Report on the CECAM Workshop on "Complex dynamics of fluids in disordered and crowded environments"

held in Lyon (28.6.-1.7.2010)

Summary

Over the past two decades, the dynamics of fluids under nanoscale confinement has attracted considerable attention. A great variety of molecular systems under different types of confinement, disordered in most cases, has been investigated using a broad spectrum of experimental techniques. At the same time, quite a few studies of simple model systems using molecular dynamics simulations were undertaken. Motivation for the rapidly increasing interest in this topic is based on both practical and fundamental reasons. On the practical and rather applied side, the study of many problems in several scientific fields, such as polymer and colloidal sciences, rheology, geology, or biophysics, would undoubtedly benefit from a more profound understanding of the dynamical behaviour of confined fluids. Furthermore, effects similar to those observed in confinement are expected in fluids whose constituents have strong size or mass asymmetry, hence widely different mobilities, and in biological systems where crowding and obstruction phenomena in the cytosol are responsible for clear separations of time scales for macromolecular transport in the cell.

Now that theoretical and simulation approaches have caught up with experimental investigations, our workshop on the complex dynamics of fluids confined in disordered environments has offered the ideal stage to bring together the different communities working in this field. In the presentations and discussions the dynamics of several kinds of fluids exposed to some disordered environment have been addressed.

In summary we have aimed with this workshop in two directions:

- to re-assemble theoreticians and simulators that work on the closely related systems mentioned above;
- to establish contact between the theoretical/simulation community and experimentalists working in this field.

Reassembling theoreticians and simulators working in this field within a workshop has fostered discussions on methodological and conceptual developments. Also the new and unexpected physical phenomena that have emerged from the recent investigations could be discussed in detail. Furthermore, the workshop has offered a forum to address difficulties encountered so far and yet unsolved problems.

Description of the scientific content and discussion at the event

The first part of the **Afternoon session** of **Day 1** was dedicated to experiment. In the first presentation **Alba-Simionesco** has has summarized new phenomena observed in liquids confined at a nanoscale level. **Monkenbusch** has reported about spin-echo experiments on linear PEO chains with different molecular weights confined in narrow nano-pores in alumina. Focus was put on the entanglement properties of the confined melt, experiments revealed a slight increase of the confining tube diameter. **Kimmich** gave an overview over a long-standing history of successful NMR experiments on coherent and incoherent transport in porous media. The first scenario described referred to adsorbate molecules of a liquid at or in the vicinity of solid surfaces. The second example presented was dedicated to the comparison of electro-osmotic flow and ionic current density in a porous model object. The central topic of the second part of this session was diffusion. **Franosch** presented results about localization transition in porous media. Relying on extensive computer simulations and scaling theory, he could explain the emergence of so-called anomalous transport in porous media and has elucidated the role of correlations in the obstacle distribution. **Gimel** has talked about computer simulations on tracer diffusion in various complex matrices, showing that the diffusion coefficient of the tracer is only a function of the volume fraction accessible to the tracer. In the last contribution, **Dean** discussed diffusion of a Brownian particle in a random potential which is a function of a Gaussian field.

The first part of the **Morning session** of **Day 2** was dedicated to colloids, both in experiment and theory. **Bechinger** talked about experiments on colloidal transport through porous media, a problem which is, from the technological point of view, of high relevance. In the subsequent contribution, **Dhont** presented results of his theoretical investigations on diffusion of spheres through networks and on charged colloids in external electric fields. Finally, **Barentin** presented results of confined diffusion of probes in a colloidal suspension, obtained via the "Fluorescence Recovery After Photobleaching" technique. By varying the probe size over two orders of magnitude, she could give evidence for deviations of the probe diffusivity from the bulk Stokes-Einstein expectations. The second half of this session

was dedicated to simulations: **Truskett** discussed structural and dynamical properties of fluids confined in small spaces. In his contribution he could demonstrate how accurate predictions of dynamics from first principles are possible for confined fluid systems. Finally, **Berthier** talked about the observation that the structure of viscous liquids approaching the glass transition is affected by the existence of a large number of amorphous metastable states. In his work he has defined and measured directly a static correlation length-scale and has found that it grows modestly but steadily when approaching the glass transition.

The first part of the **Afternoon session** of **Day 2** was dedicated to simulation studies and theoretical considerations of binary systems. **Folk** reported about the concentration and mass dependence of transport coefficients and correlation functions in binary mixtures with high mass asymmetry, a system that might be considered as a precursor of a fluid confined in a porous matrix. In the subsequent talk, **Voigtmann** talked about glass and localization transitions in binary hard sphere mixtures with very disparate sizes. Among others, glass-glass transitions are observed for this system. Finally, **Medina-Noyola** reported about the self-consistent generalized Langevin equation approach to investigate dynamic arrest, dynamic asymmetry, and non-equilibrium dynamics in simple model colloidal systems. The second part of this session was dedicated to diffusion, studied both in theory and experiment. **Kargl** reported about quasi-elastic neutron scattering experiments on fast diffusion in a slowly relaxing matrix, in particular in alkali silicate melts, which form a network of covalently bound tetrahedra. In the subsequent contribution **Horbach** discussed localization phenomena in ion-conducting glass-formers, such as mixtures of silica with alkali oxides. In the final talk, **Jardat** presented results for self-diffusion of ions in the presence of charged obstacles, obtained in Brownian dynamics simulations. In these investigations the matrix is obtained in a rapid quench of an electrolyte solution, being in equilibrium at given temperature and relative permittivity. The fluid that is immersed into this matrix is a charge and size symmetric electrolyte. For dilute matrices the diffusion of counterions of the matrix is slower than that of co-ions, while for concentrated matrices an unexpected speedup of the counterions of the matrix with respect to the co-ions is reported.

The entire **Morning session** of **Day 3** was dedicated to simulations. In the first contribution **Kurzidim** reported about the dynamic properties of a hard

sphere fluid confined in a porous, disordered matrix of hard spheres, obtained in molecular dynamics simulatiosn. The subsequent contribution, given by **Miyazaki**, dealt with dynamic properties of a closely related system, focusing in particular on the glass and on the localization transitions. Finally, **Rovere** reported about the dynamic properties of a binary Lennard-Jones mixture in a disordered matrix, calculated via Mode Coupling Theory. In his talk, **Moreno** presented results of anomalous dynamics of a two-component polymer system under confinement. To be more specific, the slow matrix formed by the majority component induces confinement effects on the fast minority component. Finally, **Gallo** reported about slow dynamics of water close to organic and inorganic surfaces. Results were obtained by computer simulations and Mode Coupling Theory for a system confined in a cylindrical pore of silica material.

The **Afternoon session** of **Day 3** was dedicated to crowding. **Metzler** reported about random motion and search processes in complex systems, focusing in particular on anomalous diffusion connected to biological systems (such as DNA, polymeric chains in translocation through a small pore in a membrane, ...). **Weiss** presented results on crowding and anomalous diffusion *in vivo*, *in vitro* and *in silico*, summarizing thereby both experimental and simulation results on proteins and tracer particles in the cytoplasm. **Yethiraj**'s talk was dedicated to crowding effects on protein association reactions, which either decrease or increase the rates of association reactions (or protein folding), depending on the nature of the crowding agents and the type of reaction. In his contribution **Dorsaz** reported about diffusion-limited reactions in crowded environments, as they are commonly found in biochemical processes such as enzyme catalysis, protein aggregation or complexation in cells. Finally, **Höfling** talked about anomalous transport in crowded membranes resolved by fluorescence correlation spectrocscopy.

The **Morning session** of **Day 4** started with theoretical contributions. **Vink** considered the critical behaviour of a fluid confined in a porous matrix, leading to random-field effects in the critical exponents. In his contribution **Archer** reported about his version of dynamical density functional theory, which represents a promising approach to the fluid mechanics of colloidal suspensions. Finally, **Krotscheck** gave a talk on two-dimensional He_3, which represents a crucial system for understanding Fermion dynamics. **Vlassopoulos** presented experimental results on the glassy dynamics in soft interpenetrable colloids, in particular on concentrated solutions of multiarm

star polymers. The preferred experimental technique is dynamic light scattering. The final presentation of this workshop, given by **Likos**, reported about phonon and hopping dynamics in cluster crystals, i.e., regular lattices formed by clusters of overlapping ultrasoft particles.

In addition, twelve posters have been presented at this workshop which could be visited after the lectures and during the coffee and lunch breaks. Attendance of these presentations was quite remarkable and reflected the fact that even more oral presentations might have been made.
Talks were in general scheduled for 40 minutes; during the preparation of the meeting we informed the contributors to schedule up to 30 minutes for the presentation itself and to reserve at least ten minutes for discussion. Thus most of the discussions in the forum took place right after the respective presentation, i.e., at a moment when the impressions were still very vivid. Discussions were highly appreciated by the participants and were considered to be very lively and constructive and mutually fertilising.

Assessment of the results & Impact of the event on the future direction of the field

We are proud to say that this workshop was attended in total by 50 participants. With respect to their home institutions, 19 of them came from Germany, twelve from France, and six from Austria. Further European nations represented at this meeting were Italy (2 participants), United Kingdom (1), Switzerland (1), Spain (1), and Greece (1). We are proud to mention that we had in total seven speakers from overseas, i.e., from the US (4), from Japan (2) and from Mexico (1).

At the workshop, 32 oral contributions have been presented by the invited speakers, in addition twelve poster presentations have been made.

Soon after our proposal was accepted by the CECAM board, we could convince the editorial board of the liquids section of Journal of Physics (Condensed Matter) to produce a special issue dedicated to the topic of the workshop. Thus, right from the first invitation to the workshop, participants were invited to contribute to this special issue. So far we have received twelve contributions, listed below. The presentation of this issue is planned for late February/early March. Of course, financial support by SimBioMa will be acknowledged.

Throughout the meeting we had the impression that a CECAM workshop dedicated to this particular subject of complex dynamics in disordered and crowded environments was highly due. The need for such a meeting was not only justified from the purely academic point of view, but also from a more applied, technological aspect as well as from an interdisciplinary point of view. The direct contact between physicist, chemists and biophysicists was highly stimulating for the discussions and mutually fertilising. The rather compact group, the premises offered by the Ecole Normmale in Lyon and the good atmosphere contributed to very lively discussions and a good means to exchange ideas and concepts.

There was general agreement that in a few years' time (two to three years from now) another workshop should be organized on this topic.

Contributions submitted so far for the special issue, to be published in Journal of Physics (Condensed Matter)

- T. Neuhaus and C.N. Likos
  Phonon dispersions of cluster crystals

- M. Hellmann, J. Klafter, D.W. Heermann, and M. Weiss
  Challenges in determining anomalous diffusion in crowded fluids

- R. Kimmich
  Distinction of rotational and translational fluctuations of molecular dynamics in complex systems: Polar liquids and polymers confined in nanometric porous media

- D.S. Dean and V. Demery
  Diffusion of active tracers in fluctuating fields

- J.-C. Gimel and T. Nicolai
  Self diffusion of non-interacting hard spheres in particle gels

- E. Stiakakis,B.M. Erwin, D. Vlassopoulos, M. Cloitre, A. Munam, M. Gauthier, H. Iatrou, and N. Hadjichristidis
  Probing glassy states in binary mixtures of soft interpenetrable colloids

- R.L.C. Vink and T. Fischer
  Fluids with quenched disorder: Scaling of the free energy barrier near critical points

- P. Gallo and M. Rovere
  Lennard-Jones binary mixture in disordered matrices: exploring the mode coupling scenario at increasing confinement

- M. Bernabei, A.J. Moreno, and J. Colmenero
  Static and dynamic contributions to anomalous chain dynamics in polymer blends

- M. Spanner, F. Höfling, G. Schröder-Turk, K. Mecke, and T. Franosch
  Anomalous transport of a tracer on percolating clusters

- S. Schnyder, F. Höfling, T. Franosch, and T. Voigtmann
  Large-wavelength anomalies in the asymptotic behavior of mode-coupling theory

- J. Kurzidim, D. Coslovich, and G. Kahl
  Dynamic arrest of colloids in porous environments: disentangling crowding and confinement

Final program of the meeting

- **Day 1 - June, 28 2010**
  - Afternoon session
    - 14:00 to 14:20 - Welcome
    - 14:20 to 15:00 - Christiane Alba-Simionesco
      Confining a liquid down to the nanoscale: more of the same or new phenomena?
    - 15:00 to 15:40 - Michael Monkenbusch
      Confined polymer chain dynamics, neutron spin-echo results
    - 15:40 to 16:20 - Rainer Kimmich
      Coherent and incoherent transport in porous media: NMR experiments and simulations on length scales from nano- to millimeters
    - 16:20 to 16:40 - Coffee Break
    - 16:40 to 17:20 - Thomas Franosch
      Localization transition in porous media
    - 17:20 to 18:00 - Jean Christophe Gimel
      Tracer diffusion in complex matrixes
    - 18:00 to 18:40 - David Dean
      Diffusion in non-Gaussian random potentials
- **Day 2 - June, 29 2010**
  - Morning session
    - 9:00 to 9:40 - Clemens Bechinger
      Colloidal transport through porous media
    - 9:40 to 10:20 - Jan Dhont
      Diffusion of spheres through networks and charged colloids in external electric fields
    - 10:20 to 11:00 - Catherine Barentin
      Confined diffusion of probes in a colloidal suspension
    - 11:00 to 11:20 - Coffee Break
    - 11:20 to 12:00 - Thomas Truskett
      Structure and dynamics of confined fluids

        * 12:00 to 12:40 - Ludovic Berthier
          Revealing growing static order in viscous liquids using confinement
    - Afternoon session
        * 14:00 to 14:40 - Reinhard Folk
          Concentration and mass dependence of transport coefficients and correlation functions in binary mixtures with high mass asymmetry
        * 14:40 to 15:20 - Thomas Voigtmann
          Glass and localization transitions in binary hard-sphere mixtures
        * 15:20 to 16:00 - Magdaleno Medina-Noyola
          Dynamic arrest, dynamic asymmetry, and non-equilibrium dynamics in simple model colloidal systems
        * 16:00 to 16:20 - Coffee Break
        * 16:20 to 17:00 - Florian Kargl
          Fast diffusion in slowly relaxing matrix as seen by quasielastic neutron scattering
        * 17:00 to 17:40 - Jürgen Horbach
          Localization phenomena in ion-conducting glassformers
        * 17:40 to 18:20 - Marie Jardat
          Self-diffusion coefficients of ions in the presence of charged obstacles from Brownian dynamics simulations
        * 18:20 to 19:00 - Discussion

- **Day 3 - June, 30 2010**
    - Morning session
        * 9:00 to 9:40 - Jan Kurzidim
          Impact of random obstacles on the dynamics of a dense colloidal fluid
        * 9:40 to 10:20 - Kunimasa Miyazaki
          Slow dynamics in random media: from glass to localization transition
        * 10:20 to 11:00 - Mauro Rovere
          Binary Lennard-Jones mixture in disordered matrices: exploring the mode coupling scenario at increasing confinement.

        * 11:00 to 11:20 - Coffee Break
        * 11:20 to 12:00 - Angel Moreno
          Confinement and anomalous dynamics in two-component polymer systems
        * 12:00 to 12:40 - Paola Gallo
          Slow dynamics of water close to inorganic and organic surfaces
    - Afternoon session
        * 14:00 to 14:40 - Ralf Metzler
          Random motion and search processes in complex systems
        * 14:40 to 15:20 - Matthias Weiss
          Crowding and anomalous diffusion in vivo, in vitro, and in silico
        * 15:20 to 16:00 - Arun Yethiraj
          Crowding effects on protein association reactions
        * 16:00 to 16:30 - Coffee Break
        * 16:30 to 17:00 - Nicolas Dorsaz
          Diffusion-limited reactions in crowded environments
        * 17:00 to 17:30 - Felix Höfling
          Anomalous transport in crowded membranes resolved by fluorescence correlation spectroscopy
        * 17:30 to 19:00 - Poster Session

- **Day 4 - July, 1 2010**
    - Morning session
        * 9:00 to 9:40 - Richard Vink
          Phase-transitions in porous media: random-field effects
        * 9:40 to 10:20 - Andrew Archer
          Dynamical density functional theory: a microscopic approach to the fluid mechanics of colloidal suspensions
        * 10:20 to 11:00 - Eckhard Krotscheck
          Two-dimensional He_3: a crucial system for understanding fermion dynamics
        * 11:00 to 11:20 - Coffee Break
        * 11:20 to 12:00 - Dimitris Vlassopoulos
          Glassy dynamics in soft interpenetrable colloids

    - 12:00 to 12:40 - Christos N. Likos
      Phonon and hopping dynamics in cluster crystals
- Discussion session
    - 12:40 to 13:00 - Discussion
    - 13:00 to 13:10 - Closing words