POSTER ABSTRACTS OF DIFFUSION FUNDAMENTALS VIII

In the following overview of the poster sessions of Diffusion Fundamentals VIII, the individual contributions are linked to the corresponding abstracts given at the end of the document.

In the program summary and in the abstracts, the underlined names indicate the designated presenters of the posters. In the abstracts, the given email addresses are those of the persons whose names are marked with an asterisk.

POSTER PROGRAM

POSTER SESSION A
"SOCIETY, ECONOMY, MEDICINE, BIOLOGY"

Tuesday, 3rd September 2019, 09:30

A01 **Dynamic extracellular space alters spatiotemporal distribution of chemical signals in brain: experiment and modeling**
S. Hrabetova[1], J. Hrabe[1,2], [1]State University of New York Downstate Medical Center, Brooklyn, NY, USA, [2]Nathan Kline Institute, Orangeburg, NY, USA

A02 **Molecules in nanopores as a model system for mimicking spreading in nature and society**
S. Hwang[1], C. Chmelik[1,2], J. Kärger[1,2], [1]Faculty for Physics and Earth Sciences, Leipzig University, Leipzig, Germany, [2]Saxon Academy of Sciences and Humanities in Leipzig, Leipzig, Germany

A03 **Along the cause-and-effect chain: On the propagation of ideas and visions within the scientific analyzer market**
D. Klank, C. Reichenbach, D. Schneider, 3P INSTRUMENTS, Germany

A04 **Measurement of diffusion of atmospheric gases in a liquid perfluorocompound by means of optical technique**
A. Mialdun[1], V. Yasnou[1], R. Rives[2], A. Coronas[2], V. Shevtsova[1], [1]Université libre de Bruxelles, Brussels, Belgium, [2]Universitat Rovira i Virgili, Tarragona, Spain

A05 **Using diffusion tensor imaging to predict transport patterns in brain**
M. Sarntinoranont, T. Mareci, University of Florida, Gainesville, FL, USA

A06 **Transient anomalous subdiffusion of DNA-binding species in the nucleus**
M. J. Saxton, Dept Biochemistry & Molecular Medicine, University of California, Davis, CA, USA

A07 **Diffusion coefficients of quinine in supercritical CO_2**
Y. Gaponenko, A. Mialdun, V. Shevtsova, Microgravity Research Center, Université libre de Bruxelles (ULB), Brussels, Belgium

A08 **Diffusion detects conformation changes during reactions of photosensor proteins**
M. Terazima, Y. Nakasone, Department of Chemistry, Graduate School of Science, Kyoto University, Japan

A09 **Imaging of 3D patterns of slow flow in porous media**
J. Wang[1], S. Haber-Pohlmeier[2], A. Pohlmeier[3], K. Pitman[1], A. Chan[1], P. Galvosas[1], [1]MacDiamid Institute for Advanced Materials and Nanotechnology, School of Chemical and Physical Sciences, Victoria University Wellington, Wellington, New Zealand, [2]RWTH Aachen University, ITMC, Aachen, Germany, [3]Research Center Jülich, IBG-3, 5 Jülich, Germany

POSTER SESSION B "SOLIDS AND POROUS MATERIALS"

Tuesday, 3rd September 2019, 15:00

B01 **Bubble diffusivity in BCC metals: atomistic mechanisms and kinetic models**
A. Antropov, V. Stegailov, Joint Institute for High Temperatures of the Russian Academy of Sciences, Moscow, Russia, Moscow Institute of Physics and Technology, Dolgoprudny, Russia

B02 **Statistical model of atoms diffusion in a crystal lattice of a metal**
S. V. Bobyr, Iron and Steel Institute of Z. I. Nekrasov, National Academy of Sciences of Ukraine, Dnipro, Ukraine

B03 **Molecular dynamics study on the diffusion behavior of water inside functionalized carbon nanotubes**
Q. Chen, B. Liu, X. Han, Zhejiang University of Science and Technology, Hangzhou, People's Republic of China

B04 **Impact of titanium doping on Al self-diffusion in alumina**
P. Fielitz[1], S. Ganschow[2], K. Kelm[3], G. Borchardt[1], [1]Technische Universität Clausthal, Institut für Metallurgie, Clausthal-Zellerfeld, Germany, [2]Leibniz-Institut für Kristallzüchtung, Berlin, Germany, [3]Deutsches Zentrum für Luft- und Raumfahrt, Institut für Werkstoff-Forschung, Köln, Germany

B05 **Direct quantification of surface barriers in nanoporous materials**
M. Gao[1,2], H. Li[1], S. Peng[1,2], M. Ye[1], Z. Liu[1], [1]Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China, [2]University of Chinese Academy of Sciences, Beijing, China

B06 **Theoretical model for mass transport and adsorption of gases in porous solids based on the frequency response method**
R. Grün, C. Breitkopf, Technische Universität Dresden, Institut für Energietechnik, Dresden, Germany

B07 **Multiscale modeling of diffusion in elastic composite materials**
S. Kaessmair, P. Steinmann, Chair of Applied Mechanics, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Erlangen, Germany

B08 **Diffusion in nanopores recorded by microscopic measuring techniques**
C. Chmelik[1,2], D. Freude[1], J. Haase[1,2], S. Hwang[1], J. Kärger[1,2], R. Valiullin[1,2], [1]Faculty for Physics and Earth Sciences, Leipzig University, Leipzig, Germany, [2]Saxon Academy of Sciences and Humanities in Leipzig, Leipzig, Germany

B09 withdrawn

B10 **Anomalous diffusion-controlled kinetics in irradiated oxide crystals**
V. N. Kuzovkov, A. I. Popov, E. A. Kotomin, Institute of Solid State Physics, University of Latvia, Riga, Latvia

B11 **Diffusion of Sn in polycrystalline α-Fe under pulsed magnetic field**
A. V. Pokoev[1], A. A. Fedotov[1], S. V. Divinski[1,2], [1]Samara University, Samara, Russia
[2]Institute of Materials Physics, University of Münster, Münster, Germany

B12 **Phase formation in aluminum alloys aged in the constant and pulse magnetic field**
J. V. Osinskaya, A. V. Pokoev, K. S. Yamschikova, Samara National Research University, Samara, Russia

B13 **Simulation of the magnetoplastic effect in copper-beryllium alloys**
D. S. Sineglazov, A. V. Pokoev, Samara National Research University, Samara, Russia

B14 **The diffusion path reversibility confirms symmetry of surface barriers**
G. Sastre[1], J. Kärger[2], D. M. Ruthven[3], [1]Instituto de Tecnologia Quimica U.P.V.–C.S.I.C., Universidad Politecnica de Valencia, Spain, [2]Faculty of Physics and Earth Sciences, University of Leipzig, Leipzig, Germany, [3]Department of Chemical and Biological Engineering, University of Maine, Orono, Maine, United States

B15 **Multiscale diffusion in porous media: from interfacial dynamics to hierarchical porosity**
U. Tallarek, D. Hlushkou, J. Rybka, A. Höltzel, Philipps-Universität Marburg, Marburg, Germany

B16 **Stationary-phase contributions to surface diffusion at C_8-modified silica mesopores**
J. Rybka, A. Höltzel, N. Trebel, U. Tallarek, Department of Chemistry, Philipps-Universität Marburg, Marburg, Germany

B17 **Concentration-dependent sedimentation and diffusion coefficient in analytical ultracentrifugation experiments**
M. J. Uttinger, S. Wawra, J. Walter, W. Peukert, Institute of Particle Technology (LFG), FAU Erlangen-Nürnberg, Erlangen, Germany

B18 **Synthesis of hierarchical TS-1 zeolites from a hydrolysis resistant polymer and their excellent catalytic performance in bulky molecules oxidation**
J. Xing[1,2], D. Yuan[1], Y. Wu[1,2], Y. Xu[1], Z. Liu[1], [1]Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China, [2]University of Chinese Academy of Sciences, Beijing, China

B19 **A vacuum set-up for fundamental studies of self- and transport diffusion in porous media**
H. Yu, M.-O. Coppens, Department of Chemical Engineering and Centre for Nature Inspired Engineering, University College London, London, United Kingdom

B20 withdrawn

POSTER SESSION C “FLUIDS”

Wednesday, 4th September 2019, 15:30

C01 **Self- and transport diffusion coefficients from NMR experiments**
D. Bellaire, K. Münnemann, H. Hasse, Laboratory of Engineering Thermodynamics (LTD), University of Kaiserslautern, Germany

C02 **Dynamic viscosity, interfacial tension and mass diffusion coefficient of *n*-hexane, cyclohexane, 2-methylpentane and CO_2 systems**
S. Yan, S. Bi, J. Cui, X. Meng, J. Wu, Key Laboratory of Thermo-Fluid Science and Engineering, Ministry of Education, School of Energy and Power Engineering, Xi’an Jiaotong University, Xi’an, China

C03 **Translational and rotational diffusion coefficients in nanofluids from polarized dynamic light scattering**
F. E. Bioucas[1], C. Damm[2], W. Peukert[2], M. H. Rausch[1], T. M. Koller[1], C. Giraudet[1], A. P. Fröba[1], [1]Institute of Advanced Optical Technologies – Thermophysical Properties (AOT-TP), Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Erlangen, Germany, [2]Institute of Particle Technology (LFG), FAU, Erlangen, Germany

C04 **Assessing diffusivities of organic compounds in ionic liquids**
J. Praus, P. Čihal, O. Vopička, Department of Physical Chemistry, University of Chemistry and Technology, Prague, Czech Republic

C05 **The thermodynamic factor: The key to understand complex diffusion behavior in fluid mixtures**
G. Guevara-Carrión[1], V. Shevtsova[2], J. Vrabec[1], [1]Thermodynamics and Process Engineering, Technical University of Berlin, Berlin, Germany, [2]Microgravity Research Center, Université Libre de Bruxelles, Brussels, Belgium

C06 **The Diffusion Research Unit, The Australian National University, Canberra: A contribution to physical chemistry and beyond**
K. R. Harris[1], W. E. Price[2], [1]University of New South Wales, Canberra, ACT, Australia, [2]University of Wollongong, Wollongong, NSW, Australia

C07 **Fick diffusion coefficients in binary fluid mixtures consisting of methane, propane, or carbon dioxide by theoretical and optical methods**
U. A. Higgoda, M. Piszko, P. Zangi, M. H. Rausch, C. Giraudet, T. M. Koller, A. P. Fröba, Institute of Advanced Optical Technologies – Thermophysical Properties (AOT-TP), Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Erlangen, Germany

C08 **Solubility of CO_2 in 2-butyl-1-octanol from (323.15 to 573.15) K at pressures up to 10 MPa**
X. Hu, J. Yang, X. Jia, S. Bi, J. Wu, Key Laboratory of Thermo-Fluid Science and Engineering of Ministry of Education, Xi'an Jiaotong University, Xi'an, China

C09 **Fick diffusion coefficients in binary liquid mixtures of *n*-alkanes or 1-alcohols with dissolved gases investigated by molecular dynamics simulations and dynamic light scattering**
T. Klein, W. Wu, M. Kerscher, M. H. Rausch, C. Giraudet, T. M. Koller, A. P. Fröba, Institute of Advanced Optical Technologies – Thermophysical Properties (AOT-TP), Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Erlangen, Germany

C10 **Simultaneous study of molecular and micelle diffusion in polyol-based microemulsions with CO_2-swollen micelles by dynamic light scattering**
M. S. G. Knoll[1], C. Giraudet[1], C. J. Hahn[2], M. H. Rausch[1], A. P. Fröba[1], [1]Institute of Advanced Optical Technologies – Thermophysical Properties (AOT-TP), FAU, Erlangen, Germany, [2]Covestro Deutschland AG, Leverkusen, Germany

C11 **Improvement of a transferable force field for the prediction of self-diffusivity, viscosity, surface tension, and density of long-chained linear and branched alkanes and alcohols up to 573 K by molecular dynamics simulations**
F. D. Lenahan, T. M. Koller, T. Klein, A. P. Fröba, Institute of Advanced Optical Technologies – Thermophysical Properties (AOT-TP), FAU, Erlangen, Germany

C12 **Viscosity measurements of *n*-dodecane and 2-butyl-1-octanol at temperatures from (298 to 475) K and pressures up to 10 MPa by vibrating-wire method**
X. Liang, Y. Fu, J. Wu, J. Kuang, Key Laboratory of Thermo-Fluid Science and Engineering of Ministry of Education, Xi'an Jiaotong University, Shaanxi, Xi'an, China

C13 **Predicting self-diffusion and transport diffusion coefficients using entropy scaling and PC-SAFT**
J. Mele[1], M. Hopp[1], A. Bardow[2], J. Gross[1], [1]University of Stuttgart, Institute of Thermodynamics and Thermal Process Engineering, Stuttgart, Germany, [2]RWTH Aachen University, Chair of Technical Thermodynamics, Aachen, Germany

C14 **Definition of frame-invariant Soret coefficients for ternary mixtures**
J. M. Ortiz de Zárate, Facultad de Física, Universidad Complutense, Madrid, Spain

C15 **Diffusivities accessible from dynamic light scattering across the two-phase boundary of an equimolar propane-methane mixture**
M. Piszko, M. H. Rausch, C. Giraudet, A. P. Fröba, Institute of Advanced Optical Technologies – Thermophysical Properties (AOT-TP), FAU, Erlangen, Germany

C16 **Reference frames and negative main Fick diffusion coefficients**
V. Shevtsova[1], T. Janzen[2], S. Kozlova[3], I. Ryzhkov[3], A. Mialdun[1], J. Vrabec[2], [1]Microgravity Research Center, Université libre de Bruxelles (ULB), Brussels, Belgium, [2]Thermodynamics and Process Engineering, Technical University Berlin, Berlin, Germany, [3]Institute of Computational Modelling SB RAS, Krasnoyarsk, Russia

C17 **The Soret effect in ternary mixtures of water + ethanol + triethylene glycol of equal mass fractions: ground and microgravity experiments**
D. Sommermann[1], T. Triller[1], M. Schraml[1], F. Sommer[1], W. Köhler[1], E. Lapeira[2], M. M. Bou-Ali[2], [1]Physikalisches Institut, Universität Bayreuth, Bayreuth, Germany, [2]Mechanical and Manufacturing Department, MPEG Mondragon, Mondragon, Spain

C18 **Interfacial tension measurements of *n*-dodecane/CO_2 from (298.15 to 573.15) K at pressures up to 10 MPa by pendant drop method**
J. Yang, S. Bi, J. Wu, Key Laboratory of Thermo-Fluid Science and Engineering of Ministry of Education, Xi'an Jiaotong University, Xi'an, China

C19 **Self-diffusivity of a homologous series of ethylene glycols: Experimental measurements, relation with viscosity, correlation and prediction methods**
J. R. Ascenso[1], M. C. M. Sequeira1, H. M. N. T. Avelino[1,2], F. J. P. Caetano[1,3], J. M. N. A. Fareleira[1], [1]Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, [2]Área Departamental de Engenharia Química, Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, [3]Departamento de Ciências e Tecnologia, Universidade Aberta, [1,2,3]Lisboa, Portugal

POSTER SESSION D
"CHEMICAL ENGINEERING AND MEASUREMENT METHODS"

Thursday, 5th September 2019, 10:30

D01 **The effects of external surface barriers on zeolite catalysts**
M. Alkhunaizi[1], T. Weissenberger[1], G. Sankar[2], M. O. Coppens[1], [1]Department of Chemical Engineering, [2]Department of Chemistry, [1,2]University College London, UK

D02 **Breakdown of the Stokes-Einstein relation for nanoparticles**
A. Baer[1], Zoran Miličević[1,2], David M. Smith[2,3], Ana-Sunčana Smith[1,2], [1]PULS Group at the Institute for Theoretical Physics, [2]Division of Physical Chemistry, Institute Ruđer Boščović, Zagreb, Croatia, [3]Computer Chemistry Center, [1,3]Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Erlangen, Germany

D03 **Multicomponent diffusion coefficients in liquids from a fully automated microfluidic setup using Raman-microspectroscopy**
C. Flake[1], J. Thien[1], C. Peters[1], H.-J. Koß[1], A. Bardow[1,2], [1]Institute of Technical Thermodynamics, RWTH Aachen, Germany, [2]Institute of Energy and Climate Research (IEK-10), Forschungszentrum Jülich, Germany

D04 **A multi-region model for reaction-diffusion process in a catalyst particle**
H. Li, M. Gao, M. Ye, Z. Liu, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China

D05 **Contribution of mesopores of hierarchically structured titanium silicalite-1 to the catalytic activity towards the methyl oleate epoxidation**
M. Dvoyashkin[1], M. Göpel[1], J. Möllmer[2], R. Gläser[1], [1]Institute of Chemical Technology, [2]Institute of Non-Classical Chemistry, Universität Leipzig, Germany

D06 **Kinetic data for the adsorption of nickel ions from aqueous solutions**
C. Hermann, B. Niemeyer, Chair for Process Engineering with Focus on Separation Technologies, Helmut-Schmidt-University, Hamburg, Germany

D07 **Particle diffusivities in free and porous media from dynamic light scattering applying a heterodyne detection scheme**
M. S. G. Knoll[1], N. Vogel[2], D. Segets[3], M. H. Rausch[1], C. Giraudet[1], A. P. Fröba[1], [1]Institute of Advanced Optical Technologies – Thermophysical Properties (AOT-TP), [2]Institute of Particle Technology (LFG), [1,2]Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Erlangen, Germany, [3]Process Technology for Electrochemical Functional Materials, Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen (UDE), Duisburg, Germany

D08 **Diffusion-wave inverse problem thermal conductivity depth-profile reconstructions using an integral equation approach**
A. Mandelis[1], D. Zheng[1,2], A. Melnikov[1], S. Kooshki[1,3], [1]Center for Advanced Diffusion-Wave and Photoacoustic Technologies (CADIPT), University of Toronto, Toronto, Canada, [2]School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an, China, [3]Mechanical Engineering, Yazd University, Yazd, Iran

D09 **Infrared Soret forced Rayleigh scattering apparatus using a single crystal diamond window to measure Soret and mass diffusion coefficient**
H. Matsuura[1], Y. Nagasaka[2], [1]School of Integrated Design Engineering, [2]Department of System Design Engineering, [1,2]Keio University, Yokohama, Japan

D10 **Interdiffusion of two polymer layers during drying**
L. Merklein, S. Raupp, P. Scharfer, W. Schabel, Institute of Thermal Process Engineering (TVT), Thin Film Technology (TFT), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany, Innovation Lab(iL), Heidelberg, Germany

D11 **Molecular dynamics studies on shale gas and fracturing fluid diffusivity in shales**
L. D. Peristeras[1], K. D. Papavasileiou[1,2], I. G. Economou[1,3], [1]National Center for Scientific Research "Demokritos", Institute of Nanoscience and Nanotechnology, Molecular Thermodynamics and Modelling of Materials Laboratory, Aghia Paraskevi Attikis, Greece, [2]Scienomics SARL, Paris, France, [3]Texas A&M University at Qatar, Chemical Engineering Program, Doha, Qatar

D12 **Shortening NMR diffusion experimental times**
W. S. Price, A. Gupta, R. Masuda, T. Stait-Gardner, A. Torres, G. Zheng, Nanoscale Organisation and Dynamics Group, Western Sydney University, Penrith, NSW, Australia

D13 **Diffusion processes in soft matter studied by field-cycling proton NMR relaxometry**
E. A. Rössler[1], M. Flämig[1], M. Hofmann[1], R. Meier[1], N. Fatkullin[2], Benjamin Kresse[3], Alexei Privalov[3], Franz Fujara[3], [1]Experimentalphysik und Nordbayer. NMR-Zentrum, University Bayreuth, Germany, [2]Institute of Physics, Kazan Federal University, Kazan, Tatarstan, Russia, [3]Institut für Festkörperphysik, TU Darmstadt, Darmstadt, Germany

D14 **Exploration of diffusional phenomena during LOHC dehydrogenation with Pt/Al_2O_3-catalysts of varying pore sizes**
P. S. Schulz, F. Auer, A. Bösmann, P. Wasserscheid, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Lehrstuhl für Chemische Reaktionstechnik, Erlangen, Germany

D15 **Beam induced dynamics in oxide glasses**
C. Tietz[1,2], T. Fritz[1], K. Holzweber[1], M. Legenstein[1], B. Sepiol[1], [1]Faculty of Physics, [2]VDS Physics, [1,2]University of Vienna, Vienna, Austria

D16 **Controlling methanol and water diffusion in Nafion via amine treatment**
M. Kludský, O. Vopička, P. Matějka, Š. Hovorka, K. Friess, University of Chemistry and Technology, Prague, Czech Republic

D17 **Diffusion measurements using a volumetric differential pressure apparatus**
J. Wang, E. Mangano, S. Brandani, University of Edinburgh, School of Engineering, UK

D18 **Adsorption and diffusion in oxyfuel combustion – Linking experiment and MD simulation through graphite structures as a first example**
C. Wedler[1], V. Angenent[2], Ö. Yönder[3], C. Hättig[3], R. Schmid[2], R. Span[1], M. Richter[4], [1]Thermodynamics, [2]Computational Materials Chemistry Group, Inorganic Chemistry II, [3]Quantum Chemistry Group, Theoretical Chemistry, [1,2,3]Ruhr University Bochum, Bochum, Germany, [4]Applied Thermodynamics, Chemnitz University of Technology, Chemnitz, Germany

D19 **Determination of diffusivities in fluid mixtures using light scattering techniques in and out of equilibrium**
W. Wu, M. H. Rausch, C. Giraudet, A. P. Fröba, Institute of Advanced Optical Technolo-gies – Thermophysical Properties (AOT-TP), Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Erlangen, Germany

D20 **Establishment of the shadowgraphy-setup for the measurements of non-equilibrium fluctuations**
D. Zapf, W. Köhler, Experimentalphysik IV, Universität Bayreuth, Bayreuth, Germany

Dynamic extracellular space alters spatiotemporal distribution of chemical signals in brain: experiment and modeling

S. Hrabetova[1]*, **J. Hrabe**[1,2]

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Brain can be considered as a porous medium. The brain cells form a *solid* phase while the liquid-filled extracellular space (ECS) forms a *porous* phase that surrounds each individual cell. Brain ECS is of a fundamental importance for brain function [1]. It serves as a reservoir for ions and a channel for diffusion-mediated transport of biologically significant molecules and therapeutics. ECS volume is the main factor governing the extracellular concentrations of these substances. Any ECS volume change may lead to a change in concentration of ions and transported substances, and this has consequences for brain function.

Volumes of extracellular and cellular phases undergo reciprocal changes during certain physiological and pathological events in brain. For example, transition from sleep to awake state is associated with a reduction in ECS volume [2, 3] and expansion of one type of brain cells [3]. Here we introduce a new phenomenon, the Transient Volume Reductions (TVR) in the ECS that appear to play an important role in sustaining epileptic seizures. Epileptic seizures represent abnormal synchronous excitatory activity in neurons. While they are often thought of as mediated by *cellular* mechanisms, there are *extracellular* mechanisms too, such as a rise in extracellular potassium and ephaptic (field) interactions. When studying epileptic seizures in hippocampus, we found TVRs that occurred in concert with epileptiform potentials (Fig. 1). We hypothesize that TVRs promote epileptiform activity and its propagation by enhancing the *extracellular* mechanisms.

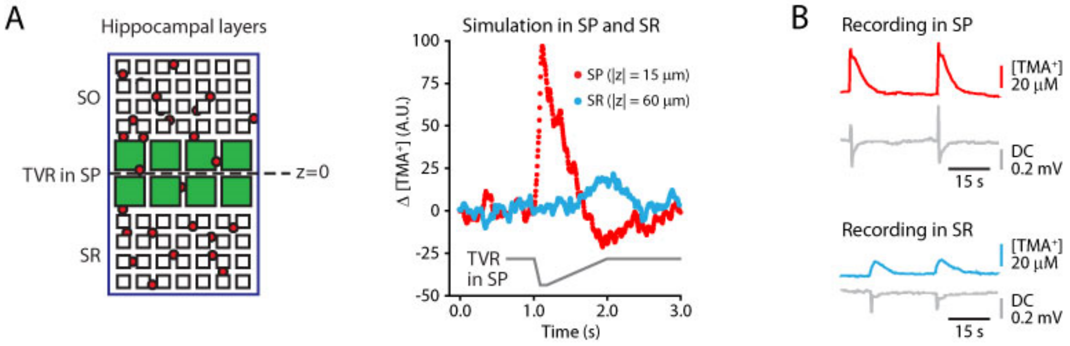

Figure 1: Transient Volume Reductions (TVR) of brain ECS. **A.** Modeling with MCell in hippocampal layers (SO, SP, SR). TVR in SP created a wave that was detected in SR. **B.** TVRs and field potentials (DC) recorded during epileptiform activity in hippocampal layers with tetramethylammonium (TMA) sensing microelectrode.

Here we ask how do the TVRs propagate in space and time and influence local diffusion and concentration of different molecules. The MCell simulator [4] recently acquired capability to incorporate time-dependent geometry. This enabled us to explore how concentration waves in the ECS can be generated by localized TVRs, possibly acting as a novel engine driving the diffusion flux. Preliminary numerical experiments with MCell suggest that TVR can generate interesting and unexpected effects. If a TVR occurs only in one layer of hippocampus, this layer acts as a transient macroscopic diffusion source and generate concentration wave of molecules endogenous to the ECS that spreads to the surrounding layers (Fig. 1). Numerical modeling is in agreement with the experiments in brain and helps us to understand the relationship between TVRs and epileptiform activity in brain.

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[1] C. Nicholson, S. Hrabetova: *Brain extracellular space: The final frontier of neuroscience.* Biophys. J. **113**, 2133-2142 (2017).

[2] L. Xie, H. Kang, Q. Xu, M. J. Chen, Y. Liao, M. Thiyagarajan, J. O'Donnell, D. J. Christensen, C. Nicholson, J. J. Illif, T. Takano, R. Deane, M. Nedergaard: *Sleep drives metabolite clearance from the adult brain.* Science **342**, 373-377 (2013).

[3] A. D. Sherpa, F. Xiao, N. Joseph, C. Aoki: *Activation of β–adrenergic receptors in rat visual cortex expands astrocytic processes and reduces extracellular space volume.* Synapse **70**, 307-316 (2016).

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Molecules in nanopores as a model system for mimicking spreading in nature and society

Seungtaik Hwang[1]*, **Christian Chmelik**[1,2], **Jörg Kärger**[1,2]

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Phenomena of diffusive spreading are ubiquitous in our world. They may be observed in nature and society, with reference to both material and immaterial objects. Examples range from the irregular movement of atoms and molecules as the elementary constituents of matter in gases, liquids and solids (with dramatically differing rates of propagation) up to the spreading of deceases and the incorporation of new words in our language [1]. Investigating molecular mass transfer within nanoporous materials is, within this context, distinguished by a number of advantages. They refer to both the objects of spreading and the conditions under which spreading occurs. On considering molecules, one operates, as a rule, with an extremely large amount of diffusants. All molecules of a given species are identical – and do (at least under conditions excluding chemical reactions) not change their identity with time. By observing mass transfer within a host system of well-defined architecture one has exact knowledge of the conditions under which mass transfer has to occur, with the option of a well-defined variation of these conditions by provident, purposeful chemical processing, ending up in well-defined changes in host structure and, hence, the propagation conditions. Compared with most of other studies, investigating molecular spreading in nanopores thus affords high statistical relevance, extended options for varying the initial and boundary conditions, high reproducibility and good prospects, given all these options, to end up with simple relations for quantitating the overall phenomena.

With reference to these advantages, the poster goes the other way round and identifies a couple of similarities where, on looking at molecular diffusion in nanoporous materials, one is able to recognize features of spreading, which may occur in quite different fields of research. The examples presented include

(i) considering molecular uptake and release with nanoporous particles as a model for, respectively, occupation of a habitat by a new species and, vice versa, for the loss of a species in this habitat [2],

(ii) the effect of additional highways on overall mass transfer [3,4],

(iii) transport impediment (and enhancement!) by diffusant interference [5],

(iv) invader-induced changes in the host system [2] and

(v) host-induced changes of the invaders [6].

References

[1] A. Bunde, J. Caro, J. Kärger, G. Vogl (Eds.): *Diffusive Spreading in Nature, Technology and Society*. Springer International Publishing, Cham, 2018.

[2] J. Kärger, T. Binder, C. Chmelik, F. Hibbe, H. Krautscheid, R. Krishna, J. Weitkamp: *Microimaging of transient guest profiles to monitor mass transfer in nanoporous materials*. Nat. Mater. **13**, 333–343 (2014).

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Along the cause-and-effect chain: On the propagation of ideas and visions within the scientific analyzer market

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As supplier and producing company in the adsorption field, we study diffusion phenomena both related to adsorption and in business field development. In the context of pure gas adsorption for texture characterization of porous materials we find phenomena which are easy to explain, e.g., the blockage of narrow micropores in Zeolith 4A dependent on the measuring temperature (see Fig. 1). Fig. 2 shows temperature profiles and breakthrough curves of mixed gas and vapor adsorption studies, measured with the 3P mixSorb dynamic sorption analyzer [3].

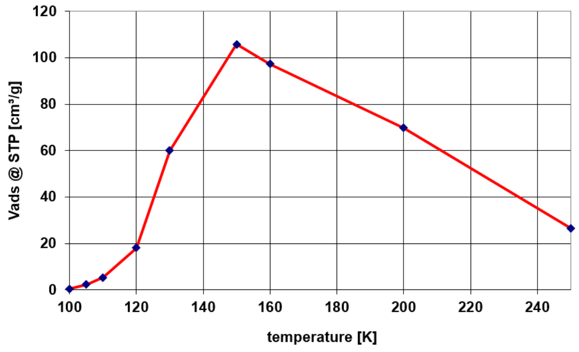

Figure 1: Nitrogen adsorption of Zeolith 4A at 101 kPa (each point taken after 48 hours), the volumes adsorbed depend on adsorptive, pressure, temperature and pore structure [1].

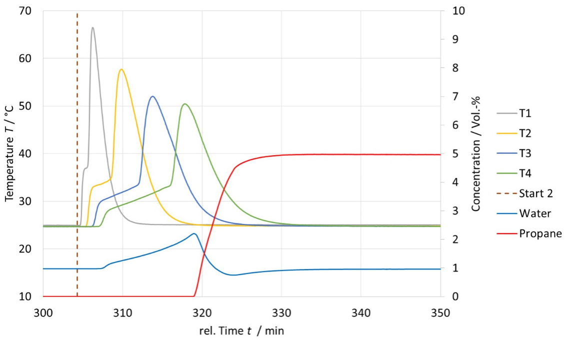

Figure 2: Competing sorption between nitrogen, water and propane in active carbon (temperature and concentration profiles), sorption of propane occurred while displacing previously adsorbed water [2].

The fact that such blocking effects in narrow micropores (Fig. 1) are still not widely known illustrates different diffusion rates of scientific information into the relevant groups of instrument users. The mixed adsorptive processes are additionally influenced by competitive effects between the adsorptive species, and that is well-known effects in the economical game. In contrast to adsorption phenomena which can be described by a Gaussian-like statistics, we find a more complex behavior of parties in economy. According to [4], the question came up how "negative Black Swans" can be prevented in our economical field of activity. We have found indications that the so-called antifragility of our organization in fact has been improved by timely movements from the forth into the third quadrant of statistical thinking (see Table 1) [5]. On this way, it can happen that the complexity of an organization increases with the antifragility, but the long-term uncertainty is reduced by specific diffusion and counter-diffusion effects.

Table 1: "The fourth quadrant", *where statistics and models fail us [4]*

I. Extremely robust to Black Swans ("thin tailed distributions")	III. Quite robust against Black Swans ("thin tailed distributions")
II. Quite robust to Black Swans (heavy tails), simple decisions or well known problems	IV. Limits of statistics, extreme fragility against Black Swans ("fat tails"), called "Estremistan"

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Measurement of diffusion of atmospheric gases in a liquid perfluorocompound by means of optical technique

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Diffusion of gas molecules dissolved in the liquid bulk is the problem that is rarely addressed experimentally, mainly due to a difficulty in sensing the presence of dissolved gas and quantifying its concentration. Approaches which are typically used to overcome the problem include either indirect methods (e.g. based on the gas dissolution kinetics [1]), or newly developed complicated sensing techniques [2].

Assessing the diffusion of gases in liquid might be needed for different reasons, for example, it is a limiting factor affecting bubble formation and growth in boiling processes. Our interest to this problem, in particular, was motivated by development of life-support systems aimed at delivery of oxygen within human body. There are at least two types of health-related applications where diffusion of O_2, N_2 and CO_2 in perfluorocarbon compounds (PFC) is important: it is artificial blood design and liquid ventilation [3]. Knowledge of diffusion rates of these gases in the liquid is of utmost importance for both applications.

But complexity of the existing measurement approaches makes them difficult to establish, while rendering the data obtained therein hard to reproduce and verify. To overcome the complication, we have tested an ability of classical diffusion measurement technique, namely, interferometry and diffusion cell, to support such measurements. We found that the high solubility of the gases in PFC together with high sensitivity of the diagnostics make the measurements well accessible.

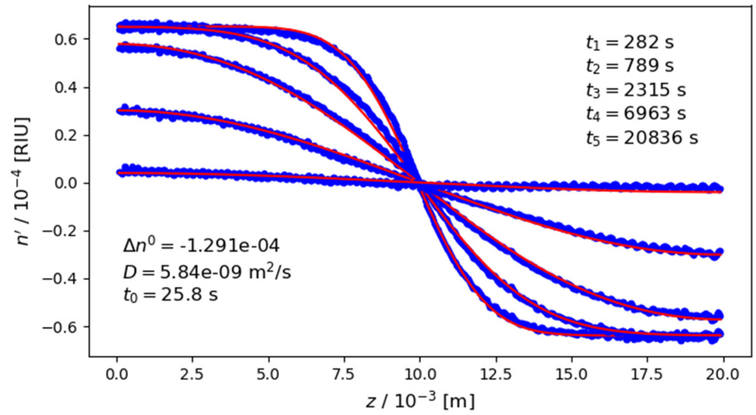

Figure 1: Refractive index profiles acquired in course of an experiment on gas diffusion in methoxy-nonafluorobutane (HFE-7100) at 298 K.

By using the approved approach, we have taken a set of measurements of diffusion of the most important atmospheric gases in a perfluorocarbon within the temperature range 288-313 K. Obtained results are in good agreement with a data for analogous systems available in literature.

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Using Diffusion Tensor Imaging to Predict Transport Patterns in Brain

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Vital nutrients, accumulated wastes and therapeutic agents are all transported by diffusion in their journey through brain tissues. 3D computational models of the brain that predict species transport have proven helpful in regional analysis of disease and drug delivery. In our group, we have developed computational models using magnetic resonance diffusion tensor imaging (DTI) data sets that account for heterogeneity and anisotropy of transport. To date, we have used these models to predict spatial depositions following brain infusions.

DTI provides measures of the effective diffusion tensor of water at each imaged voxel in the brain. We take advantage of structural information within these tensor measures in order to develop our model. Mainly, water diffusion is hindered in certain directions by aligned fiber structures (axons) within white mater regions. First, this allows us to use fractional anisotropy measures to distinguish between white matter and gray matter regions which are known to be more isotropic. Such segmentation allowed us to account for heterogenous transport properties.

Second, the axonal fiber bundle direction within white matter aligns with the eigenvector that points in the direction of maximum diffusivity. Also, the bundle structure of axons allows us to assume transversely isotropic transport properties. So long as we know transport properties in directions parallel and perpendicular to aligned fiber directions, we can build spatially varying transport tensors that account for anisotropy due to fiber alignment. For example, diffusion of a tracer agent can be constructed.

$$\mathbf{D_t} = \mathbf{V}\begin{bmatrix} D_\perp & 0 & 0 \\ 0 & D_\perp & 0 \\ 0 & 0 & D_{||} \end{bmatrix}\mathbf{V^T} \tag{1}$$

where $D_\perp$ and $D_{||}$ are tracer diffusion eigenvalues in perpendicular and parallel directions, respectively. $\mathbf{V} = [v_1, v_2, v_3]$ are the DTI measured eigenvectors at each location where $\mathbf{v_3}$ corresponds to the maximum diffusion direction. We used these methods to predict transport of large macromolecular tracers following infusions into the hippocampus of the rat brain. We also compared predictions to MR measurements, Fig. 1.

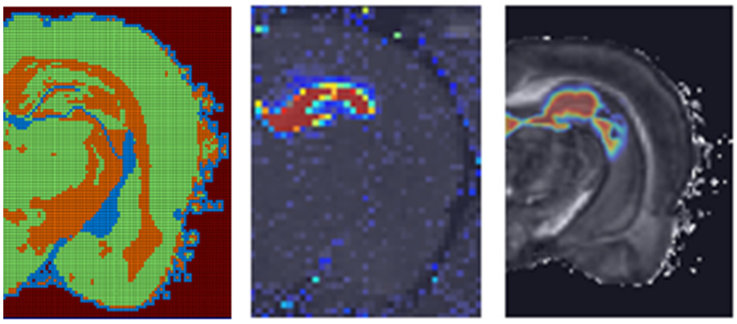

Figure 1: Brain transport model of the rat brain. (Left) Segmented region of the rat brain that based on fractional anisotropy showing white matter, gray matter, and cerebrospinal fluid regions. (Middle) MRI measures of tracer distribution and (Right) model predictions following infusion into the hippocampus.

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Transient anomalous subdiffusion of DNA-binding species in the nucleus

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Single-particle tracking experiments have measured the distribution of dwell times of various DNA-binding species — including CRISPR-Cas9, TetR, and LacI — diffusing in living cells. The observed truncated power law distribution has direct and indirect implications.

One direct implication is that the observed dwell time distribution is inconsistent with the Gaussian distribution of binding energies generally obtained from bioinformatics. Consideration of length scales of the nucleus and the measurement is essential to understanding the dwell time distribution.

Another direct implication is that a truncated power-law distribution of dwell times leads to transient anomalous subdiffusion, in which diffusion is anomalous, $\langle r^2 \rangle \propto t^{\alpha}$, $\alpha < 1$, at short times and normal, $\langle r^2 \rangle \propto t$, at long times, where $\langle r^2 \rangle$ is the mean-square displacement, t is time, and α is the anomalous diffusion exponent. The initial anomalous regime is of fundamental interest because it represents the search of the DNA-binding species for its target DNA sequence. Monte Carlo simulations are used to characterize the time-dependent diffusion coefficient D(t) and to relate the time dependence to the dwell time distribution. Time-dependent diffusion is described in terms of α, the limits D(0) and $D(\infty)$, and the crossover time between anomalous and normal diffusion. Detailed examination of the dependence of the subdiffusion parameters on the dwell time parameters is better suited to a paper than to a poster, but we give one example here. The trap concentration has a major effect on the anomalous diffusion exponent, but much of this effect is captured in D(0) and $D(\infty)$, which are easily calculated from the truncated power-law parameters, and are essential quantities to measure in experiments.

Some indirect consequences: (1). The simplest interpretation of the model is that the dwell times are actual binding times to DNA. One alternative is that the dwell times are the periods of one-dimensional diffusion on DNA in the standard combination of one-dimensional and three-dimensional search ("facilitated diffusion"), though the form of the dwell time distribution suggests a more complicated interpretation. (2). Non-target DNA sites have a significant effect on search kinetics; false positives from bioinformatic studies are potentially rate determining *in vivo*. (3). Overexpression of the DNA-binding species reduces anomalous subdiffusion because the deepest non-target binding sites are occupied and unavailable, a phenomenon well-known in the study of diffusion in catalyst pellets. (4). Both binding and obstruction affect diffusion. In the absence of a consensus model of chromatin geometry, obstruction effects ought to be characterized by experiment as well as by modeling. Suggested controls for obstruction are green fluorescent protein (GFP) as a calibration standard among laboratories and cell types, and the DNA-binding species itself with the binding site inactivated as unobtrusively as possible.

(Supported in part by NIH grant GM038133)

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Diffusion coefficients of quinine in supercritical CO_2

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It is widely recognised that the increase in atmospheric CO_2 levels due to industrial activity is the main cause of climate change. One idea is that, under the right conditions, it could be used industrially as a solvent. In its gaseous form, CO_2 is essentially a non-solvent but, in the supercritical fluid state above its critical point ($T_{cr} = 31.1°C$ and $P_{cr} = 7.38$ MPa), the density and solvation capabilities of CO_2 change dramatically compared with the gas. The key physico-chemical properties of a supercritical fluid such as density, diffusivity and dielectric constant can be easily controlled by changing the pressure and/or temperature.

Another advantage of using supercritical CO_2 ($scCO_2$) in extraction is the fact that it can easily be separated from the product by processes like adsorption, absorption or evaporation. This offers good product purity as none of the above separation processes can be detrimental to the product.

One of the ideas of using $scCO_2$ as a solvent is to extract quinine, which has been used since the 16th century to treat malaria. Quinine is not only an antimalarial medication, but it is also used for the treatment many other diseases. It is also widely used in beverages such as tonic water. Usually, the strong acids or petrochemical-derived solvents (e.g. as hexane) are used for the extraction of quinine and the final product is not clean. The use of $scCO_2$ is most promising as it does not require no pre-treatments or post purification processes. However, this application is impacted and even governed by the diffusion process but there is a lack of knowledge about transport properties of quinine in $scCO_2$.

Our objective is to investigate the diffusive properties of quinine in supercritical CO_2, and how they depend on pressure and temperature. To conduct the investigation, a dedicated experimental setup has been developed, comprising a Taylor dispersion instrument working at high pressure [1]. The solid quinine is first dissolved in ethanol and then is injected into supercritical CO_2. For this reason the first task of the study is focused on the analysis of the diffusion of pure ethanol in $scCO_2$. The second part is aimed at the diffusion of the (quinine + ethanol) solution in $scCO_2$ at different pressures and temperatures.

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Diffusion detects conformation changes during reactions of photosensor proteins

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Since conformation changes of proteins and biomolecular interactions (including protein-DNA, or protein-protein interactions) are essential processes for biological functions, detections of these processes are important in chemistry and biochemistry to understand the reactions. For the detection of these processes, a variety of techniques have been developed. UV/vis absorption spectroscopy or emission spectroscopy are very powerful to trace the time development of reactions. However, these techniques have a limitation to detect the conformation changes of proteins and biomolecular interactions. Recently, our group discovered that the translational diffusion coefficient can be a useful and sensitive probe to detect the conformation change as well as the intermolecular interaction changes. Although many techniques, e.g., dynamic light scattering, Taylor dispersion, capillary method, NMR spectroscopy, have been developed to monitor molecular diffusion, molecular diffusion has never been considered as a time dependent property during reactions. We have been developing a method based on the pulsed-laser induced transient grating (TG) technique to detect the time-dependent diffusion. Here, we repot the time-resolved detection of protein conformation changes of a blue light sensor protein of phototropin by using the diffusion coefficient.

Phototropin (phot) was found in higher plants and green algae. It consists of N-terminal blue-light sensing domains, LOV1 and LOV2 (LOV= light, oxygen, and voltage sensor), and a serine-threonine kinase domain. The LOV1 and LOV2 domains bind a FMN molecule non-covalently. Previously, conformational changes of *Arabidopsis* (*At*) phot1-LOV2 with the linker (phot1-LOV2-linker) were investigated from the view point of the changes in the molecular diffusion coefficient by the time-resolved TG method. Although the absorption spectrum change completes within a few microseconds, the diffusion coefficient detected by the TG method decreased drastically with a time constant of 1.0 ms from 9.2×10^{-11} m^2/s to 5.0×10^{-11} m^2/s. This time dependent diffusion coefficient was interpreted in terms of the unfolding of α-helices in the linker region. We extended this study to photochemical reactions of a variety of differently truncated constructs of a phot from *Chlamydomonas reinhardtii* (*Cr*) (LOV1, LOV1-hinge, LOV2, LOV2-linker and hinge-LOV2). We found that, in the dark state, LOV1 is in dynamic equilibrium between the monomer and dimer, and the main photochemical reaction is dimerization of the monomer and dissociation of the dimer. On the other hand, LOV1-hinge exists as the monomer and the photochemical reaction is the dimerization reaction associated with the unfolding of the helix of the hinge domain. The linker region including the Jα helix is rather stable upon photoexcitation. The helix of the hinge domain of hinge-LOV2 is slightly unfolded in the dark state and the major photoreaction is the dimerization event. These photochemical properties of *Cr* phot are considerably different from those of *At* phot. It should be noted that these conformation changes and the dimerization reactions cannot be detected by other optical methods, i.e., these processes are spectrally silent. These studies clearly demonstrate that the diffusion coefficient can be very useful for probing spectrally silent processes of proteins.

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Imaging of 3D patterns of slow flow in porous media

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Understanding root water uptake is indispensable for the optimization of plant growth and crop yield against the background of growing world population. One strategy to understand how root water uptake functions is the knowledge of water movement from bulk soil to the root, passing the root-soil interface: the bottleneck for water uptake. Whereas direct imaging of fluxes in the above-ground plant stem has been performed by the group of Van As [1], little is known about the 3D flow pattern, dispersion and velocities in the soil-root compartment. This is due to the heterogeneous and hierarchical structure of the root system [2], resulting in small fluid displacements of some tens of micrometer per second based on the transpiration rate of the plant. It has been shown by Spindler et al. [2] that mean flow rates of a homogeneous flow as low as 0.06 mm/s can be measured even under the influence of internal magnetic field gradients (caused by the heterogeneity of the soil as a porous material) using 13-interval stimulated echo multi-slice imaging (STEMSI).

This contribution will report on further challenges if STEMSI is used for the acquisition of water transport in a heterogeneous root phantom and around the roots of a life plant system. While a 3D MRI image of the root system with sufficient spatial resolution is necessary it is also important to obtain the full 3D information of the velocity vector for the water movement in the vicinity of the plant roots. These requirements need to be balanced against the necessary acquisition time for this 6D data set since the plant is growing and therefore changing its root system over time. To meet this requirement the concepts for Stimulated Echo Acquisition Mode (STEAM) [4] have been fully incorporated into the STEMSI method, thus enabling rapid multi-slice acquisition while retaining sufficient signal to noise ratios.

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Bubble diffusivity in BCC metals: atomistic mechanisms and kinetic models

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Release of gas fission products in nuclear fuels is a practically important phenomenon based on the bubble diffusivity in crystal lattice. The bubble diffusion coefficient can be expressed through the volume and surface self-diffusion coefficients D_{vol} and D_{surf}. In the case of an empty bubble in a bcc lattice the corresponding expression is as follows (see [1]):

$$D_{bub}(R) = D_{vol}\frac{3\Omega}{2\pi R^3} + D_{surf}\frac{3\Omega^{\frac{4}{3}}}{4\pi R^4} \,, \tag{1}$$

where Ω is an atomic volume and R is a radius of a bubble. The surface self-diffusion plays a significant role in the bubble motion in solids [2], but up to now the underlying mechanisms have not been studied well enough. In this work these mechanisms are studied via the classical molecular dynamic modelling in two representative metals: bcc U and bcc Mo.

We find the equilibrium facet shape of bubbles with different diffusion rates on different faces. We proposed the method of calculation of an average surface self-diffusion coefficient over all the bubble in [3]. The mean square displacement is found for the surface layer atoms that are identified by the Voronoi polyhedron method.

For the validation of formula (1) we calculate the bubble's diffusivities via the nonequilibrium molecular dynamics based on the Nernst-Einstein equation. On the example of a two-dimensional lattice it is shown that such a method gives correct results [4]. However in the case of facet bubbles the drift velocity can be not proportional to the applied force. It indicates a certain more complex mechanism of bubble movement. Our analysis shows that the velocity is determined by the rate of the nucleation of new steps at [110] faces (figure 1). The bubble diffusivities are obtained via the direct modelling and independently predicted by formula (1). The comparison between these results allows to correct the theory according to revealed mechanisms. Obtained results can be applied in kinetic models for computation of nuclear fuel properties. Work has been supported by the Russian Foundation for Basic Research (grant no. 18-08-01495), the grant of the President of Russian Federation for support of leading scientific schools grant NSh-5922.2018.8 and the program 5top100 of NRU MIPT.

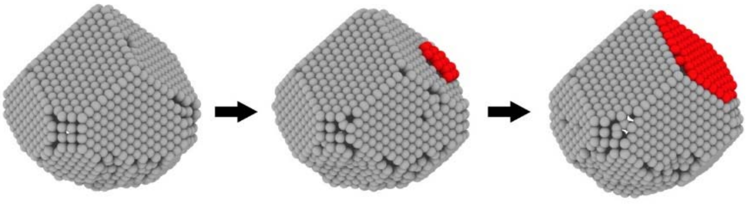

Figure 1: Surface atoms of the bubble in bcc U. The new emerging layer of the surface is shown as red atoms. Nucleation of such surface steps determines bubble mobility.

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Statistical model of atoms diffusion in a crystal lattice of a metal

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To describe the diffusion of atoms in the crystal lattice of a metal, we use the statistical model, which was previously well tested for the description of thermionic emission [1]. Atoms in the crystal lattice of a metal are held by large attractive forces, therefore the potential energy of moving, i.e. diffusing atoms is greater than the potential energy of the atoms of the crystal lattice by the value of u — the activation energy of the diffusion process.

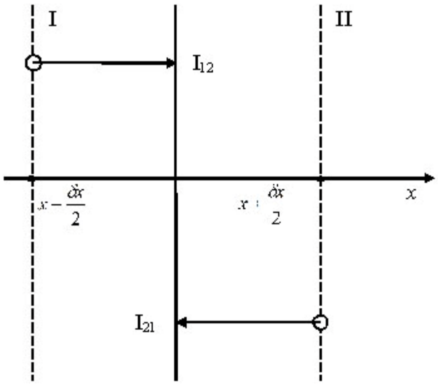

Fig. 1. Scheme of diffusion in the statistical atomic model.

Let us single out in a unit volume of metal V a unit surface perpendicular to the x axis (Fig. 1). The total flow of atoms in the positive direction of the x axis is equal to the difference in the flow I_{12} (from the plane $x – d/2$ to the plane $x + d/2$) and I_{21} (in the opposite direction) [1]. Only those metal atoms for which the energy ε is larger than the potential barrier of the lattice u can pass through this surface in the positive direction of the x axis:

$$\varepsilon = \frac{\mathrm{p}_x^2}{2\mathrm{m}} \geq u \tag{1}$$

and m is the mass of the diffusing atom. The diffusion flow I_{12} is determined by the number of metal atoms or impurities passing through a unit of surface per unit of time. To find its expression, it is necessary to calculate the distribution of atoms by impulses:

$$dN = \frac{\mathrm{V} dp_x dp_y dp_z}{\mathrm{h}^3 \exp((\varepsilon - \mu)/kT)}. \tag{2}$$

There, dN is the number of atoms in the metal whose pulse components are in the range of values between p_x and $p_x + dp_x$, $\mathrm{p_y}$ and $p_y + dp_y$, $\mathrm{p_z}$ and $p_z + dp_z$, i.e. number of particles with impulse and energy given in magnitude and direction, T – temperature. The number of atoms passing through a unit of surface per unit of time:

$$dn = \frac{dp_x dp_y dp_z}{\mathrm{mh}^3 \exp((\varepsilon - \mu)/kT)}, \tag{3}$$

Performing the well-known calculations [1], we find the diffusion flow I_{12} in the direction of the x axis:

$$I_{12} = \frac{2\pi mk^2T^2}{h^3} \exp - ((\mathrm{u} - \mu_1)/\mathrm{kT}) , \tag{4}$$

where μ_1 is the chemical potential of metal atoms on the side of plane I (Fig. 1). Similarly, we find the diffusion flow I_{21} in the direction opposite to the x axis (from plane II to plane I). The total diffusion flow is equal to:

$$Ic = I_{12} - I_{21} = \frac{2\pi mk^2T^2}{h^3} \mathrm{e}^{-\mathrm{w/kT}} \exp((\mu_1 - \mu_2)/\mathrm{kT}) . \tag{5}$$

Perform a further transformation of equation (5). If we consider the self-diffusion of atoms of a pure metal, then the difference of their chemical potential at the interplanar distance $\Delta\mu=\mu_1-\mu_2$ <<1, then $exp(\mu_1-\mu_2)/kT \approx (\mu_1-\mu_2)/kT$. According to the average theorem, we find the equation:

$$Ic = -\frac{2\pi mkTd}{h^3} \mathrm{e}^{-\mathrm{w/kT}} \frac{\partial\mu}{\partial x} \tag{6}$$

It is the statistical equation of atoms diffusion in a crystal lattice of a metal. That allows us to calculate *ab initio* the zero diffusion coefficient of atoms.

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Molecular dynamics study on the diffusion behavior of water inside functionalized carbon nanotubes

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Carbon nanotubes (CNTs) are considered feasible materials for desalination and wastewater treatment. However, it is reported that functionalized CNTs can change water flux and ion selectivity [1-2]. Therefore, it is of great importance to compare the diffusion behavior of water inside pristine CNTs to that of water inside functionalized CNTs. In this work, we utilize positively charged CNTs (with $-COO^-$) and negatively charged CNTs (with $-NH_3^+$). Detailed investigations are carried out on the systems of rigid (6, 6), (7, 7), (8, 8), (9, 9), and (10, 10) armchair carbon nanotubes, both pristine and functionalized, solvated with Lennard-Jones water fluids. We also compare different water models such as TIP5P and SPC/E to better mimic the interaction between water molecule and CNTs. Self-diffusivity statistics, molecule configurations and hydrogen bonding are computed or examined. It is found that water molecules will have more ordered structure in functionalized CNTs. In small (6,6) CNT, hydrogen bonds tend to aggregate water into a wire and lead to rapid collective drift. Functionalization of CNTs can stabilize the hydrogen bond of water molecules and enhance its lifetime. In (7,7) nanotubes and beyond, hydrogen bonding network allows the water to form regional concentrated clusters. This allows water fluid in extremely low density exhibit rather slow self-diffusion motion. Functionalization can accelerate the oriented motions of water molecules. This fundamental study attempts to provide insights into understanding nanoscale delivery system in aqueous solution.

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Impact of titanium doping on Al self-diffusion in alumina

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α-Al_2O_3 is an important refractory material which has numerous technical applications: as an in situ growing self-healing oxide scale, as a massive material and as reinforcement fibres in composites. For modelling diffusion controlled processes (creep, sintering, alpha-alumina scale growth on aluminium bearing Fe or Ni base alloys) it is necessary to study self-diffusion of the constituent elements.

However, the aluminium diffusivity is difficult to measure [1, 2] because aluminium has no natural tracer isotope, and the only suitable radiotracer is ^{26}Al, which raises two difficulties. First, ^{26}Al is artificial and causes very high production costs, and second, it has a half-life time of 7.4×10^5 years and consequently a very low specific activity, which makes it difficult to apply classical radiotracer methods. We applied Secondary Ion Mass Spectrometry (SIMS) to measure ^{26}Al depth profiles resulting from diffusion experiments [3]. This avoids the problems related to the radioactivity measurement, reduces the necessary amount of ^{26}Al per experiment considerably, and yields a much higher spatial resolution.

In this work, we studied the impact of titanium doping on Al self-diffusion in single crystalline alumina. Single α-Al_2O_3 crystals intentionally doped with different amounts of Ti (about 300, 600, 900 and 1200 wt. ppm) were used in this study. It could be shown that Al self-diffusion increases with increasing titanium doping.

The single crystals were grown by the Czochralski technique with rf induction heating. Due to a very low segregation coefficient of Ti in Al_2O_3, the doping level of the melt was about 10 times higher than the desired concentration in the solid. Such high Ti amounts entail growth instabilities and therefore the crystal pulling rate was decreased preventively with increasing Ti concentration. The incorporation of Ti was analyzed using a micro-XRF spectrometer.

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Direct quantification of surface barriers in nanoporous materials

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Successful design and application of nanoporous materials are essentially dependent on the molecular diffusion. Two mechanisms, *i.e.* surface barriers and intracrystalline diffusion, may dominate the mass transport. In the previous studies, these two mechanisms are difficult to determine with certainty by dual resistance model [1] (DRM). Here, we derive an expression of uptake rate relying solely on surface permeability, which provides a method to directly quantify the surface barriers. Subsequently, the effects of surface barriers and intracrystalline diffusion could be identified separately.

We derived that for sufficiently small time the relative uptake loading m_t/m_∞ can be described by [2]

$$\frac{m_t}{m_\infty}\Big|^{\sqrt{t}\to 0} \cong \frac{\alpha}{l}\left(\sqrt{t}\right)^2 + O\left(\sqrt{t}^3\right) \qquad (1)$$

where α is the surface permeability, t the uptake time, l the characteristic length of materials.

As shown in Fig. 1a, it is commonly accepted that *S*-shapes of uptake curves were found, and some attributed this to the effect of surface barriers. Eq. (1) can be applied to determine surface permeability α by use of initial uptake data. Then the intracrystalline diffusivity D can be obtained by fitting the whole uptake rate data with DRM. Compared to the method based on DRM with both D and α as free parameters, this approach can significantly reduce the uncertainty of the fitting results.

As can be seen from Fig.1b, the effective diffusivities measured by three macro-methods span over two orders of magnitude. After decoupling the surface barriers from overall mass transfer by Eq. (1), the intracrystalline (transport) diffusivity of methanol in SAPO-34 shows surprising consistence.

The surface barriers and intracrystalline diffusion in SAPO-34 with different crystal size and Si content were quantified, which is shown in Fig. 1c. It is found that the effective diffusivity deviates by two orders of magnitude. After decoupling the surface barriers by Eq. (1), the derived intracrystalline diffusivity is almost invariant with the changes of crystal size. Furthermore, the surface permeability shows a strong acidity-dependence, which is consistent with the observation in [3].

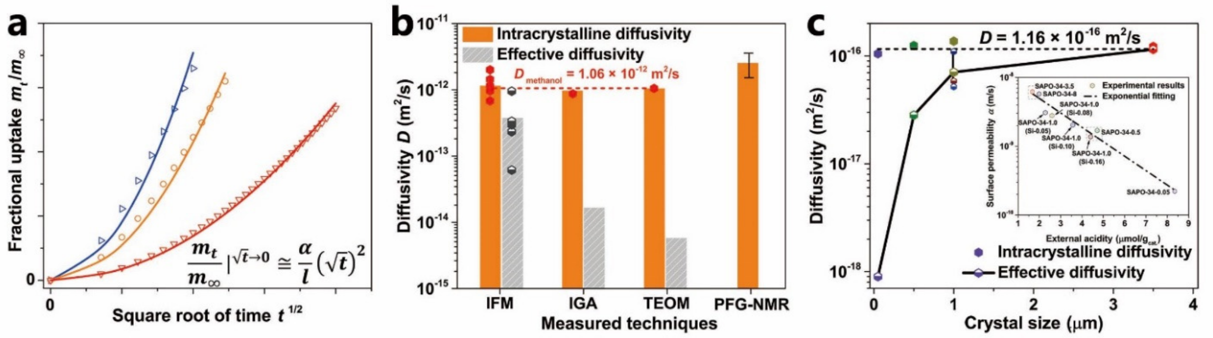

Figure 1: (a) By use of Eq. (1), the surface permeability can be directly quantified from the initial uptake rate data. (b) Diffusion of methanol in SAPO-34 under low molecular loading at 303 K. (c) Uptake of propane over SAPO-34 with different crystal size and Si content at 313 K.

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Theoretical model for mass transport and adsorption of gases in porous solids based on the frequency response method

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Detailed knowledge of mass transport and adsorption is one of the key factors in the development of novel high-performance porous materials for a wide range of technical applications. In the course of an optimization process, a quick conclusion on the properties of the pore system and its accessibility for certain sample molecules is crucial. On the other hand, predictions about the pore system can save steps in material development.

The frequency response method is a promising analysis technique for the determination of such transport processes taking place inside the pore structure. By simply recording the macroscopic quantities pressure and temperature, this method can be a meaningful tool for characterizing transport processes of gases in porous materials by combining practical measurements with mathematical modelling. The modelling of the measurement result should provide kinetic parameters such as diffusion and adsorption coefficients.

In addition, the method offers the possibility to simulate the complex mass transport and adsorption processes. For this purpose, a standard model has to be developed, since there are no standard models in a suitable simulation environment so far.

For these research purposes an apparatus is available, which is shown in Figure 1.

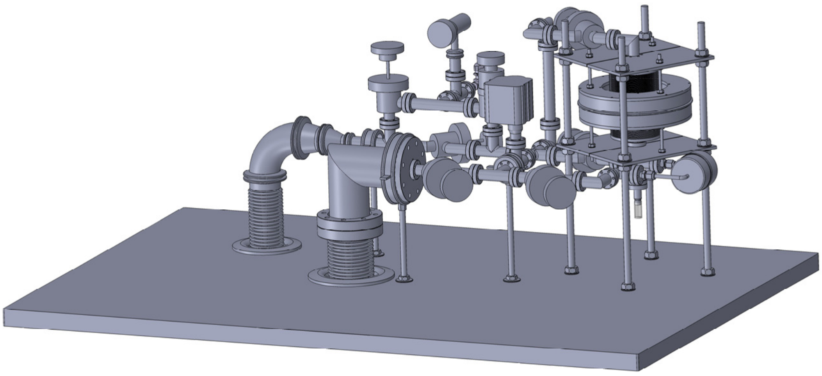

Figure 1: CAD model of frequency response installation.

Establishing this measurement method for the characterization of porous materials is the goal of current research work.

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Multiscale modeling of diffusion in elastic composite materials

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Our research features diffusion in elastically deformable solids with complex microstructure. A prominent example are electrodes of Li-ion batteries which are typically a porous compound consisting of a binder, conductive particles, and active particles, filled with an electrolyte. The charge and discharge processes are complex multi-physics problems. Based on the used materials, they may include chemical reactions, electrochemically driven diffusion, separation into lithium poor and lithium rich regions in the active particles, or swelling phenomena [1]. Here, we consider a simplified version of this problem restricting ourselves to diffusion in an elastic matrix-particle composite. In the matrix, the transport of the mobile species is described using a Fickian-type flux driven by the gradient of the chemical potential. In the particles, the mobile species tends to accumulate and build separate regions of equal concentration – either high or low. This behavior is modeled using the Cahn-Hilliard equation.

When the dimensions of the computational domain increase, it is less surprising that a direct numerical simulation is computationally extremely demanding. To circumvent this difficulty, an extended version of the computational homogenization procedure presented in [2] is employed. There, instead of modeling the body in full detail, a homogenized problem is considered. The unknown constitutive response, such as the species flux or the stress tensor, is computed from the known constitutive response of a statistically representative volume element. The coupling of the homogenized macroscopic problem with the representative microscopic problem is achieved via appropriate boundary conditions. The figure below compares the results of a direct numerical simulation with the homogenized solution. Both relevant cases, diffusion driven deformation and deformation driven diffusion, are studied. First a flux is prescribed on the left boundary. Afterwards the top left half of the body is loaded with a constant force per length. As can be seen, in the particles, the mobile species creates regions of high (red) or low concentration (blue) whereas in the matrix, the concentration field is rather homogeneous. The body expands at high concentrations and contracts at low concentrations. Under pressure, the particles prefer a low species concentration.

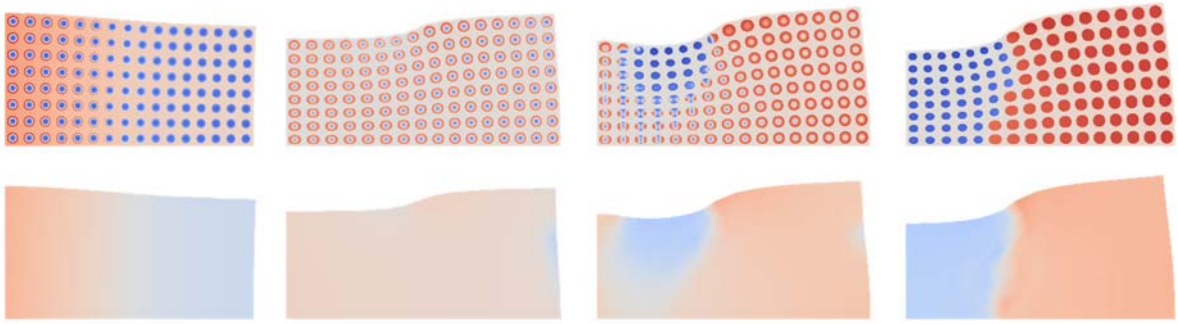

Figure 1: Deformation driven diffusion in a matrix particle composite.

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Diffusion in nanopores recorded by microscopic measuring techniques

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Diffusion, i.e. the irregular movement of, notably, atoms and molecules as the elementary constituents of matter, is among the omnipresent phenomena in nature and, moreover, often among the decisive steps deciding about the functionality of the given system. This is in particular true for many technological processes, including those based on the application of microporous materials. As a consequence of the intimate contact of the "guest" molecules in such "host" materials with their internal surface, such systems serve as excellent media for matter upgrading by separation due to molecular sieving and by catalytic conversion. In all these applications, as a matter of course, the gain in value-added products can never be faster than allowed by the rate of mass transfer between the surrounding atmosphere and the interior of the nanoporous materials. The rate of this exchange may depend on quite a number of processes. Knowledge about their relevance for the overall process is, as a consequence, an important prerequisite for ensuring operation with these materials with highest possible performance [1].

The poster presents two measuring techniques which, by their very nature, can be focused on, exclusively, microscopic dimensions, including the interior of the individual particles (crystallites) of the material under study. Correspondingly, they are referred to as "microscopic measuring techniques". The examples presented refer, in particular, to the potentials of these techniques for investigating mass transfer in complex systems.

These are, notably, zeolites with hierarchically organized pore spaces where the genuine micropore space is permeated by "transport pores" [2]. Recent progress in combining conventional pulsed field gradient (PFG) NMR diffusion measurement with magic angle spinning (MAS) [3,4] has opened up novel potentials for attaining information about the various constituents of mass transfer in such materials which, so far, were only accessible by modelling approaches [5,6].

Microimaging via IR microscopy (IRM) and interference microscopy (IFM), as the second method(s) in the focus of this poster, have similar potentials – even though, on monitoring mass transfer in hierarchical pore spaces, they have so far been only applied in the fast-exchange regime. These potentials, however, have been demonstrated already with the in-depth observation of mass transfer in mixed-matrix membranes (MMMs), where the interface between the filler (MOF ZIF 8) and the embedding polymer medium could be identified as a region of enhanced guest concentration [7].

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Anomalous diffusion-controlled kinetics in irradiated oxide crystals

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MgO, Al_2O_3 and MgF_2 are three wide gap insulating materials with different crystalline structures. All three materials are radiation resistant and have many important applications, e.g. in reactor optical windows. It is very important to predict their long-time defect structure evolution controlled by defect migration and reactions. One could estimate the diffusion coefficients of radiation defects in solids from measurements of the main defect concentration changes (oxygen vacancies called the F-type color centers, by optical absorption) under different conditions, e.g., sample heating (annealing) after irradiation.

As is well-known, the F center mobility is much smaller than that of the complementary radiation Frenkel defects -- interstitial ions. Thus, at moderate radiation fluencies and temperatures, the kinetics of the F-type center annealing is governed by their *diffusion-controlled recombination* with mobile interstitials. The basic theory (how to extract from experimental data the *migration energy* E_a of interstitials and its *pre-exponential factor*) was developed and applied to irradiated insulators in our recent study [1,2]. It is demonstrated (Fig.1), for the first time, that in three types of strongly irradiated ionic solids the pre-exponential factor of diffusion is strongly correlated with the migration energy. It was showed [2] that the correlation of these two parameters satisfies the so-called *Meyer–Neldel rule* (MNR) [3] observed more than once earlier in glasses, liquids, and disordered materials, but not yet in the irradiated materials.

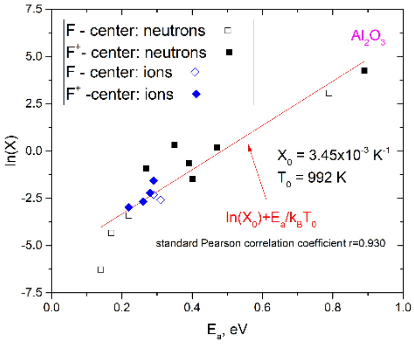

Figure 1: Correlation of the effective diffusion energies and its pre-exponents for neutron and ion-irradiated Al_2O_3.

We have shown for all three materials that with the increase of radiation fluence (dose) both the migration energy and its pre-exponent are *decreasing*, irrespective of the type of irradiation. We discuss the origin of this phenomenon. Thus, in this study, we demonstrated that the dependence of defect migration parameters on the radiation fluence plays an important role in the quantitative analysis of the radiation damage kinetics and long time damage development of real materials and cannot be neglected.

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Diffusion of Sn in polycrystalline α-Fe under pulsed magnetic field

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The experimental investigations of Sn diffusion in ferromagnetic α-Fe within the pulsed magnetic field by X-ray diffraction analysis were performed. The pulsed magnetic field was found to influence significantly the diffusion coefficients of Sn in α-Fe.

Pulsed magnetic field was shown [1] to influence significantly hetero-diffusion in ferromagnetic materials. In particular, diffusion of Al and Sn in ferromagnetic α-Fe-based solid solutions reveled a resonant behavior [2, 3] which was explained by a reorientation of atomic pairs in accordance with Zener's mechanism under magnetostrictive stresses imposed by application of the pulsed magnetic field to the α-Fe crystal lattice.

The present study reports the impact of pulsed magnetic field on diffusion of Sn in polycrystalline α-Fe in the temperature interval of 730-830°C. The magnetic field intensity and the frequency are varied in the ranges of 39.8–557.2 kA/m and 1–21 Hz, respectively. The X-ray diffraction analysis is applied to determine the Sn diffusion coefficients. Both, retardation and enhancement of the diffusion coefficient of Sn in α-Fe are observed in dependence on the pulse frequency. The diffusion rate of Sn in α-Fe reveals evidently a resonant behavior which depends substantially on the magnetic field intensity. This behavior is explained by inelastic interactions between the stresses induced by mobile defect complexes (pairs of solute atoms or higher order complexes) and magnetostrictive fields appearing in polycrystalline α-Fe crystal lattice under pulsed magnetic field. Furthermore, elastic interactions of dislocations with moving domain walls during reversal magnetization could provide a further contrition to the observed diffusion behavior.

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Phase formation in aluminum alloys aged in the constant and pulse magnetic field

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In the report the results of phase formation and magnetoplastic effect (MPE) researches in five alloys on the Al-basis with additives Mg, Li, Zn, Cu, Si, Fe and Mn, aged in a constant magnetic field (CMF) and pulse magnetic field (PMF), are presented.

Preliminary the samples subjected to annealing in the furnace at the air atmosphere, then quenched in water at a room temperature. Further the quenched samples are artificial aged in vacuum in CMF and PMF and without it. Microstructure, MPE, phase content and parameters of thin structure of a residual α-matrix of samples have been investigated by methods of metallography, microhardness, X-ray structure and phase analysis.

Ageing of the Al-basis alloy without imposing magnetic field leads to increase in intensity and broadening of the diffraction lines corresponding α-solid solutions that testifies to processes of an alloy relaxation at ageing temperature.

Inclusion CMF influences on phase formation process and structure relaxation period of aged alloy to equilibrium content. Imposing CMF changes value of thin structure parameters of α-solid solutions and at that the structure of alloys at imposing CMF and at negative sign of MPE becomes more homogeneous and fine granulated. In this cases, changes of microhardness of aged alloy up to ~20 % in relation to value of microhardness of an alloy after ageing without CMF are observed. Thus, evidencing a «negative» MPE. Application of a PMF always entails a decrease in the microhardness as compared to the case of annealing in zero field by approximately 50 % and, as a result, enhanced plasticity, which suggests a «positive» MPE.

Regularities of MPE for the Al-basis alloys is assigned in connection of their structure and thermomagnetic processing. Possible physical mechanisms of MPE in investigated alloys and the modes of ageing determining them optimum physicomechanical properties are discussed.

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Simulation of the magnetoplastic effect in copper-beryllium alloys

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Experimental studies of the aging of BrB-2 beryllium bronze in a constant magnetic field (PMF) show a noticeable “negative” magnetoplastic effect (MPE), which consists in reducing the ductility of the alloy and increasing the microhardness to 30% [1]. In some cases, the using a accompanied by the formation of structural formations — coherent scattering blocks — with a size of less than 100 nm [2], which we have identified as the nano-magnetoplastic effect (NMPE). It is of interest to search for optimal aging regimes that lead to the greatest effects of MPE and NMPE, and to establish the physical mechanisms of these effects.

We solved a range of particular problems using density functional theory and phase field method aimed at modeling MPE and NMPE arising in model copper-beryllium alloys after aging of hardened alloy in a constant magnetic field [1]. In particular, calculations were made of the energy states of binary residual solid solutions of copper-beryllium with different concentrations of beryllium, and the phase energy of the γ-CuBe phase formed during decomposition with and without external CMF superimposed. It is shown that the energy state of the residual solid solution weakly depends on the inclusion of CMF, while the imposition of CMF gives a significant gain in the energy of the states of the γ-CuBe phase.

The results obtained are consistent with experimental data on the X-ray phase analysis of copper-beryllium alloys aged in CMF and without it, which indicate a higher quantitative content of the γ-CuBe phase formed in CMF.

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The diffusion path reversibility confirms symmetry of surface barriers

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The resistance perceived by guest molecules upon entering or leaving a microporous host material (the "surface barrier") is known to often surpass the influence of diffusion in its interior on the overall rate of molecular uptake and release [1, 2]. Our knowledge of the relevant mechanisms of surface permeation, however, is still rather limited. This is related to the difficulties in its direct measurement which, given the "nanoscopic" extension of the relevant space scale, notably exceed the difficulties which do exist with already the diffusion measurement. A question discussed in this context refers to the possibility that the resistance perceived by the molecules on entering the pore space may differ from that perceived upon leaving [3-5].

In first MD simulations in zeolite MFI with partial surface blockade using benzene as a probe molecule [6], with increasing surface blockage molecular exchange rates were found to be slowed down following the relevant relations adopted from effective medium theory [7]. The diffusion path lengths covered during the simulations, however, turned out to be too short for yielding a sufficiently large enough number of adsorption-desorption events.

The situation totally changed on considering methane as a probe molecule. Now many thousands of ad- and desorption paths could be followed. They confirmed complete symmetry of the diffusion paths during adsorption and desorption and, hence, of also the surface resistance [8].

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Multiscale diffusion in porous media: From interfacial dynamics to hierarchical porosity

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The transport of liquid and solutes in porous media over widely different time and length scales, ranging from specific interactions with the surface (and the associated interfacial dynamics) to the effective pore diffusion through hierarchical porosity, is central to many environmental and technological processes. This interplay between surface functionality and hierarchical porosity requires, on the one hand, a detailed molecular-level picture of sorption, reaction, and mobility, and realistic geometrical models of hierarchically porous media on the other, to establish (and apply) quantitative morphology–functionality–transport relationships for the tailored preparation of ever more selective and efficient materials for storage, separation, and catalysis.

We present a modelling approach that allows us to determine effective transport properties covering a hierarchy of length scales, from the detailed molecular-level picture at the surface and the interfacial dynamics, emerging from molecular dynamics (MD) simulations [1], to diffusion in physical reconstructions of hierarchical porosity, simulated by a Brownian dynamics approach [2,3].

A key message of this work is that interfacial phenomena resolved by the MD simulations have a strong influence on the effective diffusivity resulting on a macroscopic scale, an effect that is usually difficult to assess and quantify or even remains unknown. This influence can be adequately reflected by the presented multiscale simulation approach, which embeds the relevant interfacial dynamics along the hierarchical porosity and associated molecular diffusion path.

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Stationary-phase contributions to surface diffusion at C_8-modified silica mesopores

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The structure, dynamics, and mobility of binary solvents and solute molecules at adsorbent surfaces play an important role in adsorption, catalysis, and separation. When investigating chemical systems, information gained by experimental data is often limited to the macroscopic view. Molecular dynamics (MD) simulations allow new insights on molecular processes and offer the possibility to study the molecular-level picture at solid-liquid interfaces in detail.

In previous work, we investigated the distribution and mobility of binary water (W) – acetonitrile (ACN) mixtures and four typical aromatic hydrocarbon analytes (benzene, ethylbenzene, acetophenone, and benzyl alcohol) in C_{18}-modified silica slit pores, mimicking the conditions in reversed-phase liquid chromatography (RPLC), by MD simulations [1]. The data showed that analytes are retained by a combination of partitioning into and adsorption onto the bonded-phase chains [1]. Furthermore, the local diffusive mobility of the analytes parallel to the surface goes through a maximum in the ACN ditch, an ACN-rich border layer around the terminal parts of the bonded-phase chains, because the solvent composition there is more conducive to analyte mobility than the W-rich mobile phase [1,2]. In this study, MD simulations were carried out for the four analytes in silica slit pores with two different C_8 surface modifications to gain information about the influence of grafting density and chain length on surface diffusion. The first silica surface was modified with 3.11 µmol C_8 chains/m^2 and endcapped with 0.93 trimethylsilyl (TMS) groups/m^2. For the second surface (high-density C_8 (hd-C_8)), all endcapping groups were replaced by additional C_8 chains. Due to the increased grafting density, the C_8 chains are more stretched, resulting in a so-called picket-fence structure. For a 70/30 (v/v) W/ACN mobile phase, analyte surface diffusion increases from C_8 over C_{18} to hd-C_8 and for 20/80 (v/v) W/ACN, the increase results in the order of C_8, hd-C_8 and C_{18}. For the W-rich mobile phase, the bonded phase contributes positively to surface diffusion. In addition, we show that a shorter chain length of the bonded phase results in a larger overlap between the adsorption and partitioning peak of the analytes

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Concentration-dependent sedimentation and diffusion coefficient in analytical ultracentrifugation experiments

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Experimental data of analytical ultracentrifugation (AUC) experiments is defined by sedimentation and diffusion transport of molecules in solution. While the sedimentation properties define the position of the measured sedimentation boundaries, information on the diffusion is included in the broadening. Both effects are then analysed with well-established finite element solutions of Lamm's equation The results from this multidimensional analysis provide e.g. molecular mass or size distributions or information on core-shell structures [1,2]. Moreover, it is known that the properties of macromolecules and particles in AUC experiments are influenced by concentration-dependent sedimentation and diffusion coefficients, which are described by two interaction terms k_s and BM. While the Gralen coefficient k_s represents hydrodynamic interactions, the second virial coefficient B is a thermodynamic quantity and is used to correct for non-ideal diffusional properties throughout AUC experiments [3]. Here, we show that by analyzing these parameters via AUC, information of the global interaction of particles in solution can be retrieved. Hence, the second virial coefficient was determined for a lysozyme model system as a function of the pH of the solution from AUC experiments Figure 1 (left) presents the retrieved values for BM from the AUC measurements as black bars. It can be concluded that the interaction term BM is a measure for stability and the tendency of the system to aggregate as it follows the trend of the zeta-potential representing charge-charge interactions. Theoretical considerations from DLVO theory show that with increasing pH of the solution, the contribution from an electrostatic potential decreases and thus predict a decreasing interaction term with increasing pH, as can be seen in Figure 1 (right). This approach paves the way for a direct correlation between global interaction potentials in solution and parameters obtained from AUC experiments.

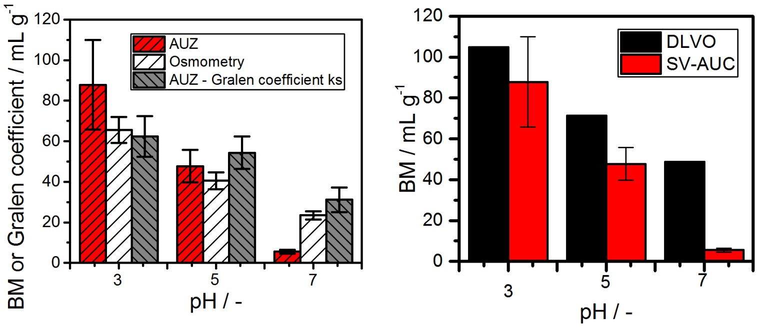

Figure 1: Left: Second virial coefficient from SV AUC experiments (grey bars), osmometric measurements (red bars) alongside the Gralen-coefficients (Grey bars). Right: Second virial coefficient from DLVO theory (black bars) alongside the values from SV-AUC experiments (red bars).

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Synthesis of hierarchical TS-1 zeolites from a hydrolysis resistant polymer and their excellent catalytic performance in bulky molecules oxidation

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The traditional TS-1 zeolite is a typical microporous material, the diffusion of bulky molecules in TS-1 is greatly affected.[1] Besides, because of the highly hydrolyzable titanium source, the preparation of TS-1 requires complex synthesis conditions. Moreover, the difference in hydrolysis rate between the silicon source and titanium source tends to increase the difficulty of titanium insertion into the framework, and it is easy to generate extraframework Ti species during the synthesis. We propose a method of synthesizing hierarchical TS-1 from highly hydrolysis-resistant polymers containing titanium and silicon (Fig. 1a). This method completely solves the above problems and can conveniently and stably synthesize high-quality TS-1 free of extraframework Ti species. The TS-1 zeolite synthesized from the polymers exhibits excellent reaction performance in the oxidation of n-hexane and cyclohexene.

SEM and TEM images of the TS-1 zeolites synthesized with the polymers are displayed in Fig. 1b. TS-1 zeolites synthesized from polymers is a kind of nano domain aggregated MFI with a mean size around 300 nm. We further investigated the characterizations of the low-temperature N_2 physical adsorption (Fig. 1c). It revealed that TS-1 synthesized from polymers has a higher external surface area (134 m^2g^{-1}) than the samples synthesized by conventional methods (48 m^2g^{-1}).

The catalytic performance of TS-1 synthesized from polymers was evaluated by the oxidation reactions of n-hexane and cyclohexene. The results in Fig. 1e shows that the catalytic activity of TS-1 synthesized from polymers (TS-1-P) was much higher than that of TS-1 synthesized by conventional processes (TS-1-C), regardless of the oxidation reaction of n-hexane or cyclohexene.

Cyclohexene has a molecular dimension of about 0.5 nm. Thus, in contrast to n-hexane, cyclohexene suffers from strong diffusion constraints when diffusing in the 10-ring pores. Contrary to linear alkenes, molecular diffusion is the rate-determining parameter for the first oxidation reaction. The superiority in oxidation performance of TS-1 synthesized from polymers is mainly attributed to the sample had a high external surface area and hierarchical structure, which leads to the reactant being easily accessible to the active sites, especially for cyclohexene, which is a relatively larger molecule compared with n-hexane.

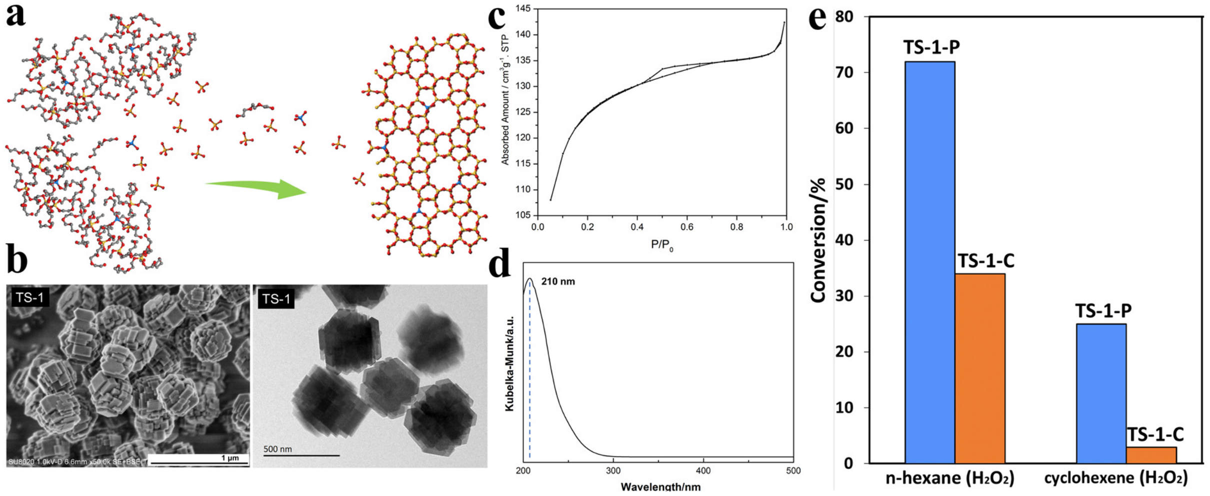

Figure 1: (a) Schematic illustration of synthesizing TS-1 zeolites. (b) SEM and TEM of TS-1-P. (c) N_2 adsorption-desorption isotherms of TS-1-P. (d) UV-Vis spectra of TS-1-P. (e) Oxidation of n-hexane and cyclohexene over TS-1-P. Reaction condition: cat., 50 mg; alkene and H_2O_2, 10mmol. CH_3OH, 10ml; 333K; 4h.

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A vacuum set-up for fundamental studies of self- and transport diffusion in porous media

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Diffusion in disordered porous media attracts a lot of attention because of its considerable importance to industrial processes, such as molecular separations, heterogeneous catalysis and oil recovery [1]. In heterogeneous catalysis, the molecules diffuse through the pore network and react on the active sites on the pore walls. The geometrical disorder of porous systems intensely influences molecular transport processes that occur inside the pore network [2]. In mesoporous materials, Knudsen diffusion is often the predominant transport mechanism for gases, where the mean free path of the molecules is much larger than the pore diameter, so that molecule-wall collisions dominate molecular transport.

Despite its practical relevance, direct experimental insight of the effect of fractal surface roughness on Knudsen diffusion in porous media has never been obtained. This may be due to the complexity of real porous media, where effects of pore shape, surface roughness, and pore connectivity are combined. Modeling [2,3] nevertheless suggests significant effects of fractal surface roughness on Knudsen diffusion. Such theoretical results can form the basis for comparison with carefully designed experiments on model pores or porous media to validate the theory.

Here, we propose experiments that emulate processes that occur in disordered mesoporous media, on a macroscopic scale, by using a special designed high-vacuum system and 3D-printed channels to investigate features of complex porous media, such as fractal pores [3]. This set-up allows us to validate Knudsen diffusion theory in complex geometries more directly than has ever been the case. Some preliminary results will be shared, including features of the vacuum set-up, and Knudsen diffusion results in channels of varying geometry, including channels with a 3D-printed fractal surface.

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Self- and transport diffusion coefficients from NMR experiments

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Self-diffusion coefficients give insight into the mobility of molecular species and serve as benchmark variables for molecular modeling. Nuclear magnetic resonance (NMR) spectroscopy is an excellent method for the measurement of self-diffusion coefficients: In the present work, a pulsed gradient stimulated echo (PGSTE) pulse sequence was employed for their determination in binary and ternary liquid systems at 298 K and 1 bar. To ensure a high quality of the measurements, a preliminary gradient mapping was carried out. The experimental results are compared to molecular simulation data by Guevara-Carrion et al. [1] for binary systems (acetone/toluene, acetone/ethanol and acetone/cyclohexane) and to molecular simulation data that was determined in the present work for the ternary system acetone/toluene/cyclohexane.

Data on the self-diffusion coefficient was also extrapolated to infinite dilution, where the self- diffusion coefficient is equal to the transport diffusion coefficient. Furthermore, transport diffusion coefficients were determined from measurements with field gradient NMR, which yields quantitative spatially- and time-resolved information on the concentrations.

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Dynamic viscosity, interfacial tension and mass diffusion coefficient of *n*-hexane, cyclohexane, 2-methylpentane and CO_2 systems

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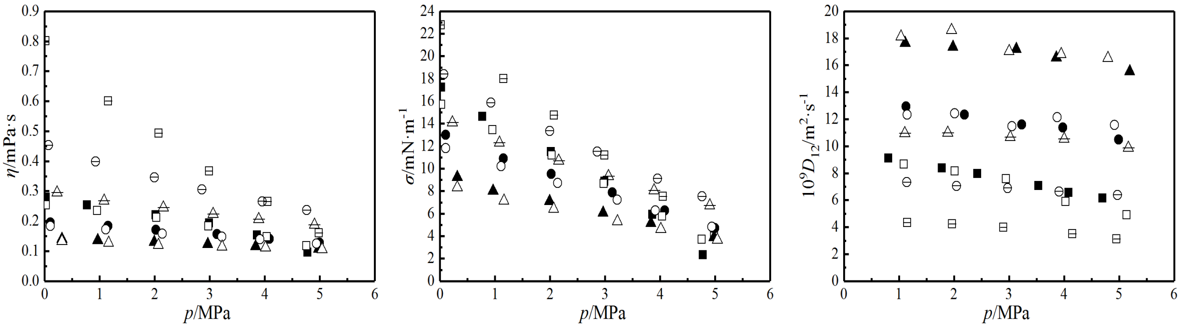
Dynamic viscosity, interfacial tension and mass diffusion coefficient of CO_2 in hydrocarbons are the fundamental transport properties in the CO_2 flooding technology applied in oil exploitation, which can improve the oil recovery rate effectively and complete the geological burial of CO_2 [1]. In this work, *n*-hexane, cyclohexane and 2-methylpentane were selected to represent linear-alkanes, cycloalkanes and branched alkanes, respectively. Based on the light scattering method, the viscosity, interfacial tension and mass diffusion coefficient of *n*-hexane/CO_2, cyclohexane/CO_2 and 2-methylpentane/CO_2 were measured in order to explore the change trend of thermophysical properties of the systems with the same carbon atom number but different molecular structures. The experiments were conducted at the temperatures of 303 K, 343 K and 383 K and at pressures up to 5 MPa. The expanded uncertainties ($k = 2$) of dynamic viscosity, interfacial tension and mass diffusivity were 2.5%, 2% and 5%, respectively. The experimental results show that *n*-hexane and 2-methylpentane with similar molecular structure have more similar values of properties, while cyclohexane with cyclic structure has lower thermophysical properties than the others.



n-hexane/CO_2: (■) $T = 303$ K; (●) $T = 343$ K; (▲) $T = 383$ K; cyclohexane/CO_2: (⊟) $T = 303$ K; (⊖) T=343 K; (△,—) $T = 383$ K; 2-methylpentane/CO_2: (□) $T = 303$ K; (○) $T = 343$ K; (△) $T = 383$ K

Figure 1: Dynamic viscosity, interfacial tension and mass diffusion coefficient of *n*-hexane, cyclohexane, 2-methylpentane and CO_2 systems.

Acknowledgments:

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Translational and rotational diffusion coefficients in nanofluids from polarized dynamic light scattering

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Nanofluids representing nanometer-sized solid particles dispersed in liquids are of interest in many fields of process and energy engineering, e.g., heat transfer, catalysis, and the design of functionalized materials [1]. The physical, chemical, optical, and electronic properties of nanofluids are strongly driven by the size, shape, surface potential, and concentration of the nanoparticles. For the analysis of diffusive processes in nanofluids allowing access to, e.g., particle size and its distribution, dynamic light scattering (DLS) is the state-of-the-art technique. It is based on the analysis of microscopic fluctuations originating from the random thermal movement of particles in the continuous liquid phase at macroscopic thermodynamic equilibrium. For anisotropic particles or particle aggregates, besides translational diffusion also rotational diffusion occurs. To obtain the sum of the orientation-averaged translational (D_T) and rotational (D_R) diffusivities by depolarized DLS [2], a homodyne detection scheme is usually applied which can hardly be fulfilled in the experimental realization. Furthermore, the experiments are restricted to limited ranges for temperature, particle concentration, and viscosity.

The objective of this work is to show the applicability of polarized DLS for the simultaneous study of translational and rotational diffusion in nanofluids. For this, the polarized component of the scattered light modulated by the random motion of anisotropic particles was studied to simultaneously resolve D_R and D_T. To investigate opaque nanofluids reliably, a DLS setup was established where sufficiently low laser powers are applied and the scattered light is analyzed in reflection direction. By ensuring a heterodyne detection scheme where much stronger reference light is superimposed to the scattered light, the uncertainties of the measured diffusivities could be reduced. As model system, water-based nanofluids containing stabilized gold nanorods with a volume fraction of 10^{-5} were investigated from 271 to 323 K. To account for variations in the particle concentration and in the viscosity of the liquid phase ranging between 0.5 and 9.0 mPa·s, volume fractions of the gold nanorods from 10^{-5} down to 3.7×10^{-6} and water-glycerol mixtures with glycerol volume fractions up to 0.67 were studied at 303 K.

In agreement with theory [2], the measured correlation functions of the polarized component of the scattered light intensity contain two superimposed exponentials which appear on different time scales. The slower mode is associated with the isotropic component of the scattered light, i.e. with the translational diffusivity. The faster mode is connected to the combined translational and rotational motion of the gold nanorods. On average, the orientation-averaged D_T and D_R values measured by DLS at 303 K are $(8.9 \pm 0.7)\times10^{-12}$ $m^2\cdot s^{-1}$ and $(7.9 \pm 3.4)\times10^{3}$ s^{-1}. Compared to these values, the D_T and D_R data predicted by the stick hydrodynamic theory [3] based on results for length and aspect ratio of the gold nanorods analyzed from scanning electron micrographs agree with the experimental data. For D_T and D_R, temperature-dependent behaviors described by a modified Andrade-equation and decreasing trends with decreasing particle volume fractions below 4×10^{-6} were found. For all measurements performed at a particle volume fraction of 10^{-5} in connection with the water-based systems as a function of temperature and the water-glycerol-based systems at 303 K, generalized relations between the ratio of the diffusivities to temperature and the dynamic viscosity of the liquid phase were observed. Here, a weaker viscosity-dependent trend is given for D_R than for D_T.

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Assessing diffusivities of organic compounds in ionic liquids

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While equilibrium dissolution of volatile compounds in ionic liquids (ILs) has been studied for numerous systems, diffusivities of such compounds in the ILs have not commonly been assessed in most studies [1, 2]. We thus report on the diffusivity of methanol and ethanol in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [BMIM][NTf2].

Transient absorption of the single-component vapours in [BMIM][NTf2] was measured using sorption microgravimetry: IL was first degassed by exposing it to vacuum and then exposed to the vapours while mass of the solution was measured over time. Experimental data were evaluated by using Fick's second law.

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{1}$$

The model of the transient absorption into the one-dimensional liquid body upon its idealized instantaneous exposure was taken from the literature [3]. This model was then modified to reflect the realistic pressure dependences in the apparatus.

The knowledge of the diffusivities of volatile components in ILs enables to utilize extraction units outside equilibrium and, potentially, enhance their performance. Besides that, knowledge of diffusivities of volatile compound in ILs allows for the targeted preparation of IL-based separation membranes.

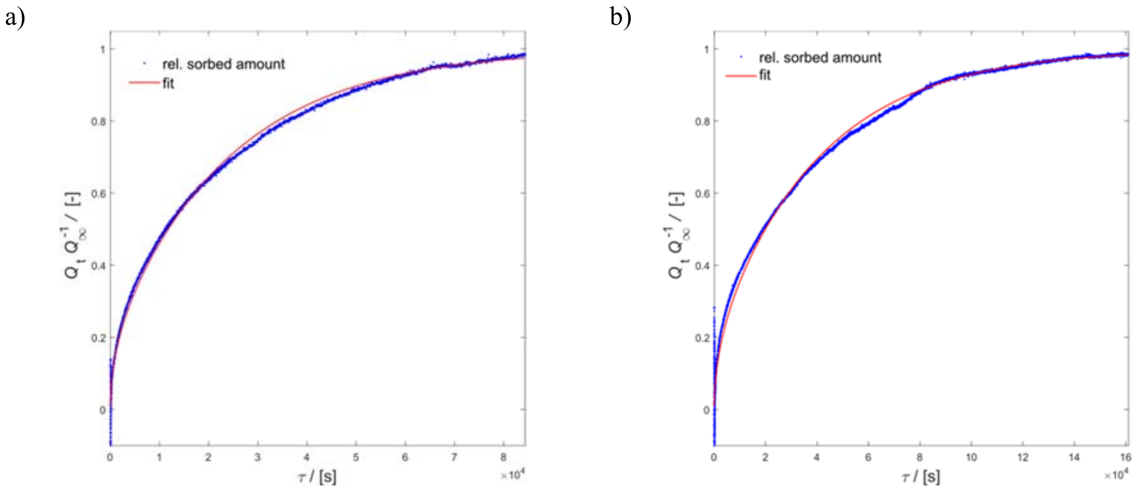

Figure 1: Transient absorption of methanol (a) and ethanol (b) vapour in [BMIM][NTf2].

Acknowledgement

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The thermodynamic factor: The key to understand complex diffusion behavior in fluid mixtures

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Separation processes in chemical engineering, such as distillation, absorption or extraction, are affected by diffusion. In recent years, molecular modelling and simulation has become an alternative tool not only to accurately predict dynamic properties of fluids, but also to interpret experimental data because it offers access to microscopic details which are often inaccessible with experimental techniques. In preceding work of our group [1,2,3], it was shown that transport properties of pure fluids, binary and ternary mixtures of non-polar, polar and hydrogen-bonding species can be accurately predicted with simple, non-polarizable molecular models.

We present the results of a molecular simulation study of fluid mixtures, where complex diffusion behavior has experimentally been found and offer an explanation based on the hydrodynamic and thermodynamic components of the Fick diffusion coefficient. Special attention is paid to mixtures near critical and demixing regions, where in many cases strong discrepancies between different measurements of the Fick diffusion coefficients are found. Also molecular simulations are challenging in these regions and require extensive sampling due the presence of pronounced density fluctuations.

In molecular dynamics simulations, the Fick diffusion coefficient is typically calculated from the Maxwell-Stefan diffusion coefficient and the derivative of the chemical potential in form of the thermodynamic factor. Because the chemical potential cannot be measured by experiment, this factor is usually estimated from vapor-liquid equilibrium or excess enthalpy data, employing an equation of state or an excess Gibbs energy model. Nevertheless, it can also be sampled by molecular simulations, as it was done in this work.

Near the infinite dilution limit, the thermodynamic factor is usually assumed to be unity and to have an insignificant influence on the value of the Fick diffusion coefficient. However, under certain conditions, even for solvent concentrations of a few mole percent only, the thermodynamic factor may approach values of zero, having a major impact on the Fick diffusion coefficient. For example, the thermodynamic factor of a 1 mole% mixture of benzene in carbon dioxide may reach values around 0.5 in the near-critical region. Thus, the anomalous behavior of diffusion found experimentally in this region for this mixture and the strong composition dependence of the Fick diffusion coefficient can be rationalized, if the thermodynamic factor is taken into account.

Furthermore, for highly non-ideal mixtures and those approaching a demixing region, the contribution of the thermodynamic factor to the observed Fick diffusion coefficient may become much more important than the hydrodynamic contribution given by the Maxwell-Stefan diffusion coefficient

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The Diffusion Research Unit, The Australian National University, Canberra: A contribution to physical chemistry and beyond

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The Australian National University was established in Canberra in 1946-48 to be a research university of international standing under the post-war Chifley federal government. At that time Australia had only six universities, all in the main population centres, the state capitals. Canberra, as the country's capital housed the national Parliament, but had yet to be developed as a true city. Under Adelaide-born Marcus Oliphant (later Sir Mark), a nuclear physicist and former student of Rutherford who had contributed to the Manhattan Project, the Research School of Physical Sciences was established in 1949. Reg Mills (1917-2001), a New Zealander, joined the Department of Radiochemistry in 1954, bringing skills in using radio-tracer methods to make precise measurements of the diffusion of ions in electrolyte solutions to test theoretical predictions. In 1964 he set up the Diffusion Research Unit which he led until his retirement in 1982. He was succeeded by Lawrie Woolf (1934-2019), a West Australian who, having joined DRU in 1966, continued the outstanding work of the unit until his retirement in 1998. During this period of 32 years, DRU was host to many distinguished visitors and young scientists from many countries who came to learn diffusion techniques. Mills and Woolf adapted the Stokes diaphragm cell for radiotracer measurements and McCool, Collings and Woolf developed a high-pressure cell for self-diffusion measurements. Mills established the first accurate values for self-diffusion coefficient of water over a range of temperature [1]. These are now the basis for calibration of all NMR apparatus used in diffusion measurements and certain applications of Magnetic Resonance Imaging in medicine. In addition, Harris and Woolf determined the self-diffusion of water and 18-oxygen water over a wide range of pressures and temperatures [2]. DRU carried out extensive studies of isotope effects, i.e. the effect of molecular mass, on molecular and ion diffusion. These are used extensively by hydrologists and soil sciences in understanding the age and flow of water in artesian water supplies.

Here we detail these and other contributions made by DRU in fields such as molten salts, liquid state physics, refrigerants, cryogenic liquids, food chemistry, electrolyte and non-electrolyte solutions, and the theory of mass and charge transport processes in solutions. These illustrate the wide use and fundamental importance of diffusion processes in diverse areas of Science and Technology.

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Fick diffusion coefficients in binary fluid mixtures consisting of methane, propane, or carbon dioxide by theoretical and optical methods

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Fluid mixtures containing natural gas components such as methane, propane, and carbon dioxide are important in many areas of process and energy engineering. For the optimum design of apparatuses and processes related to such systems, the exact knowledge of mass diffusivities as a function of temperature, pressure, and composition including the specification of their uncertainties is necessary. For this, experimental techniques and theoretical approaches including molecular dynamics (MD) simulations are needed to provide a reliable database. Although theoretical approaches have to be normally validated with experimental data, they are helpful to understand macroscopic properties as mass diffusivities from a molecular perspective. Within an ongoing research project at AOT-TP, Fick diffusion coefficients in binary fluid mixtures consisting of methane, propane, or carbon dioxide should be accurately determined over a wide region of thermodynamic states ranging from the superheated vapor over the gas state and supercritical region up to the compressed liquid state by theoretical and optical methods.

With holographic interferometry applied for a Loschmidt cell (HILC), the instationary diffusion process observable in binary fluid mixtures subjected to a defined initial macroscopic concentration gradient is investigated. From the analysis of the temporal change in the partial molar density in both half cells applying two interferometers, the concentration dependency of the Fick diffusion coefficient D_{11} was accessed in the superheated vapor and gaseous state at pressures between 0.05 MPa and 0.5 MPa and at temperatures of 293 K and 313 K [1]. With dynamic light scattering (DLS) experiments in macroscopic thermodynamic equilibrium, the dynamics of microscopic fluctuations in composition is studied by the temporal analysis of the scattered light intensity. In this way, absolute D_{11} data were accessible as a function of concentration in the supercritical and compressed liquid state around the two-phase boundary at pressures between 9 MPa and 12 MPa and temperatures between 283 K and 363 K. The measurement results obtained by HILC and DLS with expanded uncertainties of about 5% served as reference for equilibrium MD simulations calculating thermophysical properties from the analysis of the statistical motion of molecules. Based on a simultaneous consideration of kinetic and thermodynamic contributions, D_{11} values were calculated by MD simulations over the entire concentration range at pressures between 0.1 MPa and 12 MPa with statistical expanded uncertainties of about 10%. For these calculations, besides molecular models or force fields from literature, newly developed ones derived from *ab initio* calculations for the pure fluids in the limit of zero density [2] were employed as alternatives. For the investigated range of thermodynamic states including temperatures between 293 K and 353 K, the simulated D_{11} values obtained with the new *ab initio*-based models are in better agreement with the experimental results.

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Solubility of CO_2 in 2-butyl-1-octanol from (323.15 to 573.15) K at pressures up to 10 MPa

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China is rich in coal resources, whereas oil-gas resources are relatively in shortage. Currently, coal dominates the supply and consumption of energy in China, accounting for 69.6% of total energy production and 60.4% of total energy consumption in 2017 [1]. A majority of coal is directly combusted for power generation, steel and cement industries, and residential and commercial heating, which has caused severe energy waste and environmental problems. Therefore, in recent years, the Chinese government is now taking an active role to promote the utilization of clean coal technologies (CCTs), including clean coal power generation, coal conversion, pollution control and carbon capture. A number of factories using CCTs have already stepped into the commercialization stage [2].

Coal gasification combined with the Fischer-Tropsch process converting coal into synthetic liquid fuels is one of the promising CCTs. The Fischer-Tropsch process involves complex gas-liquid systems, primarily long chain hydrocarbons and its mixtures with H_2, CO, H_2O or CO_2 gases. The conversion efficiency of the Fischer-Tropsch process for coal is around 47.3% to 53.6% (lower heating value basis) [3]. To further optimize and improve the Fischer-Tropsch process, it is vital to understand the thermophysical properties of reactants and products involved in this process.

2-Butyl-1-octanol ($C_{12}H_{26}O$) is one of the representative alcohols of the Fischer-Tropsch process and one of the most easily acquirable long chain alcohols. In this work, solubility of CO_2 in 2-butyl-1-octanol is measured by isochoric-saturation method over the temperature range of (323.15 to 573.15) K and at pressures up to 10 MPa. The expanded uncertainties ($k = 2$) of temperature, pressure and solubility are 20 mK, 1.6 kPa and 3%, respectively. The Peng-Robinson equation of state combined with the van der Waals mixing rule is used to correlated the experimental data.

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Fick diffusion coefficients in binary liquid mixtures of *n*-alkanes or 1-alcohols with dissolved gases investigated by molecular dynamics simulations and dynamic light scattering

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Systems based on liquids containing dissolved gases are of interest in many areas of chemical and energy engineering such as separation processes, catalysis, and hydrogen storage by liquid organic hydrogen carriers. One key property required for the optimum design of corresponding processes is the diffusion coefficient. In a current research project, the benefits of experimental and modeling methods are combined to get a fundamental understanding on the influence of varying molecular species and thermodynamic state on the diffusive mass transport in liquids with dissolved gases.

The objective of the present study is to characterize the molecular diffusion in binary systems consisting of liquids and dissolved gases via the study of the Fick diffusion coefficient. For this, the strategy was to combine the benefits of dynamic light scattering (DLS) experiments and molecular dynamics (MD) simulations. To account for variations in the polarity of the solvents and the size of the solutes, binary mixtures of the solvents *n*-hexane (*n*-C_6H_{14}) or 1-hexanol (1-$C_6H_{14}O$) with the dissolved gases hydrogen (H_2), helium (He), carbon monoxide (CO), nitrogen (N_2), and carbon dioxide (CO_2) were investigated at temperatures between (303 and 423) K. While for the gases H_2, He, CO, and N_2, which show low solubilities in the solvents, investigations were limited to relatively small mole fractions below 0.05, the entire concentration range was studied for mixtures with CO_2 at mole fractions between 0.01 and 0.95. From DLS measurements studying microscopic concentration fluctuations at macroscopic thermodynamic equilibrium, the Fick diffusion coefficient could be accessed with typical expanded uncertainties smaller than 5%. These results provide a database to validate equilibrium MD simulations. The quantities directly accessible by the simulations are the self-diffusion coefficients of both components and the Maxwell-Stefan diffusion coefficient. The latter property was combined with the thermodynamic factor obtained from the simulations or equations of state to determine the Fick diffusion coefficient with typical expanded statistical uncertainties of 10%.

The main findings of the present study may be summarized as follows. At conditions approaching infinite dilution of the dissolved gas, the self-diffusion coefficient of the gas and the Fick diffusion coefficient of the mixtures were found to be equal [1], which is in agreement with theory. For a given gas and temperature, the mass diffusivities in *n*-C_6H_{14} and in 1-$C_6H_{14}O$ correlate with the behavior of the solvent viscosities. While the matching mass diffusivities for systems containing CO and N_2 follow the expected trend, the larger values for the systems containing the heavier He in comparison with those containing the lighter H_2 could be related to the smaller size of He. It could be shown that the MD simulations can also represent the non-ideal concentration dependency of the Fick diffusion coefficient obtained by DLS for the CO_2-based mixtures [2]. Radial distribution functions and hydrogen-bonding statistics calculated by the MD simulations show that the slowing-down of the Fickian diffusion with increasing CO_2 mole fraction is caused by a distinct structural organization in the binary mixtures. An indication for this behavior could also be received by Raman spectroscopy performed simultaneously with the DLS measurements.

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Simultaneous study of molecular and micelle diffusion in polyol-based microemulsions with CO_2-swollen micelles by dynamic light scattering

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Microemulsions are of interest for many technical applications, *e.g.*, in the form of polyol-based systems with nanometer-sized supercritical carbon dioxide (CO_2)-swollen micelles as a starting point for the production of high-performance insulation foams. In such systems investigated in the present study, dissolved CO_2 as well as CO_2-swollen micelles formed by surfactants diffuse inside the polyol-based continuous phase of the microemulsion. These processes can be described with a molecular and a micelle diffusion coefficient, respectively.

While the determination of molecular diffusion coefficients of gases dissolved in various kinds of liquids by dynamic light scattering (DLS) is well-established at our institute since about five years, we have shown only recently that a proper use of this method also gives access to the translational micelle diffusion coefficient for such systems. In the given technical example, the latter diffusion coefficient is of particular interest for the insulation foam production because it can be used to derive information on the micelle size *via* the Stokes-Einstein relation.

In the present contribution, it is shown for the first time that the simultaneous study of both diffusion processes in microemulsions can be realized successfully by DLS. As the diffusion process of micelles is much slower than that of molecular solutes, the corresponding DLS signals analyzed in the form of intensity correlation functions appear on different time scales and can be separated by an appropriate data evaluation procedure. To determine the correct diffusion coefficient values from the obtained correlation times, it is necessary to identify the detection schemes for the different hydrodynamic modes. For the contribution from translational micelle diffusion, a homodyne detection scheme could be ensured, which means that sufficiently pure scattered light from the micelles was analyzed. For the contribution from molecular diffusion, it was proven with the help of an additional model system that light scattered by strong scatterers such as particles or micelles superimposes the much weaker scattered light modulated by fluctuations in species concentration on a molecular scale. Thus, it acts as sufficiently strong reference light to achieve heterodyne conditions for the hydrodynamic mode related to molecular diffusion.

Besides other experimental details, it is demonstrated that also absorbing samples can be investigated by implementing a newly developed technique analyzing scattered light in reflection direction as well as by a careful selection of the laser wavelength and power to minimize the effect of local sample heating caused by laser light absorption.

All determined diffusion coefficients for a given system show an increasing trend with increasing temperature. The presence of CO_2 increases the translational micelle diffusion coefficient despite the detectable swelling of the micelles. This can be related to the decreasing viscosity of the polyol mixture when CO_2 is dissolved therein. Hydrodynamic diameters of the non-swollen and CO_2-swollen micelles determined from the translational diffusion coefficients are in good agreement with literature data. The effective diffusion coefficient related to the molecular diffusion processes only observable in the presence of CO_2 in the microemulsion is in agreement with that measured without the presence of micelles and in the same order of magnitude as binary diffusion coefficients reported for similar systems without inhomogeneities. Additionally, it is shown that the surfactant concentration affects the hydrodynamic diameter of non-swollen micelles for the systems studied.

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Improvement of a transferable force field for the prediction of self-diffusivity, viscosity, surface tension, and density of long-chained linear and branched alkanes and alcohols up to 573 K by molecular dynamics simulations

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Systems based on long-chained linear and branched alkanes and alcohols are of interest in many areas of process and energy engineering, such as the production of highly valued petroleum products. For an efficient process design, reliable information on the transport and equilibrium properties of such systems is required. An ongoing research project at AOT-TP aims to contribute to a fundamental understanding of the thermophysical properties of long-chained hydrocarbons and related alcohols as well as their corresponding mixtures with and without dissolved gases. A special focus is on viscosity and surface tension, as they govern heat, mass, and momentum transport in continuous phases and across phase boundaries. In addition to experiments providing an ensured database, molecular dynamics (MD) simulations are used to predict thermophysical properties. The accuracy of these predictions depends on how well the molecular interactions are described by the underlying force fields (FFs). Published FFs are typically transferable to a variety of molecules, but their performance in predicting both transport and equilibrium properties up to large temperatures can be limited. Extending a FF to be transferable also across temperature and pressure is imperative for predicting properties at process-relevant conditions, where experiments are expensive or technically challenging.

The objective of the present study is to further develop a transferable FF for the reliable prediction of transport and equilibrium properties of long-chained alkanes and alcohols at vapor-liquid equilibrium for temperatures between 298 and 573 K by MD simulations. As model systems, the linear alkanes *n*-dodecane, *n*-hexadecane, *n*-triacontane, and *n*-tetracontane, related branched isomers 2,2,4,4,6,8,8-heptamethylnonane (HMN) and squalane as well as the linear and branched alcohols 1-dodecanol, 1-hexadecanol, 1,12-dodecandiol, 2-butyl-1-octanol, and 2-hexyl-1-decanol were selected. We are therefore able to probe, over the complete temperature range, the effects of alkyl chain length, branching, and hydroxylation on the calculated results for the equilibrium properties self-diffusivity, surface tension, and density, as well as the transport property viscosity. For the representative testing set consisting of *n*-dodecane, *n*-octacosane, 1-dodecanol, and HMN, three well-established FFs are evaluated: the all-atom L-OPLS FF, which considers each atom explicitly, and the TraPPE and MARTINI FFs, which approximate the molecules in the form of pseudo united atoms and coarse-grained beads. The best-performing FF at ambient conditions is chosen for further optimization in order to accurately predict both the equilibrium and transport properties at higher temperatures. As reference, our own experimental data for viscosity and surface tension, determined with surface light scattering (SLS), and density, determined with a vibrating-tube densimeter, were employed.

Over the complete temperature range, the MARTINI FF gives on average the worst representation for the studied systems and properties among the three investigated FFs. The TraPPE FF shows the best prediction for the static properties surface tension and density, but significantly underestimates viscosity and overestimates the self-diffusivity. At temperatures around 298 K, the L-OPLS FF is the best representative for predicting all four properties of interest and is therefore chosen for further development. As temperature increases, the L-OPLS FF increasingly underestimates the density, leading to an underestimation of the viscosity and surface tension of the various test systems as well. It is therefore expected that a temperature-dependent correction to the prediction of densities will improve the prediction capability of the FF for the other properties as well. This correction is achieved by adjusting the Lennard-Jones parameters and partial charges of the atoms as a function of temperature, resulting in improved predictions for the transport and equilibrium properties over the complete temperature range. The optimized FF is then transferred to the seven remaining substances and predictions are compared to the experimental data.

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Viscosity measurements of *n*-dodecane and 2-butyl-1-octanol at temperatures from (298 to 475) K and pressures up to 10 MPa by vibrating-wire method

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Due to high oil price, energy safety and climate change, the Fischer-Tropsch synthesis has attracted much attention [1]. Through the Fischer-Tropsch process, synthesis gas ($CO + H_2$) from coal gasification can be converted into hydrocarbon and alcohol fuel with no sulfur and no nitrogen. Viscosity affects the fluid mobility and the heat and mass transfer rate, and further determines the power requirements for the pump and mixer. To further optimize and improve the Fischer-Tropsch process, it is vital to understand the viscosity of reactants and products involved in this process.

n-Dodecane and 2-butyl-1-octanol are two representative substances which are frequently involved in the synthesis of Fischer-Tropsch. The molecular structure of *n*-dodecane is similar to multicomponent hydrocarbons [2], and there are many viscosity data reported in literature for *n*-dodecane, so the viscosity measurement of *n*-dodecane can serve as a validation of the apparatus and supplement the existing experimental data as well. However, to the authors' best knowledge, the viscosity data of 2-butyl-1-octanol was mentioned only in one paper [3], and it merely shows a figure of the pressure-dependent viscosity of 2-butyl-1-octanol at 294 K, without exact data.

In the present work, a vibrating-wire apparatus was developed to measure the viscosity of *n*-dodecane and 2-butyl-1-octanol over the temperature range of (298 to 475) K with a total uncertainty less than ±20 mK, and at pressures up to 10 MPa with the accuracy of 0.1%. The expanded uncertainty of viscosity with a level of confidence of 0.95 ($k = 2$) is estimated to be 2.0%. The hard-sphere model was used to correlate the viscosity data. Besides, the average absolute deviation and the maximum absolute deviation between the experimental data and the calculated data from hard-sphere correlation were evaluated, respectively.

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Predicting self-diffusion and transport diffusion coefficients using entropy scaling and PC-SAFT

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Many approaches for the prediction of transport diffusion coefficients D_{ij} require knowledge of self-diffusion coefficients of pure substances D^{self} or diffusion coefficients at infinite dilution D^0. With the scarce availability of experimental data, we show approaches for the calculation of these properties in our study.

To describe and even predict self-diffusion D^{self} using only a thermal equation of state, the entropy scaling method proposed by Rosenfeld [1] provides an impressively simple but accurate approach. Rosenfeld found a monovariable dependence between residual entropy and transport properties. We use the PCP-SAFT equation of state [2] to calculate residual entropies. With a suitable correlation function the entropy scaling method for self-diffusion coefficients shows good agreement with experimental data for all available systems. We show results for various chemical families in the entire fluid region [3].

For the calculation of diffusion coefficient at infinite dilution D^0 most approaches from literature use variations of the Stokes-Einstein (SE) Equation [4]. Despite the crude assumptions inherent in the SE equation for molecular species, some approaches lead to satisfying results for many systems, but require many input parameters and some define various equations for specific chemical families. To overcome these problems, we develop a modified SE approach to estimate D^0 using only D^{self} and viscosity η of the corresponding pure substances. Both, D^{self} and η [5], are calculated through entropy scaling. Further, we extended our new approach by an entropy dependent function to correct for inaccuracies of SE concerning solved gases. So far, we achieved promising results in the calculation of D^0 for mixtures of various species. The next step of our work will be the application of the presented approaches for D^0 and D^{self} into well-known approaches for D_{ij}.

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Definition of frame-invariant Soret coefficients for ternary mixtures

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When a steady temperature gradient is applied to a multi-component liquid mixture thermodiffusion induces a separation of its components, and concentration gradients develop in the system. In the case of a binary liquid mixture, after some transient, a non-equilibrium steady state is reached where a constant (in time) concentration gradient is established. In isotropic fluids the applied temperature gradient and the induced concentration gradient are always parallel (or antiparallel). To quantify thermodiffusion in binary mixtures, the so-called Soret coefficient S_T (units of K^{-1}) is defined as proportional to the ratio of these steady concentration and temperature gradients, namely,

$$x(1-x)S_T\,\nabla T=-\nabla x, \tag{1}$$

with x is the (average) concentration of the mixture in mole fraction. The concentration prefactor $x(1-x)$ in the definition (1) of the Soret coefficient of a binary mixture makes the S_T value invariant under change in concentration representation. Indeed, if *w* is concentration in mass fraction, one has:

$$\frac{\nabla x}{x(1-x)}=\frac{\nabla w}{w(1-w)}, \tag{2}$$

and, consequently, the numerical value of S_T will be identically the same, independently of whether it is computed like in Eq. (1) with concentrations in mole fraction x, or by

$$w(1-w)S_T\,\nabla T=-\nabla w, \tag{3}$$

with concentration in mass fraction w.

In a ternary mixture there are two independent concentrations, x_1 and x_2, so that one initially needs two independent Soret coefficients $S_{T,1}$ and $S_{T,2}$ to describe thermodiffusion in it. Our purpose here is to show how to introduce a concentration prefactor in the definition of Soret coefficients for a ternary mixture that retains the frame-invariance that the S_T of Eq. (1) has for binaries. The inconvenience is that such a prefactor has to be in the form of a matrix. Then, if for a steady state one defines Soret coefficients in a ternary mixture as:

$$\begin{bmatrix} x_1(1-x_1) & -x_1x_2 \\ -x_1x_2 & x_2(1-x_2) \end{bmatrix}\begin{pmatrix} S_{T,1} \\ S_{T,2} \end{pmatrix}\nabla T=-\begin{pmatrix} \nabla x_1 \\ \nabla x_2 \end{pmatrix}, \tag{4}$$

the resulting Soret coefficients, $S_{T,1}$ and $S_{T,2}$, are independent of whether concentrations are expressed in mole or mass fraction. This can be shown by simple differentiation of the relationship between concentrations in mass and mole fractions in a ternary mixture, which gives:

$$\begin{bmatrix} x_1(1-x_1) & -x_1x_2 \\ -x_1x_2 & x_2(1-x_2) \end{bmatrix}^{-1}\begin{pmatrix} \nabla x_1 \\ \nabla x_2 \end{pmatrix}=\begin{bmatrix} w_1(1-w_1) & -w_1w_2 \\ -w_1w_2 & w_2(1-w_2) \end{bmatrix}^{-1}\begin{pmatrix} \nabla w_1 \\ \nabla w_2 \end{pmatrix}, \tag{5}$$

similar to Eq. (2) for binaries.

The frame-invariance ideas presented here can be extended [1] to unsteady situations, by introducing frame-invariant thermodiffusion coefficients, as well as to generic multi-component mixtures.

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Diffusivities accessible from dynamic light scattering across the two-phase boundary of an equimolar propane-methane mixture

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Dynamic light scattering (DLS) is a well-established contactless technique for studying diffusive processes for a large variety of systems and thermodynamic states. In fluids and fluid mixtures at macroscopic thermodynamic equilibrium, spontaneous microscopic fluctuations give rise to a Rayleigh-Brillouin spectrum analyzed by DLS. In the case of a binary fluid mixture, the Rayleigh component of the spectrum consists of two contributions or hydrodynamic modes associated with thermal and mutual diffusivity. The intensity ratio of the mode associated with the mutual diffusivity to that one associated with the thermal diffusivity is called Rayleigh ratio and depends on the given thermodynamic state. Although the applicability of DLS for the simultaneous measurement of thermal and mutual diffusivity has been demonstrated for various binary mixtures, experimental situations occur where only one hydrodynamic mode is observable, e.g., if both diffusivities match. In the case of different diffusivities, also only a single mode can be resolved if the intensity of one mode is much larger than that of the other mode. Here, the type of diffusivity behind the single hydrodynamic mode observable in the experiments depends on the Rayleigh ratio. While for Rayleigh ratios much larger than one the detectable mode is associated with the mutual diffusivity, Rayleigh ratios much smaller than one indicate that the observed mode is connected with the thermal diffusivity.

In order to identify which diffusivity is accessible by DLS near a phase boundary, heterodyne DLS experiments and theoretical calculations for the Rayleigh ratio were performed for an equimolar propane-methane mixture at various states across the two-phase boundary. In total, the mixture was studied at 125 different thermodynamic state points including the gaseous, supercritical, and compressed liquid regions. The present measurements document that in the compressed liquid phase and along the vapor-liquid equilibrium, both diffusivities can be determined simultaneously. In the compressed liquid phase far from phase transitions, calculated and experimental Rayleigh ratios agree within combined uncertainties. Only one hydrodynamic mode could be observed in the supercritical, near-critical, and gaseous regions. At pressures and temperatures above or close to the critical isochore, the theoretically calculated intensity of the mode associated with the mutual diffusivity was found to be two orders of magnitude larger than the one related to the thermal diffusivity. Furthermore, the behavior of the detectable diffusivity along different isobars crossing the compressed liquid and supercritical states follows the expected trend for the mutual diffusivity. In the low-density gas region, however, the hydrodynamic mode is attributable to the thermal diffusivity. Between the gas regions with low and high density, no remarkable differences in the intensities of the two modes as well as in the thermal and the mutual diffusivity can be found. Here, an effective diffusivity describing both transport properties at the same time is determined by DLS.

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Reference frames and negative main Fick diffusion coefficients

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Recently, the scientific community has taken ternary mixtures more into focus because they can be seen as prototypes for truly multicomponent mixtures. Fick diffusion coefficients depend on the order of components because in Fick's law for a ternary mixture the fluxes of two components are written explicitly, while the third component serves as a reference component. Moreover, the numerical values also depend on the reference frame, for which the diffusive fluxes are expressed. Only the eigenvalues of the Fick diffusion matrix are independent on the order of components and the reference frame. There are three common reference frames for expressing Fick's law: volume-, mass- or molar-averaged. There is therefore a variety of diffusion coefficients in use. The Fickian diffusion coefficients are measured in the volume reference frame, the governing equations for thermodiffusion (Soret) are written in the mass reference frame and molecular dynamic simulation are done in the molar reference frame. Understanding the bridge between them is of particular interest for the researchers [1].

Another important point concerns the existence of negative main Fick diffusion coefficients in non-ideal solutions sometimes discussed in literature. The thermodynamic stability conditions [2] require that the sum of the main diffusion coefficient has to be positive

$$D_{11}+D_{22} > 0$$

and does not require the main diffusion coefficients to be individually positive. Negative main Fick diffusion coefficients violate physical intuition because they indicate that species oppose their dilution even in the absence of cross diffusion effects. Note that the negative main diffusion coefficients reported in the literature usually appeared in the course of transformations between different reference frames or when changing the order of components

In this study, the dependence of diffusion coefficients on the reference frame is thoroughly analyzed for seven ternary mixtures of different types. The key finding of this study is that negative values of main diffusion coefficients in ternary only appear in molar reference frame due to relatively large experimental uncertainties of cross diffusion coefficients measured in volume reference frame, which are propagated and amplified by frame transformation. Another highlight of this study is the existence of a strong similarity between main diffusion coefficients in the volume and mass reference frames for seven considered mixtures of different types.

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The Soret effect in ternary mixtures of water + ethanol + triethylene glycol of equal mass fractions: ground and microgravity experiments

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Measurements of the Soret and thermodiffusion coefficients of a symmetric ternary mixture with equal mass fractions of water, ethanol, and triethylene glycol have been performed by two-color optical beam deflection (2-OBD) and the thermogravitational column technique (TGC) in the laboratory and under microgravity conditions in the SODI apparatus aboard the International Space Station. The results from all three experimental techniques agree within the experimental error bars, which result mainly from the inversion of the contrast factor matrices. TGC shows by far the lowest, 2-OBD the highest error amplification. The microgravity measurements are in between. The agreement with the microgravity results shows that thermosolutal convection could be well controlled in the 2-OBD experiments by a proper orientation of the temperature gradient. Despite the different condition numbers, the results are invariant under the choice of the independent compositions.

Based on the orientation of the confidence ellipsoid in the ternary composition diagram, not all coefficients are equally affected by experimental errors. Although there are appreciable uncertainties for water and ethanol, the Soret and the thermodiffusion coefficients of triethylene glycol could be obtained with a good accuracy due to the favorable orientation of the confidence ellipsoid. We have found that water behaves thermophobic, corresponding to a positive Soret coefficient, whereas both ethanol and triethylene glycol are thermophilic with negative Soret coefficients. This resembles the behaviour of the binary system ethanol/water above the ethanol concentration of the sign change. [1]

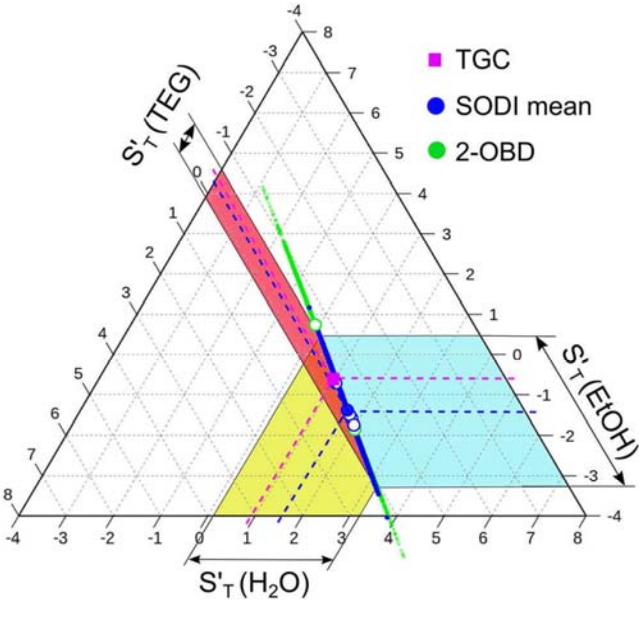

Figure 1: Ternary diagram of the Soret coefficients obtained with the three different experimental setups. The colored regions correspond to a standard deviation of ±3σ based on a Monte-Carlo simulation. Figure from reference.

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Interfacial tension measurements of *n*-dodecane/CO_2 from (298.15 to 573.15) K at pressures up to 10 MPa by pendant drop method

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In recent years, crude oil (a natural source of hydrocarbons) has become the main raw material for the production of liquid fuels and the majority of valuable chemical compounds. Nevertheless, other sources of hydrocarbons are being explored due to oil depletion or an increase in oil price on the world market. In this sense, the Fischer-Tropsch synthesis has received much attention for its potential to produce chemical feedstocks and liquid fuels without the production of environmentally harmful compounds encountered in direct hydrogenation. However, the conversion efficiency of the Fischer-Tropsch process is not very ideal [1]. To further optimize and improve the Fischer-Tropsch process, it is vital to understand the thermophysical properties of reactants and products involved in this process.

The interfacial tension, which is in connection with the stability of contacting fluid phase, is a crucial property for the understanding and eventual improvement of synthesis efficiency of liquid hydrocarbons. A number of methods for measuring the interfacial tension of two fluids are available [2]. But most methods are only suitable for experiments at ambient conditions and lack robustness and simplicity for implementation in a high pressure apparatus. The main method suitable for elevated pressures is the pendant drop method using axisymmetric drop shape analysis, based on integration of the Young-Laplace equation.

In the present study, a new high temperature and high pressure pendant drop apparatus was developed and tested with *n*-heptane over the temperature range from (298.15 to 498.15) K, and a good agreement between the experimental data and literature could be found. With the new apparatus, the interfacial tension measurements of *n*-dodecane/CO_2 were carried out over the temperature range from (298.15 to 573.15) K and at pressures up to 10 MPa. The combined expanded uncertainties of temperatures, pressures and interfacial tension with a level of confidence of 0.95 ($k = 2$) are estimated to be 18 mK, 12 kPa and less than 2.4% over the entire temperature and pressure range, respectively. Based on the experimental data, the interfacial tension is correlated according to van der Waals equation, and the deviations with the literature data are compared and analyzed.

Acknowledgments

The authors acknowledge the financial support of the National Natural Science Foundation of China (No. 51761135116).

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Self-diffusivity of a homologous series of ethylene glycols: Experimental measurements, relation with viscosity, correlation and prediction methods

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This work reports the self-diffusivity measurements of liquid diethylene, triethylene and tetraethylene glycols from 293 K to 343 K by the PGSE-NMR technique. The dependence of the diffusion coefficients with both the temperature and the molecular mass of the oligomers for the interpretation of their local structure was studied.

The diffusivity results are interpreted by means of a Stokes-Einstein-Sutherland-type equation. The hydrodynamic radius, obtained directly from the self-diffusion coefficients, is compared with the van der Waals and the hard sphere radii [1].

The viscosity and density data needed for the radii calculation were recently published by this group [2]. This study is part of a programme of measurements of thermophysical properties, namely, viscosity, self-diffusivity and density, aiming to study the correlation of the transport properties of ethylene glycols [3]. Ultimately the work will involve the prediction of thermophysical properties of liquid PEGs.

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The effects of external surface barriers on zeolite catalysts

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Zeolites are attractive heterogeneous catalysts due to their crystalline structure, high surface area and thermal stability. However, conventional zeolites display diffusion limitations in many relevant catalytic processes. The slow diffusion rate through the extended network of micropores leads to low catalyst utilisation and can, furthermore, lead to reduced selectivity and catalyst lifetime. Thus, hierarchical zeolites have received considerable attention over recent years. The pore network of hierarchical zeolites contains at least one additional, larger pore system, interconnected to the zeolite micropores. This allows for the efficient transport of reagents to, and products away from the active sites confined in the micropores by shortening the diffusion path length [1]. Thus, the incorporation of hierarchical porosity can enhance the diffusion and reduce or even eliminate diffusion limitations in zeolite catalysts [2]. In addition to enhanced catalyst utilisation, increasing the external surface area and maximising the rate of intracrystalline diffusion could also lead to improved catalyst life times.

Nevertheless, recent experimental and computational work suggests that external surface barriers in zeolite-based, hierarchical catalysts might play a significant role in affecting overall transport and reaction rates in such catalysts [3]. Rao *et al.* [4] demonstrated the existence and impact of surface barriers on the alkylation of benzene with ethylene by comparing reactor simulations with experimental results.

In recent work in our group, ZSM-5 zeolites with similar bulk properties were prepared with different external surface properties, using different synthesis methods and conditions. The synthesized materials were studied extensively using different characterisation techniques to determine their chemical, structural and textural properties. This set of catalysts was then used for appropriate catalytic experiments to investigate the impact of surface barriers on the catalytic properties of zeolites. This knowledge will be important to understand how surface barriers can be either avoided or exploited.

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Breakdown of the Stokes-Einstein relation for nanoparticles

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The Stokes-Einstein (SE) relation [1,2] is one of the most fundamental equations for diffusive transport of particles dissolved in fluid media. While derived and verified on the macroscale with large particles like gamboge granules [3], experiments show the failure of the application on the nanoscale for small molecules such as sucrose and urea [4]. This raises the question, which conditions need to be satisfied for the SE relation to hold. While one central aspect is the mass ratio of the particle to the solute molecules, surface interactions and solvent ordering might play important roles, leading to a critical particle size [5]. On the nanoscale, molecular dynamics (MD) simulations gained popularity to tackle such issues, even though further issues arise. Most prominent are finite system size effects [6] and the correct calculation of transport coefficients using Green-Kubo relations [7,8].

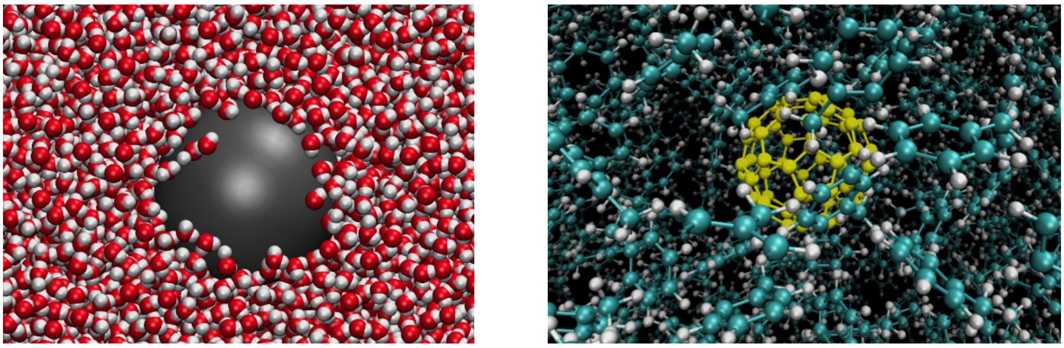

Figure 1: Snapshots of two simulated systems: (left) partially realistic system of a Lennard-Jones sphere in water, (right) full realistic system of a fullerene C60 in toluene.

We run extensive MD simulations of all-atom, coarse-grained and toy model systems (Fig. 1) to tackle physical aspects like the mass ratio and simulation aspects like the system size systematically. This allows us to estimate the range of applicability of the SE relation to systems of dissolved nanoparticles and the requirements for accurate simulation and analysis of transport coefficients like the diffusion and friction coefficient over a wide set of parameters [9].

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Multicomponent diffusion coefficients in liquids from a fully automated microfluidic setup using Raman-microspectroscopy

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Experimental data on diffusion in fluids are valuable input for modeling and design of chemical processes. Still, experimental data are often lacking since conventional diffusion experiments are time- and material-consuming. Material consumption is a particular critical issue for screening of new systems containing expensive components of limited availability.

In this work, we present a measurement setup for time- and material-efficient determination of multicomponent diffusion coefficients in liquids. The measurement setup consists of an inverse confocal Raman-microscope and a microchannel. Thereby, the setup combines the advantages of microfluidics and Raman-microspectroscopy: Small microfluidic dimensions inherently reduce both sample consumption and measurement time, since diffusion lengths are short; Raman-microspectroscopy allows for rapid simultaneous in-situ quantification of all components with a high spatial resolution.

The chosen microchannel geometry and experimental parameters ensure stable steady-state flow of two liquid phases next to each other. Mass transfer occurs only perpendicular to the flow direction. At different retention times of the fluids in the channel, Raman spectra are collected along the channel cross-section. Spectral analyses yield spatially resolved concentration profiles. From the concentration profiles, the mutual diffusion coefficients are determined by least-squares fitting of diffusion process model. The experimental setup has already been successfully applied in measuring multicomponent diffusion coefficients [1]. The results show that the presented setup allows rapid and reliable determination of diffusion data using small sample volumes.

However, until now, one experiment provides diffusion coefficients for only one mean mixture composition. Each experiment requires about 30 minutes for preparation and about another 30 minutes for start-up, in which time and material are lost. Additionally, samples are prepared manually by weight in a time-consuming and error-prone step. In fact, these steps mainly determine the overall time and accuracy for diffusion measurements.

Here, we present the automation of the microfluidics diffusion setup to further reduce experimental time and effort. In the automated setup, independent syringe pumps feed pure components into a micro-mixer to prepare mixture samples by volume before entering the microchannel. By changing the volumetric flow rates of the syringe pumps during the experiment, diffusion coefficients can be measured for multiple mixture compositions in one experiment. This procedure avoids tedious manual sample preparation and only needs one start-up period for several mixture compositions.

The results show that the presented setup saves time and sample volume for the measurement of diffusion data needed for process modeling and design.

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A multi-region model for reaction-diffusion process in a catalyst particle

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Zeolite catalysts have large applications in a variety of industrial sectors, such as FCC and MTO. In practice, catalyst particles used in industrial reactors have complicated porous structures, in which pores with hierarchical sizes may co-exist [1, 2]. As shown in Fig. 1(a), an industrial catalyst particle is composed of micro-pore zeolites and meso/macro-pore catalyst support. Despite the reaction–diffusion process inside the zeolites, the transport and thus the reaction in an industrial catalyst particle are also highly related to the fraction, size, and position of the micro-pore zeolites. Here, a multi-region model based on the unified Maxwell–Stefan diffusion theory was developed to investigate the reaction–diffusion processes within catalyst particles formed by micro-pore zeolites and meso/macro-pore support [3]. By simulating the process of alkylation of benzene over a single catalyst particle formed with H-ZSM-5 zeolites, the effects of volume fraction, size and spatial distribution of H-ZSM-5 zeolites on the effectiveness factor of the catalyst particle were then investigated and discussed.

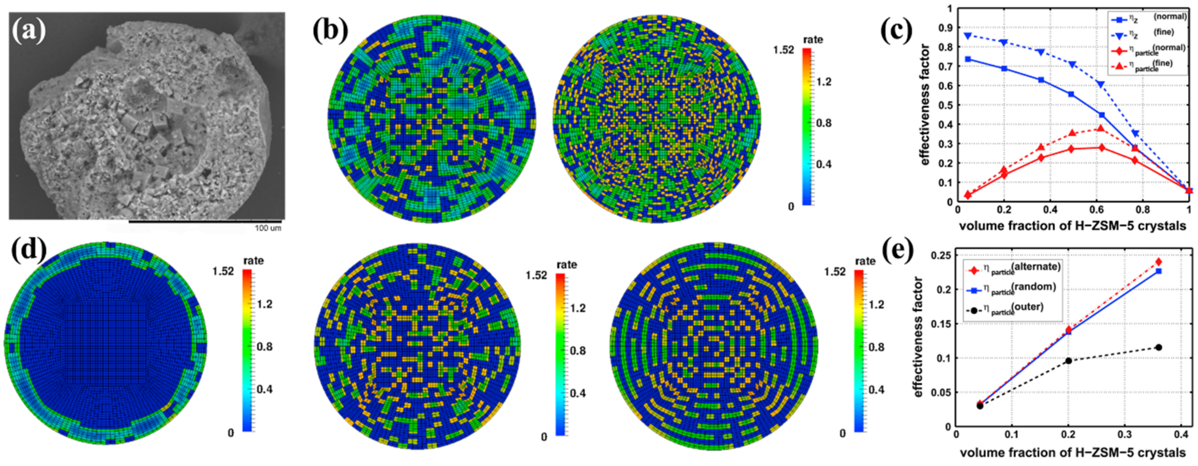

Figure 1: (a) Interior of catalyst particle used in industrial process. (b) The distribution of zeolite and reaction rate inside catalyst particle with volume fraction of H-ZSM-5 of 0.62. (c) Effectiveness factor as a function of volume fraction of H-ZSM-5 for both normal and fine crystal sizes. (d) The spatial distribution of zeolites and reaction rate inside catalyst particle. (e) Effectiveness factor for zeolites with different spatial distribution.

As shown in Fig. 1(b, c), our simulations verified that the catalyst particle composed by fine size of zeolites has higher effectiveness factor than that composed by normal size of zeolites. Our simulations suggest that the intracrystalline diffusion resistance within the zeolite region is decisive for the effectiveness factor of the catalyst particle. In Fig. 1(d, e), our simulations indicate that the effectiveness factor of outer distribution deviates significantly from that of the other two distributions when the volume fraction of zeolites is increased. The alternate distribution has the best catalytic performance when the volume fraction of zeolites is lower than 0.36.

It is shown that the multi-region model developed in this work is a potential bottom to up tool for reaction-diffusion processes inside a catalyst particle exhibiting multi-scale time characteristic. The possible applications include rational design for catalyst encountered in many industrial applications.

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Contribution of mesopores of hierarchically structured titanium silicalite-1 to the catalytic activity towards the methyl oleate epoxidation

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In micro- and mesoporous materials, transport of fluids with molecules of dimensions comparable with those of the pores often determines the overall rate of processes such as adsorption or catalysis as a result of diffusion limitations. While the vast majority of self-diffusion studies are focused on transport characteristics of low molecular-weight species, in particular short-chain hydrocarbons, far less diffusion data are reported for higher molecular-weight compounds with molecular dimensions of up to several nanometers, such as proteins, fats and oils or long-chain hydrocarbons.

The present contribution demonstrates first successful experimental results on molecular self-diffusion coefficients of methyl oleate (MO) confined to mesopores of catalytically active molecular sieves with a hierarchical micro-/mesopore system [1]. The pore hierarchy has been introduced into the initially microporous titanium-containing silicalite-1 (TS-1) catalyst by alkaline treatment and by pseudomorphic transformation.

The self-diffusion processes of MO in pelletized TS-1-based catalysts containing mesopores of 3-40 nm pore width as a result of a post-synthetic treatment were investigated by means of pulsed field gradient (PFG) NMR. Three different diffusion regimes in the treated catalysts were observed: i.) intra-crystalline diffusion within mesopores, ii.) long-range diffusion in the mesopore and in the inter-crystalline space of a pellet, and iii.) bulk-like diffusion in the voids between and outside the pellets. The intra-crystalline diffusivities are approximately two orders of magnitude lower compared to those of diffusion in the bulk phase at the same temperature. In the parent microporous TS-1, no diffusion of MO within the crystallites was observed (as expected).

The experimental data suggest that the mesopore network of the hierarchical micro-/mesoporous TS-1-based catalysts is well interconnected and accessible for MO molecules at room temperature. This, however, does not rule out possible existence of isolated mesopores being not accessible for methyl oleate. In such case, introduction of mesopores might not facilitate the intra-crystalline transport, as reported in Ref. [2]. The obtained self-diffusion coefficients allow the estimation of the time required for MO to diffuse through the entire pellet at room temperature. Moreover, the diffusivities differ for the materials with different width fractions of intra-crystalline mesopores.

In addition to the diffusion experiments, water sorption studies were performed. These were aimed at addressing the possible change in the surface hydrophobicity of the studied catalysts after application of alkaline treatment and pseudomorphic transformation. This, in turn, might influence the activity of the catalyst for MO epoxidation. Thus, the observed differences in activity of the hierarchical TS-1-based catalysts reported in Ref. [3], will be discussed in the context of the mesopore accessibility and the surface hydrophobicity.

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Kinetic data for the adsorption of nickel ions from aqueous solutions

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The global demand for clean water is constantly increasing due to increasing population numbers as well as worldwide economic growth. With the limitation of clean water as a resource, the treatment of wastewater attaches particular importance. Over 80 % of the global wastewater is discharged without any treatment [1]. Especially untreated industrial process water causes environmental pollution and consequently affects human health. Pollutants are often valuable materials, such as nickel, which is widely used in metal working industry as well as a component in lithium ion accumulators and catalysts. Clean water technology based on adsorption as a sustainable alternative to established end-of-pipe-technologies could be able to provide both water purification and material recovery.

For the development of such processes, experimental data of the adsorption behavior are necessary. Experiments were carried out to study the nickel adsorption kinetics and diffusion for functionalized silica based adsorbents (pore sizes of 100 Å and 1000 Å) at temperatures of 5 °C, 20 °C, and 60 °C with initial concentrations of 34 µmol/L, 340 µmol/L, and 3400 µmol/L, respectively.

The results in Figure 1 contain the adsorption kinetics for the first 10 seconds with an initial nickel concentration of 34 µmol/L and adsorbent pore size of 100 Å. The data show pure adsorption kinetics within the first second until a plateau is reached. It is assumed that during this time the nickel ions get in contact with the outer surface of the adsorbent. After this plateau, the adsorption takes place at the inner surface of the adsorbent. The leveling of all three temperature dependent curves (Figure 1) shows clearly that the velocity of the binding mechanism is displaced by the rate of diffusion as the limiting factor of the adsorption process. Effects of temperature, concentration, and pore size onto the adsorption process will be discussed. A modelling of the obtained data is in progress.

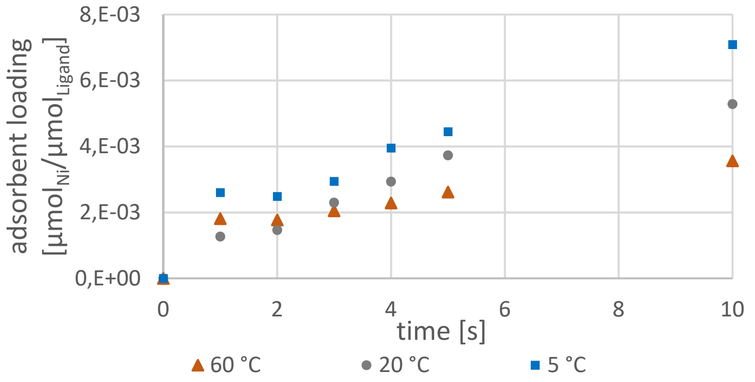

Figure 1: Adsorption kinetics with initial concentration of 34 µmol/L and adsorbent pore size of 100 Å.

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Particle diffusivities in free and porous media from dynamic light scattering applying a heterodyne detection scheme

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Diffusive processes in particulate systems play a significant role in a large variety of natural and technical processes. It is well known that the diffusive mass transport is slower in porous media in comparison to that in free media, i.e. in absence of confinements induced by a porous solid material. Porous media may consist of a myriad of interconnected structures with different pore sizes, pore geometries, and degrees of disorder, where each structure results in a characteristic diffusive mass transport. Diffusive transport on different length scales is hard to probe and differentiate experimentally. At present, fluorescence correlation spectroscopy (FCS) and dynamic light scattering (DLS) relying on a homodyne detection scheme are used to study diffusive mass transport in porous media. These techniques, however, are restricted to confined particulate systems containing fluorescent particles for FCS experiments, and to solvents with a refractive index matching the one of the porous matrix for homodyne DLS experiments. In a homodyne detection scheme, the scattered light detected and analyzed has to be sufficiently pure to ensure the validity of the corresponding working equation evaluated in context with DLS measurements. Owing to the effects of stray light, this condition is no longer given if the refractive indices of the solvent and the porous medium are different. In principle, this restriction can be overcome by ensuring a heterodyne detection scheme for DLS measurements, where the scattered light is superimposed with sufficiently strong coherent reference light.

In the present contribution, the applicability of a heterodyne detection scheme has been demonstrated for a dispersion saturating a porous medium consisting of inverse opals. These possess spherical pores with a diameter of 300 nm being approximately equal to the diameter of the pore opening. The binary particulate system consists of spherical gold nanoparticles with a hydrodynamic diameter of about 20 nm dispersed in water with a particle volume fraction of 3×10^{-6}. The hydrodynamic diameter was determined via the Stokes-Einstein relation using diffusivity values measured for the dispersion in free medium. For the porous medium, the measurements performed with a heterodyne detection scheme document that even if the refractive index of the dispersion is not matching the refractive index of the inverse opals, signals related to the particle diffusive process are observable in the intensity correlation functions. Studies performed under the same conditions with pure water saturating the porous medium demonstrated that the signals observed for the dispersion are rising from the diffusion of particles under the confinement of the porous skeleton and are not related to experimental artefacts. Heterodyne DLS experiments on the confined dispersion were conducted at different scattering angles in order to probe diffusive processes on different length scales. On average, the diffusive process in the confined dispersion was found to be 6.2 times slower than that in free medium. In addition, clear differences were observed between diffusive processes at the subpore length scale and at a larger length scale also integrating interconnected pores, cracks, and channels. The structures of the porous media were characterized by scanning electron microscopy and conventional microscopy.

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Diffusion-wave inverse problem thermal conductivity depth-profile reconstructions using an integral equation approach

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The thermal-wave boundary-value problem in a semi-infinite thermophysically inhomogeneous solid:

$$\frac{\partial}{\partial x}\left[k(x)\frac{\partial T(x,t)}{\partial x}\right]=C(x)\frac{\partial T(x,t)}{\partial t}\quad ;\quad t\geq 0\,;\,0\leq x<\infty\text{ ; with} \tag{1a}$$

$$-k(0)\frac{\partial T(x,t)}{\partial x}\bigg|_{x=0}=\frac{1}{2}F_0e^{i\omega_0 t}\quad\text{and}\quad C(x)\equiv\rho(x)c(x)\quad , \tag{1b}$$

where F_0 is the incident (photo)thermal flux, $\rho(x)$ is the density, $k(x)$ is the thermal conductivity and $c(x)$ the specific heat of the material; ω_0 is the modulation angular frequency. Introducing the Green function, $G\left(x\,|\,x_0\right)$, approach yields the formal solution to the inhomogeneous problem in the frequency domain in the form of a Fredholm-type integral equation:

$$T(x;\omega_0)=-i\omega_0\int_0^\infty G(x|x_0)T(x_0;\omega_0)C(x_0)dx_0-k(0)G(x|0)\left[\frac{dT(x_0;\omega_{0)}}{dx_0}\bigg|_{x_0=0}\right] \tag{2}$$

Solving this equation results in an inverse relation between the thermal conductivity depth profile and the inverse Laplace transform of the thermal diffusion-wave frequency response:

$$\frac{1}{k(x)}=\frac{d}{dx}\left(L^{-1}\left[\frac{T(0;p)}{p}\right]\right);\ L^{-1}\text{ denotes inverse spatial Laplace transformation.} \tag{3}$$

Figure (1a) shows inversion pairs (conductivity and frequency response) in the case of constant thermal conductivity, in agreement with the well-known analytical solution [A. Mandelis, *Diffusion-Wave Fields*, Springer, New York 2001, Chap. 2.1]. Figure (1b) shows the inversion pair in the case of an increasing *k(x)* depth profile. The method is currently being applied to the non-destructive reconstruction of thermophysical depth profiles in manufactured solids such as metal powder compacts used for parts in the automotive industry.

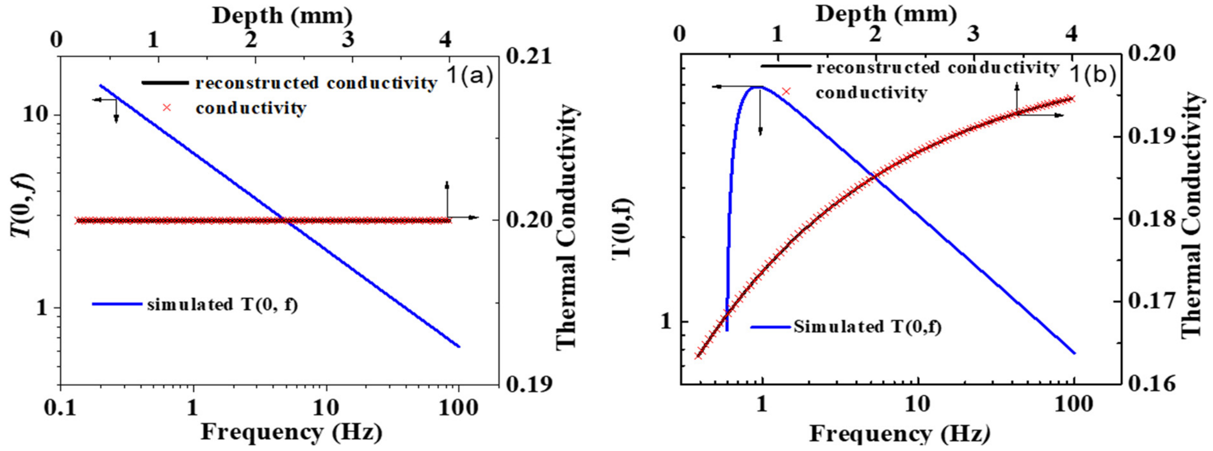

Figure 1: Conductivity and frequency response in case of constant thermal conductivity (a) and increasing conductivity depth profile.

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Infrared Soret forced Rayleigh scattering apparatus using a single crystal diamond window to measure Soret and mass diffusion coefficient

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The Soret effect describes a mass transport phenomenon driven by a temperature gradient, while the driving force of the mass diffusion is a concentration gradient. We have developed an experimental apparatus to measure Soret coefficient and mass diffusion coefficient in aqueous solutions based on the optical holographic grating technique which we call the infrared Soret forced Rayleigh scattering (IR-SFRS).

The IR-SFRS apparatus [1] is shown in Figure 1. Mass transport in a sample is induced by the heating laser with the wavelength of λ = 9.7 μm and observed by the probing laser of λ = 639 nm. By using an infrared laser, measurements without a dye can be performed, while the SFRS apparatus with visible light lasers [2,3] requires adding a dye to samples. A single crystal diamond window is used in a sample cell, because the incident side window should transmit both lasers.

To evaluate the validity of the apparatus, we performed experiments on aqueous ethanol solutions at a temperature of 298.2 K. The Soret coefficient and the mass diffusion coefficient were compared with the experimental works by other groups.

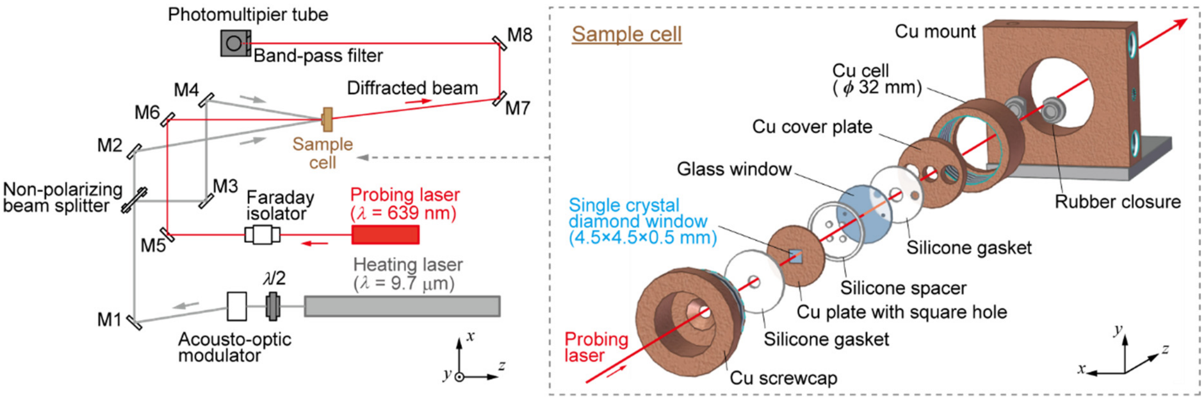

Figure 1: Optical system of the infrared Soret forced Rayleigh scattering (IR-SFRS).

Acknowledgment

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Interdiffusion of two polymer layers during drying

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For solution-processed multilayer coatings the interdiffusion of the single layers is of great importance for the product quality. For example, in the case of organic light-emitting diodes (OLEDs), the required device architecture consists of several functional nano-layers. State-of the-art processing is step-by-step coating of a wet film including drying, before the following functional layer is applied on top as wet film. During this process, the solvent of the top wet film could dissolve the dry bottom layer and thus cause a solid interdiffusion, which would affect the OLED functionality. While layer interdiffusion must be prevented for the fabrication of OLEDs, a controlled interdiffusion is required for other multilayer applications. Therefore, a fundamental understanding of the interdiffusion behavior in solution-processed multilayers has to be developed.

Up to now, there exist only a few investigations on the interdiffusion of two solids in presence of a solvent. In this study, a general model for the description of diffusion in polymer double layers was developed in order to predict the interdiffusion of the three components. The validation of the model is based on experimental investigations of different polymer-polymer-solvent systems using Inverse Micro Raman Spectroscopy (IMRS). With this measurement method, the local distribution of each component of the double layer system can be determined at different times (see Figure 1). The thickness of the investigated double layers is in the micrometer range. The influence of various parameters such as solvent content or polymer chain length on the interdiffusion behavior is of particular interest [1].

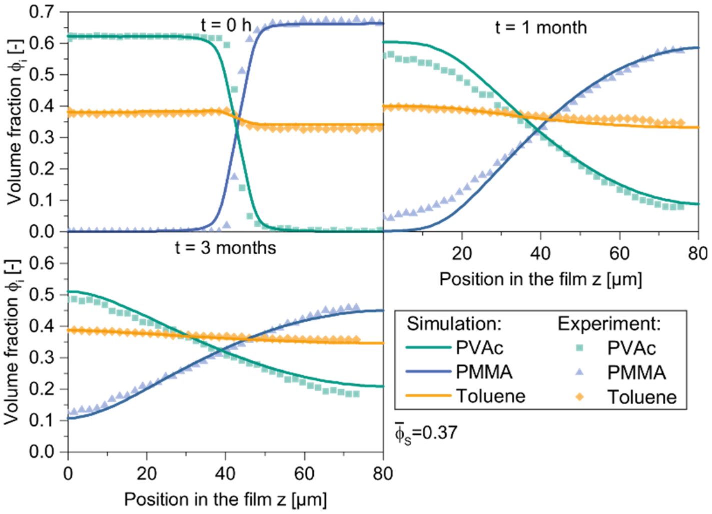

Figure 1: Comparison of simulation (solid lines) and experiment (symbols). Concentration profiles are displayed for PMMA-PVAc-toluene at 20 °C and an average toluene content of 37 vol% [2].

In the future, not only covered double layers (without solvent evaporation), but also drying systems will be considered. As a result, a large number of new challenges arises, such as the description of film shrinkage or skin formation.

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Molecular dynamics studies on shale gas and fracturing fluid diffusivity in shales

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The steady decline in conventional fuel resources as well as their environmental footprint has led to the question of efficient exploitation of unconventional hydrocarbon reservoirs. Shale gas, which is natural gas hosted in shale formations, has revolutionized the energy industry [1] and the global abundance of shale and mudrock formations has generated great hope in producing high quality transportation fuels, which lack aromatic hydrocarbons, generate lower emissions and can be directly used to cover industrial and consumer needs. Shale formations are chemically and structurally diverse, containing kerogen, clay, calcite and quartz, in analogies that vary substantially from region to region. Kerogen is a microporous amorphous solid and the major component of the organic matter scattered in the potentially lucrative shale formations hosting shale gas. A deeper understanding of the way kerogen porosity characteristics affect the transport properties of hosted gas is important for the optimal design of the extraction process [2]. To this end, we employed molecular dynamics (MD) simulations to investigate the role of porosity on the adsorption and transport behavior of shale gas in overmature type II kerogen found in many currently productive shales. The diffusion of CH_4, C_2H_6, and CO_2, both as pure components and as constituents of the quaternary mixture, was investigated at temperatures of 298.15 and 398.15 K and pressures of 1 and 250 atm. The diffusion was found to be anisotropic and the maximum component of the diffusion coefficient correlates linearly with the limiting pore diameter (LPD), indicating that the controlling step of the transport process is the crossing of the limiting pore region [3]. On the other hand, clay minerals are hydrous aluminosilicates, characterized by an extensive network of micropores and mesopores. Among them, kaolinite is one of the most abundant on Earth and is commonly encountered in shales. Fracturing fluids are mostly water-based and contain a number of chemicals in small volumes such as methanol and citric acid as well as elevated levels of Sr^{2+}, Na^{+} and Cl^{-} ions and naturally occurring radioactive materials (NORM) such as Ra^{2+} isotopes. Our MD simulations of model fracturing fluids in kaolinite slit pores at ambient temperature and pressure showed that confinement results in mobility reduction of all components compared to the bulk, with this reduction being especially pronounced near kaolinite’s gibbsite surface due to extensive hydrogen bond formation. Citric acid has a more profound effect on mobility compared to methanol, since the formation of clusters hinders the motion of all fluid components [4]. Given the experimental difficulties in probing the relevant mechanisms at the aforementioned scale, our results are expected to assist in predicting the fate of fracturing fluids additives and contribute towards formulation and design of environmentally friendly fracturing fluids that limit the amount of NORM released from a shale without compromising the extraction process.

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Shortening NMR diffusion experimental times

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NMR diffusion measurements have become the method of choice for measuring diffusing due to their wide applicability, speed of measurement, enormous range of accessible diffusion coefficients (from gas $\sim 10^{-6}$ m^2s^{-1} to large polymers $\sim 10^{-15}$ m^2s^{-1}), and the ability to measure diffusion over a specified timescale, Δ, which greatly adds to the power of NMR diffusion measurements as it allows the ability to probe porous media [1,2]. The weakness of NMR diffusion measurements lies in their inherent insensitivity. Consequently, many experiments are in theory possible but in practice would simply consume too much spectrometer time and therefore become impractical. Even in cases where the total measurement time is not a limitation, making the measurement faster expands the horizons of diffusion measurements to study reaction kinetics [3,4], as well as simply increasing throughput.

We have been developing new approaches for increasing the speed of NMR diffusion measurements with particular emphasis on generally applicable techniques that are both simple yet do not come at the cost of reduced information (e.g., loss of chemical shift information or loss of the specified diffusion measurement timescale, Δ).

Here we demonstrate that it is possible to shorten NMR diffusion measurements by more than 70% without any loss in accuracy by a trivial change in the experimental acquisition procedure. Specifically, NMR diffusion measurements are typically run as an arrayed experiment in which a particular gradient value, g (i.e., the arrayed variable) is chosen and the experiment is repeated for a set number of scans (*NS*). The arrayed variable is then incremented and a signal acquired averaged over *NS*. This procedure is typically repeated for something like 15 gradient values in total. Conventionally, NMR diffusion measurements are performed with the same *NS* at each iteration of the experimental parameter despite the SNR being more than sufficient for many of the iterations. However, enormous time saving can be found by varying *NS* as a function of the experimental parameter (i.e., g in this case) and the signal normalised by the number of scans used at each iteration [5]. Hence, this **new normalisation approach** requires far fewer total scans. The method can even be combined with other techniques to increase efficiency [6,7].

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Diffusion processes in soft matter studied by field-cycling proton NMR relaxometry

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With the availability of commercial (electronic) field-cycling (FC) relaxometers together with recent progress of home-built instruments, NMR relaxometry has gained new momentum investigating the dynamics in liquids, polymers, and plastic crystals [1-3]. The method provides the frequency dependence (dispersion) of the spin-lattice relaxation rate $R_1(\omega)$. Commercial machines cover a frequency range of 10 kHz – 30 MHz, home-built ones may achieve 100 Hz – 40 MHz [2]. Most of the studies employ protons. Here, the relaxation is caused by fluctuations of the magnetic dipole-dipole interaction, and one has to distinguish intra- and intermolecular relaxation pathways. The intermolecular relaxation caused by translational diffusion dominates at low frequencies whereas rotational dynamics at high frequencies, i.e., rotational and translational relaxation contributions are more or less separated in $R_1(\omega)$. The latter displays a universal low-frequencies dispersion law which allows determining the diffusion coefficient $D(T)$ without taking recourse to isotope dilution experiments. This is demonstrated for simple liquids and polymer melts in comparison to results from field gradient (FG) NMR. Sub-diffusive translation found in polymers caused by Rouse and entanglement dynamics is accessed by singling out the full intermolecular relaxation rate $R_1^{\text{inter}}(\omega)$ via isotope dilution experiments. By Fourier transformation, the segmental mean square displacement (msd) as a function of time is revealed [4], thus competing with neutron scattering (NS) experiments [5]. Complementing the msd data by that from FG NMR, nine decades in time are covered and all four diffusion regimes forecast by the tube reptation (TR) model are revealed (cf. Figure 1) [4].

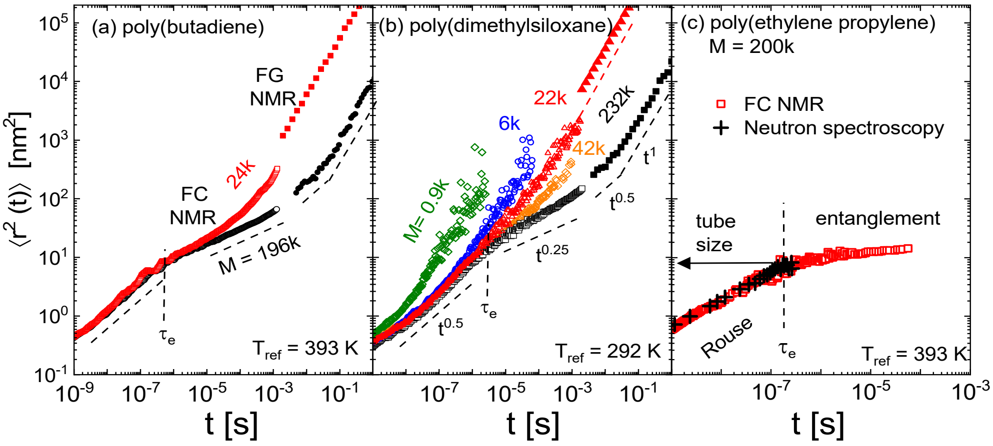

Figure 1: Segmental msd $\langle r^2(t)\rangle$ of different polymer melts as revealed by FC ^{1}H NMR relaxometry: Concerning PB and PDMS, the FC data (open symbols) of selected *M* was complemented toward long times by FG ^{1}H NMR (closed symbols). For high *M* the power-law regimes (I-IV) of the TR model are indicated (dashed lines). Concerning PEP, NS data is included (Wischnewski et al. PRL **90**, 058302, 2003).

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Exploration of diffusional phenomena during LOHC dehydrogenation with Pt/Al_2O_3-catalysts of varying pore sizes

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The use of Liquid Organic Hydrogen Carrier (LOHC) systems has recently gained great interest as they are a promising alternative for energy storage and transport. In a previous work the system dibenzyltoluene/perhydro-dibenzyltoluene (H0-DBT/H18-DBT) was proposed to be a suitable LOHC-candidate [1].

To further forward the LOHC-technology the development of an active dehydrogenation catalyst is of high importance. In this context, Pt/Al_2O_3-catalysts have proven to fit the requirements quite accurately, but, as it is the case in most heterogeneously catalyzed reactions, suffer from diffusional limitations. Thereby the effective diffusivity of the reactant molecules in the pores of the porous catalyst is significantly reduced compared to molecular diffusion. In liquid-phase reactions this becomes significant when the ratio of the molecular diameter of the reactant to the pore diameter of the catalyst support material is in the range of 1:10 [2]. As the H18-DBT molecule has a maximum expansion of approximately 1,4 nm and the pore size of common alumina supported catalysts is about 10 nm, this could strongly affect the dehydrogenation reaction.

To investigate the existence of diffusional limitations in the dehydrogenation of H18-DBT and perhaps overcome them, different alumina support materials with varying pore sizes were used to prepare the Pt/Al_2O_3-catalysts. Batch experiments and PFG NMR experiments were performed to determine the influence of the catalyst pore diameter on the rate of diffusion of reactants and therefore on the activity of the catalyst. As a result, an optimum pore size could be obtained.

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Beam induced dynamics in oxide glasses

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Atomic scale X-Ray Photon Correlation Spectroscopy (aXPCS) is a powerful technique to study the dynamics on an atomic scale by using high-intensity coherent X-ray radiation. Improvements on synchrotron sources gives rise to ever increasing possibilities to study materials. Concomitantly the effects of the beam on the materials under investigation are of grand importance. While most studies of beam damages focus on structural changes, aXPCS presents the unique possibility to study the effect of high-flux X-rays on the dynamics in hard condensed matter. Such effect on the dynamics is termed beam-induced dynamics (BID) and was recently found [1] for some classes of materials [2]. aXPCS is a prime candidate for investigations of beam induced dynamics. On the other side BID opens new opportunities for aXPCS research.

In this work the results of our recent studies of beam-induced dynamics on alkali borate glasses are presented. One of the most important results is that the inverse of the correlation times is directly proportional to the X-ray flux. BID is further dependent on sample thickness and depends on the irradiation history in addition to the thermal history. Moreover, the beam-induced dynamics lack a significant temperature dependence on their own and indeed gives rise to significant structural alterations, i.e. beam damage. First results indicate that both thermally activated dynamics and BID can occur at the same time. Finally, several possible explanations for BID will be presented as well as a short outline for the future of aXPCS measurements.

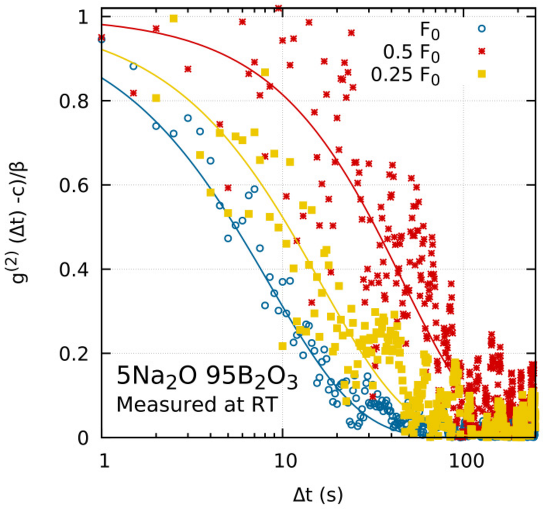

Figure 1: Flux dependency of the auto correlation function.

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Controlling methanol and water diffusion in Nafion via amine treatment

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Nafion is being used worldwide as a constituent of separation membranes [1-3] and as a proton-conductive membrane in fuel cells [4] and membrane in the chlor-alkali industry [5]. In these applications, the relation between methanol and water diffusivities is crucial. As Nafion is a polymeric perfluorosulfonic acid skeleton which is terminated by reactive sulfo-groups, we provide to control the diffusivity of water and methanol by treating Nafion with primary amines. Nafion was thus modified with a series of three primary amines and sodium hydroxide. All modified membranes were tested using vapour sorption microgravimetry method; sorption capacities and diffusion coefficients were measured [2] and compared to those of pure Nafion and of its sodium salt. The modifications of Nafion by ethanolamine and benzylamine resulted in the elimination of the degradation (spontaneous darkening), which is typical to pure Nafion [1-3]. Interestingly, Nafion modified with ethanolamine showed higher diffusivity of water than of methanol, which contrasts with the properties of all other Nafion modifications, pure Nafion and its sodium salt.

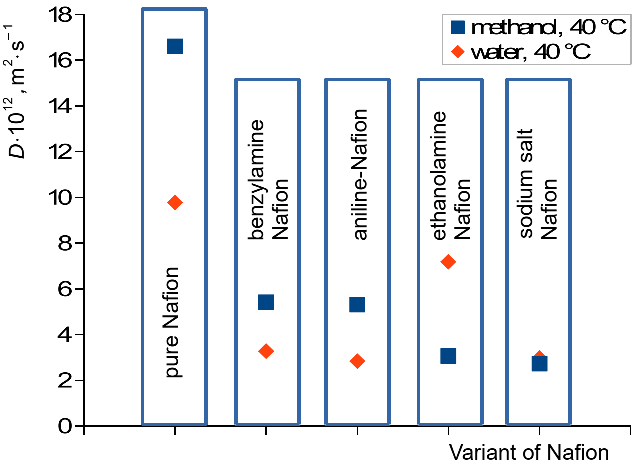

Figure 1: Diffusivities of water and methanol in modified Nafions at 40 °C and vapour activity of 0.5.

Acknowledgement

Financial support obtained from the Czech Science Foundation, projects 13-32829P and 18-08389S, and from specific university research (MSMT No 21-SVV/2019) is gratefully acknowledged.

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Diffusion measurements using a volumetric differential pressure apparatus

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In a recent work, we have demonstrated the use of commercial volumetric systems to study the gas transport mechanism in porous adsorbents, providing guidelines and recommendations to ensure the proper use of the methodology to obtain reliable kinetic constants [1].

On the base of these findings, we have designed and built an innovative differential volumetric system for the measurement of adsorption equilibrium and kinetics. The system (figure 1) is equipped with a differential and an absolute pressure transducer as well as thermocouples to measure the temperature of the dosing and the uptake cells, including the direct measurement of the sample temperature. The principle of operation is based on following the differential pressure between two symmetric branches (namely, sample and reference) as the gas expands from the dosing to the uptake volumes.

Double-branch volumetric systems present some key advantages compared to conventional single-branch ones. The use of the differential pressure (as opposed to absolute) significantly improves the quality of the transient pressure signal allowing high accuracy kinetic measurements over the entire range of absolute pressures considered. The apparatus is specifically designed for kinetic measurements therefore particular effort was dedicated to minimise dosing and uptake volumes, hence allowing accurate kinetic and equilibrium measurements with a small amount of sample (<100 mg). An additional advantage of the system is in its modular design, which allows to test different configurations to evaluate and compare different ways in which the experiment can be carried out using the same setup.

In addition to the details on the apparatus, we present kinetic tests carried out on a number of adsorbents using different gases to determine the capabilities (and the limits) of the technique for weak and strongly adsorbed systems. In order to properly interpret the results a detailed model of the system was also developed. The model includes the kinetics of the valve as well as possible imbalances present in the system and offers a direct way to identify different transport mechanisms.

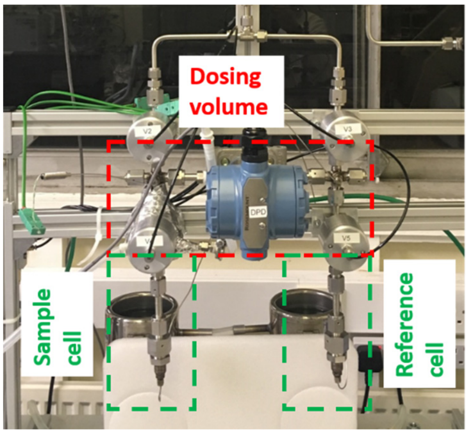

Figure 1: Differential volumetric apparatus for high pressure kinetic measurements.

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Diffusion Fundamentals VIII – Diffusion Phenomena Moving People
September 1st to 5th, 2019 in Erlangen, Germany

Adsorption and diffusion in oxyfuel combustion – Linking experiment and MD simulation through graphite structures as a first example

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During combustion and gasification reactions of solid fuels, gaseous mass transfer is of utmost importance. Gas molecules diffuse through the boundary layer into the porous structure of the fuel, adsorb on the surface, and the gas-solid reaction takes place. Then, the reaction products desorb and diffuse back into bulk phase, where possible further oxidation reactions take place. In combustion modelling, this mass transfer is either neglected or considered in terms of effective diffusion coefficients. However, those coefficients are neither determined by adsorption or diffusion experiments nor modelling, they are derived by fitting the experimentally determined combustion rate to the used conversion model.

Within the framework of the Collaborative Research Centre 129 Oxyflame (CRC), funded by the German Research Foundation, we measure adsorption capacities and kinetics for different gases and solid fuels. Effective diffusion coefficients are calculated from the experimental data by using appropriate models for the adsorption kinetics. Moreover, the mass transfer is modeled using molecular dynamics (MD) simulations. The results of these atomistic simulations are compared to data from macroscopic adsorption experiments. To establish a sound basis for comparison, graphite (see Figure 1) of different porosity, which is also the most fundamental form of the main compound of solid fuels, was selected as adsorbent.

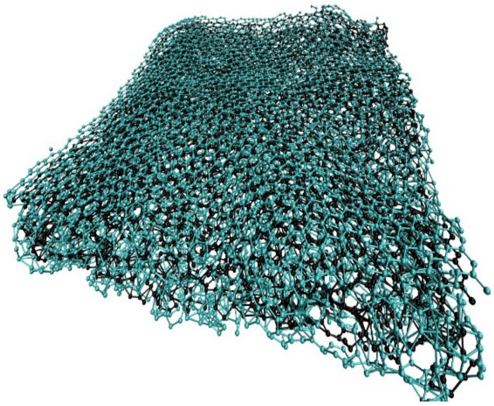
Figure 1: Graphitic structure.

In this work, we present adsorption capacities and kinetics for graphite determined with a commercially-available but deliberately modified gravimetric sorption analyzer (Rubotherm, Germany – since 2016, TA instrument, USA). These measurements are conducted with some of the most relevant gas species during oxyfuel combustion, which are carbon dioxide, oxygen and methane. Our investigations serve as base-line experiments for the evaluation of the MD simulations, since graphite has in contrast to natural solid fuels, like biomass or coal, a clearly defined structure.

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Diffusion Fundamentals VIII – Diffusion Phenomena Moving People
September 1st to 5th, 2019 in Erlangen, Germany

Determination of diffusivities in fluid mixtures using light scattering techniques in and out of equilibrium

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For the understanding and design of numerous natural and technical processes, accurate knowledge about diffusivities in fluid mixtures is important. In general, the experimental and theoretical determination of transport properties including mass and thermal diffusivity as well as thermodiffusion coefficient remains quite challenging until today. Even in the case of binary liquid mixtures, discrepancies can be found between the mutual diffusivity data obtained by different techniques, which are clearly outside their combined uncertainties. Thanks to the advancement of light sources and detection units, contactless light scattering techniques relying on the analysis of equilibrium, non-equilibrium, and forced fluctuations have attracted great attention for the characterization of several diffusive processes during the past two decades. Nevertheless, the different light scattering techniques have not been compared in a rigorous manner so far, although they possess individual pros and cons in connection with their applicability for a given thermodynamic state and diffusivity range as well as their precision, accuracy, and uncertainty.

In the present contribution, at first, the methodological principles and the experimental realization of dynamic light scattering (DLS), shadowgraphy, and forced Rayleigh scattering (FRS) will be presented. Then, the different techniques will be compared focusing on their application for the determination of diffusivities in fluid mixtures. The measurement of thermal and mutual diffusivity by DLS is based on the analysis of statistical fluctuations in temperature or entropy and composition in macroscopic thermodynamic equilibrium. It depends on the fluid characteristics and thermodynamic state whether or not both properties can be accessed simultaneously. In the presence of a macroscopic gradient at steady state, the analysis of long-ranged non-equilibrium fluctuations by shadowgraphy allows the simultaneous determination of the thermal and the mutual diffusivity as well as of the thermodiffusion coefficient. The application of a macroscopic gradient, however, restricts corresponding investigations to the one-phase region. The third light scattering technique, the FRS technique, involves gratings induced by the interference of two laser beams. From the analysis of the formation and relaxation of the resulting temperature and concentration gratings, the thermal and the mutual diffusivity as well as the thermodiffusion coefficient of mixtures can be determined. For performing FRS measurements, the addition of an absorbing dye contaminating the fluid of investigation is often necessary. While the use of small disturbances prevents advective flows, the FRS method might be inefficient close to first- or second-order phase transitions. By identifying the capabilities of each technique, guidelines for their reliable application within thermophysical property research are given for specific conditions. For this, the different techniques were examined by their application for different reference systems including binary mixtures of toluene and isooctane.

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Establishment of the shadowgraphy-setup for the measurements of non-equilibrium fluctuations

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As part of the ESA project "NEUF-DIX" we want to investigate the thermodynamic relaxations of non-equilibrium fluctuations (NEF). For this we planned a completely new shadowgraphy-setup, from the arrangement of the necessary components (like the light source or the Camera) up to the construction of a new fluid cell. We oriented ourselves to the well-known similar constructions from F. Croccolo, in Aglet [1] and A. Valati, in Milan [2]. Form the necessary temperature gradient, which needs to be parallel to the gravitational axes, we constructed the cell completely out of teflon and on a table with a leveling mechanism. The temperature gradient is generated by two peltiers (AMS TB-109-1,4-1,5CH with a 13mm hole) placed horizontally above and below the fluid cell. In addition to an intense and incoherent light source (Superlum SLD), we need a high-resolution, fast camera, to which we chose the Hamamatsu Orca Flash V2 and in the future the Hamamatsu Orca Fusion. The complete setup is seen in Figure 1.

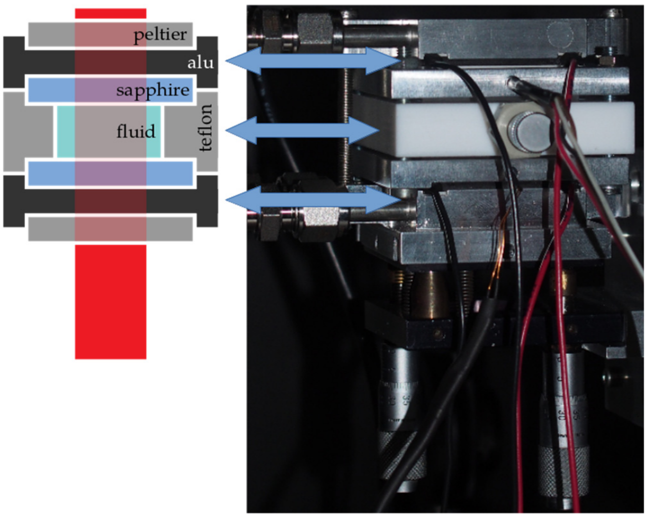

Figure 1: Sketch (left) and real image (right) of the thermally regulated fluid cell.

The considered solutions will be ternary mixtures of toluene, cyclohexane and polystyrene (4700 g/mol). The main interest is in the slowing down processes of the fluctuation-relaxations by high polymer concentrations. Due to the neighborhood to the glass transition temperature T_g, the diffusion D and thermodiffusion D_T are several decades smaller and therefor more available. Experimentally, the external temperature gradient induces an concentration gradient in the opposite direction due to the Soret effect. The fluctuations couple to these gradients and express themselves for small scattering vectors q in a strong q^{-4} dependency.

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