.....	16	Kou K.....	44	Sabirov D.Sh.....	35
Baybulova G.Sh.....	11, 22	Kozak N.V.....	20, 25	Saitgalina A.D.....	35
Beletskaya A.V.....	38	Kozanecki M.....	36	Sannikova N.A.....	37
Benedek G.....	24	Kraus P.....	24	Saramak J.....	36
Bulgakov R.G.....	35	Krivilyov M. D.....	10	Scotti R.....	40
Campi D.....	24	Kuz'menko N.E.....	34	Serbin A.V.....	42
Chirskaya N.P.....	12	Kuz'menko N.E.....	38	Shubenkova E.G.....	13
Chizhov Y.V.....	9	Lachinov A.N.....	11, 22	Snyga Yu.G.....	38
Chzhu O.P.....	13	Larin S.V.....	28	Stishenko P.V.....	15
Colmenero de Leon J.....	18	Lobko Eu.V.....	25	Strikhanov M.N.....	37
D'Arienzo M.....	40	Lukasheva N.V.....	28, 41	Sukharev V.M.....	37
Despotuli A.L.....	14	Lysogorskiy Y.....	26	Svetushkov N.N.....	39
Dyson P.J.....	44	Lyulin S.V.....	28	Tadiello L.....	40
Ernst W.E.....	24, 32	Mayrhofer-Reinhartshuber M.....	24	Tamtögl A.....	24
Evseeva S.I.....	15	Mirsakiyeva A.....	27	Tayurskii D.....	26, 31
Fedorov M.V.....	17	Morazzoni F.....	40	Timan S.A.....	23
Fominykh O.D.....	16	Mukhamedzyanova D.F.....	34	Tolmachev D.A.....	41
Frolov A.I.....	17	Nazarychev V.M.....	28	Tsvetkov V.B.....	42
Galiev A.F.....	11	Nedopekin O.....	26, 31	Tukhbatullina A.A.....	35
García-Yoldi I.....	18	Nevidimov A.V.....	29	Veselovskiy A.V.....	42
Garipova R.R.....	35	Nikitenko V.R.....	37	Voronina E.N.....	12
Giordano L.....	33	Novikov L.S.....	12	Wahba L.....	40
Golovin A.....	43	Pacchioni G.....	33	Yakimansky A.V.....	28
Gordeev G. A.....	10	Perevalov T.V.....	30	Yan N.....	44
Gritsenko V.A.....	30	Petrova A.....	31	Yu V.....	27
Gurtovenko A.A.....	28	Pichugina D.A.....	34, 38	Yuan X.....	44
Halagan K.....	19	Polanowski P.....	19	Zalevsky A.....	43
Hubina A.V.....	20	Popova S.V.....	21	Zavyalova E.....	43
Ishbulatova R.I.....	21	Pototschnig J.V.....	32	Zhdanov E.R.....	11, 22
Iskakov R.....	27	Prada S.....	33	Zvereva E.E.....	44
Kalimullina L.R.....	11, 22				



Fund for Infrastructure and Educational Programs

The Fund for Infrastructure and Educational Programs was founded during the reorganization of the Russian Corporation of Nanotechnologies. It stimulates nanotechnology infrastructure building to support innovation in the country. The Fund for Infrastructure and Educational Programs primarily focuses its activity in these areas:

- Formation of infrastructure for nanotechnology
- Development of human resources for the nanoindustry
- Market development for nanotechnology products
- Improvement of the legislative framework for innovation
- Standardization and certification of nanoproducts and evaluation of their safety
- Refinements in metrology
- Popularization of nanotechnology and nano-enabled products

The highest governing body of the fund is its Supervisory Council, which is chaired by Alexey Ponomarev, Vice President, Skolkovo Institute of Science and Technology (Skolkovo Tech). In accordance with the charter of the fund, the council determines priorities for its activities, establishes its strategies, and sets its budget.

The Management Committee is the fund's collegial executive body. It is chaired by RUSNANO CEO Anatoly Chubais. Andrey Svinarenko is CEO of the Fund for Infrastructure and Educational Programs.

Moscow Metro Map



Copyright © 2002 by InfoServices International, Inc., NY, USA