

SoftComp – now in its fifth year as a NoE – is becoming more and more of a focal point for soft matter science in Europe. The attractiveness of SoftComp shows itself in particular in the large number of outstanding research groups that recently sought membership in SoftComp, even though the benefits of EU-funding will end soon and membership will require a membership fee. The SoftComp Network Governing Board recently accepted as new members: 1. University of Fribourg, Center for Nanomaterials, Switzerland (Prof. Schurtenberger); 2. Laboratoire Matière Molle et Chimie, ESPCI, Paris, France (Prof. Leibler); 3. Imperial College, London, United Kingdom (Prof. Maitland); 4. Università La Sapienza, Rom, Italy (Prof. Sciortino); 5. Université Catholique de Louvain, Belgium (Prof. Bailly); 6. group headed by Prof. Tribet, ESPCI, Paris, France. In contributing significantly to all network areas, these new members will further reinforce the strength of SoftComp.

Regarding the scientific contributions, this newsletter contains two articles which highlight the scientific work in SoftComp. The first article by J. Colmenero et al. emphasizes the importance of computer simulations from an experimental point of view – in the present case to interpret and understand neutron scattering data on the slow dynamics of melts of glass-forming polymers. The second article by J. Vermant and P. Clegg explains the importance of thin viscoelastic layers at surfaces. From the historic use of oil to still waves at high sea, a bridge is built to current research on colloid-laden interfaces, which are a stepping stone to the design of new materials.

Hugo Bohn & Dieter Richter

news letter

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Doing Molecular Dynamics Simulations on Polymers as Neutron Scattering Practitioners

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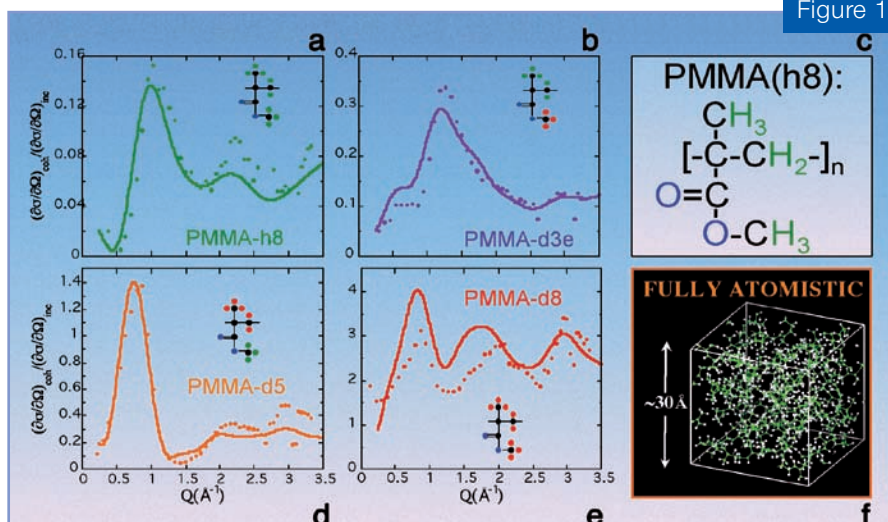
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Computer simulations in general – i.e. *ab-initio* methods, molecular dynamics simulations, Monte Carlo methods, etc. – are considered to be something in between theoretical approaches and experimental tools. However, roughly speaking, there are two different ways of performing simulations: (i) from the point of view of a theoretician and (ii) that of an experimentalist. In the first case, the focus is on simulating simple systems that capture the essence of a given problem and which can be used to check theories and theoretical concepts. No direct connection with real systems is usually invoked. In the second case, the

focus is on mimicking real systems as much as possible. Therefore, validation of the simulated system by comparing it with experimental results becomes crucial. Once the simulated system has been validated – at least for the particular problem we are dealing with – we can take advantage of the simulations, for instance, to calculate magnitudes that are not experimentally observable or that extend the parameter range beyond the experimental capabilities. By means of this feedback between experiments and simulations, we can try to understand a given problem and also check theories approach that we. This is

Figure 1



Ratio between the coherent and incoherent differential cross sections measured by neutron diffraction with polarization analysis at 300 K (dots) or calculated from the MD simulations at 580 K (lines) for differently labelled PMMAs. The schematic representation of the monomer shows the labelling: black dots are C atoms, blue dots are O atoms, green dots are H atoms and red dots are D atoms.

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Doing Molecular Dynamics Simulations on Polymers as Neutron Scattering Practitioners (continued)

the followed over the last few years performing fully atomistic molecular dynamics (MD) simulations of polymer systems as neutron scattering practitioners. Our ultimate goal has always been to unravel the structure and dynamics of such systems. Neutron scattering techniques represent the right tools for validating fully atomistic MD simulations of polymer systems. First of all, they cover the relevant length and time scales (see below). Moreover, the classical Van Hove formalism allows the magnitudes measured to be easily calculated by neutron scattering from the simulated atomic trajectories.

Polymer systems are built from big molecules known as macromolecules. As a consequence, the structural and dynamic properties of polymer systems (we will focus here on amorphous polymers and polymer melts) strongly depend on a hierarchy of length and time scales. This is schematically shown in Fig. 1. At short and intermolecular length scales (of the order of 10 Å) and thereby relatively short time scales, amorphous polymers and polymer melts behave similarly to other glasses and glass-forming materials. However, at larger length scales (of the order of the radius of gyration of the macromolecule), the chain character of macromolecules emerges and polymer systems display universal properties. Obviously, the characteristic times of the dynamic processes at these large scales depend on the length of the macromolecules (molecular weight) and can be very long, sometimes beyond the possibilities of MD simulations. Therefore, at larger scales, only coarse-grained methods that neglect the chemical details can be used. Fully atomistic simulations are now only possible at the intermolecular or scales up to several hundred monomers (Fig. 1f). The MD simulations were carried out by the group from San Sebastián and in

neutron scattering experiments in collaboration between the groups in San Sebastián and Jülich – a nice example of collaborative research within the framework of SoftComp.

Unraveling structure

The local structure, i.e. the so-called short-range order, of many polymer materials, is still poorly understood. In a diffraction experiment, this local structure emerges at momentum transfers $Q > 0.5 \text{ \AA}^{-1}$, where the diffraction patterns of different polymers show a number of broad peaks. In many cases almost nothing is known about the particular atomic or molecular

correlations contributing to these peaks, i.e. about the actual short-range order in real space.

The local structure of polymer systems has been traditionally investigated by means of X-ray diffraction which delivers data on the correlation of all carbon atoms. Neutron diffraction combined with selective deuteration allows to be accessed differently weighted atomic correlations – in the case of fully deuterated samples, the actual structure factor $S(Q)$, where all of the atoms contribute equally. Neutron diffraction with polarization analysis allows the strong background arising from the protons to be avoided by separating the so-called incoherent scaling. Figure 1 shows of

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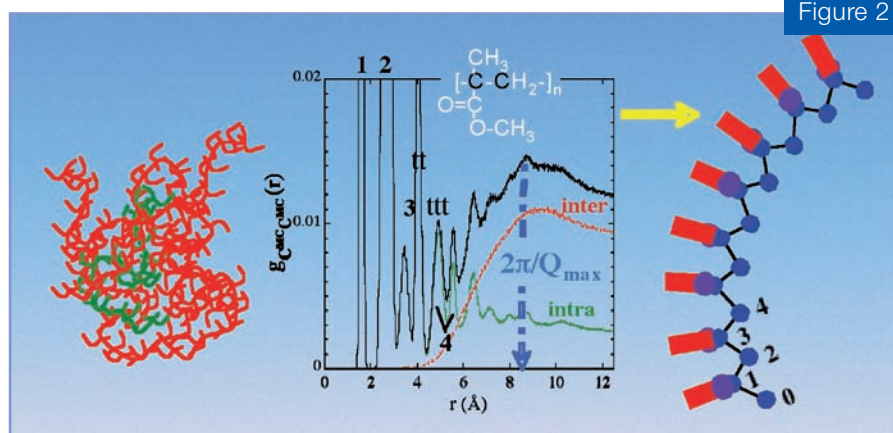
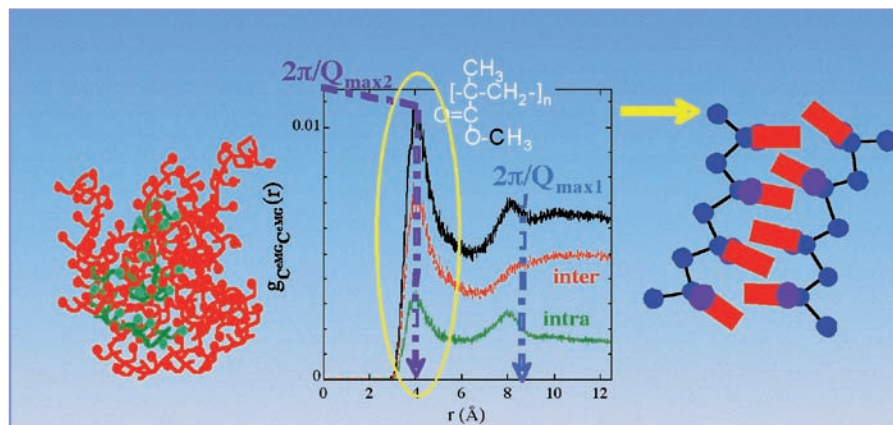


Figure 2



Radial probability distribution functions involving the carbons in the main chain (top) and in the ester methyl groups (bottom). The green curves have been calculated for atoms within the same chain (intrachain correlations), while the red ones correspond to atoms belonging to different chains (interchain correlations). The black curves display the sum of both. On the right, the structural feature is deduced.

an example four different partial structure factors corresponding to different deuteration levels of syndiotactic poly(methyl metacrylate) (PMMA, Plexiglass)^[2]. MD simulations on a realistic sample allow us to go beyond a qualitative analysis. For example, analysis in real space is possible, as is a separation of the inter- and intrachain contributions to the correlations. Of course, first of all, we need to have a realistically simulated cell. The experimental partial structure factors facilitate validation. Fig. 2 shows the direct comparison of neutron diffraction and simulation results without any adjustment. Taking into account the difference in temperature of measurements (300 K) and simulation (580 K – we need this high T to reach equilibrium in the simulated times), we can conclude that the agreement is quite good. Now we can see how the simulations can further contribute to unravelling the atomic correlations.

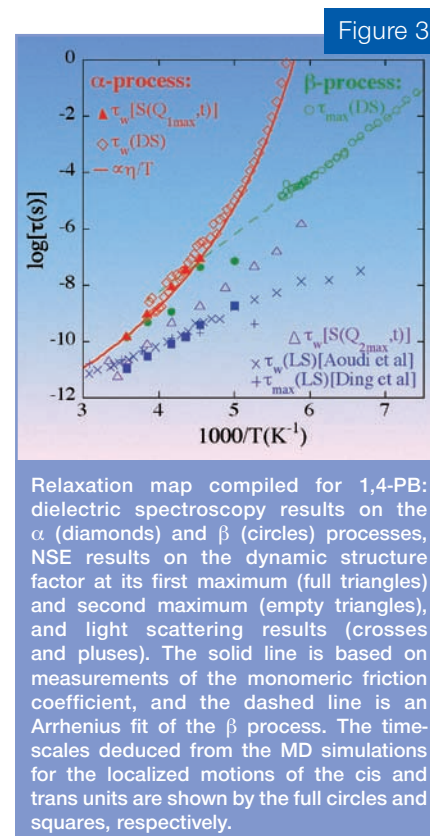
This may be done in Q-space^[2] but more importantly also in real space. There, we can inspect the radial density function corresponding to different key atoms. For instance, let us first consider the main-chain carbons. In Fig. 2(a) the inter- and intramolecular contributions have been separated. This analysis shows that the main peak at Q_{\max} in the reciprocal space is purely of interchain nature, suggesting again a strong short-range order. Moreover, the analysis of the sequence of intrachain peaks indicates that there is a persistent all-trans structure which is in agreement with the high experimental values reported for the characteristic ratio C_{∞} ^[4,5,6], i.e. with a locally rather stiff chain. We can also see that intrachain correlations also contribute at rather large distances, which are likely reflected in the shoulder of the main peak in the reciprocal space.

A similar analysis of the ester methyl group is shown in Fig. 2(b). Here,

the most relevant feature is the strong contribution of both, inter- and intramolecular correlations just at the same distance, which coincides with the Van der Waals radius of a methyl group. This suggests some interdigitation of the side groups, which again is in agreement with the nano-phase separation precursor effect previously mentioned.

Resolving dynamic processes

Now we move to another example dealing with the local dynamics of 1,4-polybutadiene (PB) close to the glass-transition temperature T_g ^[7,8]. First of all, it has to be emphasized that this is a very difficult range for neutron scattering experiments because the dynamic processes are usually too slow to be resolved. PB is, in principle, a very simple main-chain polymer which is considered as a canonical system for the study of glass-transition phenomena and is also very important for industrial applications. There is a high worldwide production of this polymer for very different purposes: in tires for modifying other polymers or even in golf balls! In a pioneering experiment in 1996^[9,10], the dynamic structure factor of PB was measured by neutron spin echo (NSE) at the second maximum of $S(Q)$. This peak was attributed to local intrachain correlations^[1]. The analysis of those NSE resulted in a value for the average activation barrier of the local motions involved that was very similar to that obtained from dielectric spectroscopy for the secondary β relaxation below and above T_g . This was a very encouraging finding, but unfortunately the absolute values of the time scales deduced from both techniques differed by more than two orders of magnitude (see Fig. 3), preventing a direct identification of both processes. Qualitatively, the atomic local motions were interpreted as being due to local reorientations of



the cis and trans units (see scheme in Fig. 4)^[10]. After this work, other results from optical techniques were also reported^[11,12] which agreed with neither the neutron scattering data nor the dielectric data. As can be appreciated from Fig. 3, we were facing quite a puzzling situation!

In an attempt to address this question, we carried out MD simulations^[7,8] of a realistic PB sample with a similar microstructure to that of the real chains. The simulations were run for a very long time ($\sim 1 \mu\text{s}$) to equilibrate the system as best as possible in the difficult temperature range under consideration (about 20 K above T_g). The results were carefully validated using neutron scattering data addressing structural as well as dynamical properties on both protonated and deuterated samples^[7,8,13]. Once the cell was validated, we calculated the radial probability distribution functions corresponding to the different

Doing Molecular Dynamics Simulations on Polymers as Neutron Scattering Practitioners (continued)

kind of hydrogens in PB – something which, unfortunately, is impossible to measure with neutrons. Figure 4 shows the emergence of a second peak in the distribution function – an indication of local motion. Moreover, different hydrogens in the different units move in a different way. Taking a look on longer times, diffusion contributions (broadening of the distribution and shift to longer distances) are also visible at this low temperature. They become more dominant as the temperature increases (see Fig. 4). All of these results suggested that we construct a simple model combining hopping in an asymmetric double-well potential and some anomalous diffusion processes [7,8]. The model nicely fits the results in real space, as can be seen in Fig. 4. From the fits, we obtained the hopping times of cis and transunits, which are shown in Fig. 3. They turn out to be rather different. The dielectric results are rather compatible with the timescales observed for the cis-units jumps. This is reasonable, since it is the cisunit that carries the dipole moment of PB. On the other hand, the NSE values are rather close to those obtained for the local process of the transunits. Apparently, the short-time window accessed by this technique is more sensitive to the fast motions occurring in the sample. The reason why the optical measurements also seem to give similar values for the relaxation times is still unclear. However, we can conclude that our MD simulations have put the controversial puzzle into context and the key result was that cis and transunits behave in a rather different way displaying very different relaxation times.

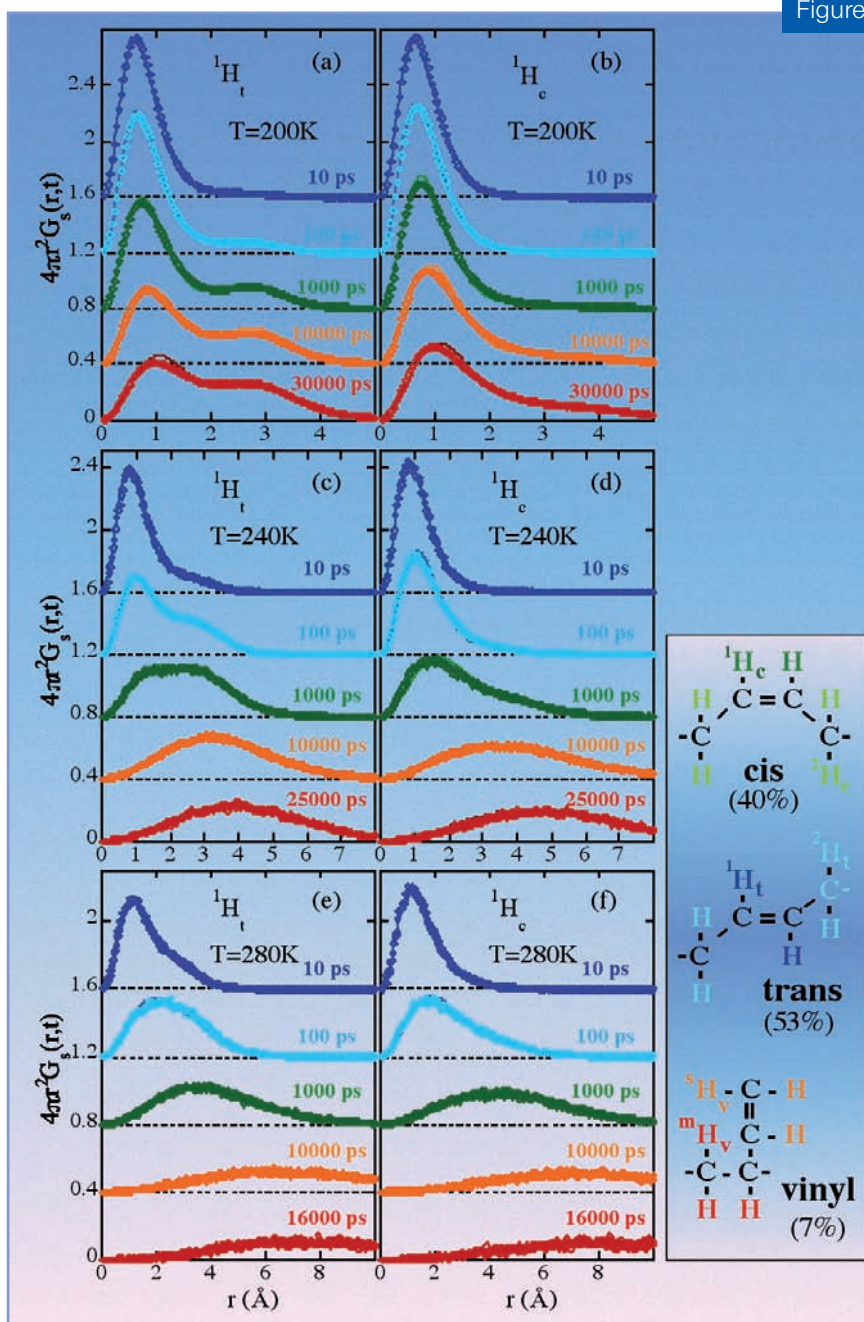
Conclusions

Fully atomistic MD simulations provide a unique route for unravelling the details of the short-range order and the mole-

cular motions at local scales of glass-forming polymers. First of all, a rigorous check was performed of the realism of the simulated cell by direct comparison with experimental data on the real sample. This can be best realized using neutron scattering results on samples with

different deuteration levels. Once the simulated cell has been validated, valuable information can be extracted which is not accessible experimentally. We have proven the power of this strategy with two recent examples of everyday polymeric materials.

Figure 4



Radial probability distribution function calculated at 200 K (a,b), 240 K (c,d) and 280 K (e,f) at the different times indicated for $^1\text{H}_t$ (a,c,e) and $^1\text{H}_c$ (b,d,f). For clarity, the origins are shifted to the levels displayed by the horizontal dotted lines. The solid lines show the description obtained by the proposed model.

From stilling the waves to novel material design

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Particularly during the summer season, one is often confronted with thin rainbow-like patterns when thin oil layers sit on the surface of water, e.g. in a harbour or a lake. These striking optical properties of thin oil films have been noticed and recorded by mankind for millennia, as have the peculiar mechanical properties of such films. Pliny the Elder, the Roman nobleman responsible for the first encyclopaedia, recorded how the surface of water could be made smooth by depositing a thin layer of oil on the surface. This useful effect was employed by divers who descended from the sea's surface carrying a quantity of olive oil that would be dispensed to calm the action of small waves and surface eddies. Benjamin Franklin made similar observations during a diplomatic journey to England after noticing that the wake following different ships was either smooth or highly rippled. The captain of his vessel explained to him that smooth wakes could very well be caused by the release of oily residue by the ship's cook following the cleaning of cookware. Franklin was intrigued by this observation and he carried out some oil-spreading experiments in a small pond near Clapham Common, England. He was surprised to see how efficient even a teaspoon of oil was, as it was able to smooth about half an acre of the pond. These experiments, which were later published as a letter to the Royal Philosophical Society of London in 1774 motivated Lord Rayleigh to calculate the thickness of a monolayer (see e.g. ^[11]).

About a hundred years later, the Belgian scientist Joseph Plateau studied the phenomenon of surface tension and he was the first to prove

experimentally that molecular forces act in a very thin surface layer. Plateau put a lot of effort into investigating the laws governing the formation of soap films. He noticed that molecules at interfaces also affected the mobility or the dynamics of interfaces. Plateau, who – despite being blind – was a very careful and talented experimentalist, described the damping of a compass needle on a surfactant-laden interface in comparison with the behaviour of a pure interface. To explain this, Plateau postulated the existence of a *surface viscosity* ^[12]. Lord Kelvin later pointed out that the Plateaus experiment probed a viscoelastic rather than a purely viscous resistance, as the rotational motion of the needle wipes the surface clean and creates surface gradients in concentration, which lead to viscoelastic stresses. Interfacial, rheological material functions were introduced by Joseph Valentin Boussinesq (1842-1929) to explain observations concerning why small drops and bubbles may sometimes pass through a liquid under the action of gravity with the same speed as solid spheres. Boussinesque demonstrated that the presence of a surface shear viscosity at the interface can convert the settling velocity of a droplet or bubble and cause the same result as a solid sphere if that viscosity is sufficiently large ^[13]. In addition to possessing an enhanced viscosity, interfaces may also be viscoelastic, i.e. exhibit behaviour inbetween a viscous liquid and an elastic solid. Such complex fluid surfaces are ubiquitous in nature (e.g. in human lungs) and in technological applications (e.g. in food and consumer-care products).

Within Softcomp, researchers in different groups are trying to get to

From stilling the waves to novel material design

grips with the surface dynamics. They are trying to measure it, to control the dynamics using self-assembled structures and to use the control over interfacial dynamics to create novel soft composite materials.

Measurements

Since the time of Plateau, several measuring devices have been proposed for investigating the properties that govern the mobility and dynamics of interfaces. Recently, the focus has been on devices that measure the surface shear viscosity and elasticity in a rigorous manner. One of the challenges when measuring the properties of two-dimensional interfaces is that the real world is three-dimensional. When applying a deformation to the interface, this will automatically entail a deformation to the bulk. When selecting the measurement geometry, this needs to be considered, and an optimal geometry has the maximum amount of perimeter at the interface with respect to the surface in contact with the bulk. From this perspective, needles or rings are better geometries than the classically used disks or bicone geometries. Figure 1 shows an example: a sensitive magnetic rod rheometer, originally developed by the group headed by G. Fuller at Stanford University, and which is now being used by groups within Softcomp, in which a magnetic rod is dragged through a channel by an externally generated magnetic field^[4]. Likewise, novel double wall ring devices that can be mounted in rotational instruments facilitate the exploration of a wider range of dynamic conditions while maintaining sensitivity. For both the magnetic rod and the double wall ring device, numerical simulations enable us to separate the interface and bulk contributions and automatically correct for subphase drag effects. Future research will be aimed at diversifying these techniques and applying them to

even more complex fluid interfaces, such as membranes and biologically relevant systems.

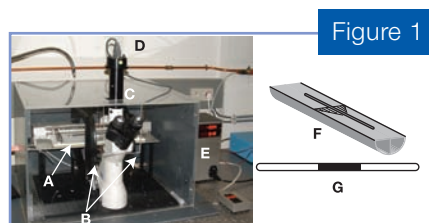


Figure 1
 Interfacial stress rheometer. (A) Langmuir Trough, (B) Helmholtz coils that generate a controlled magnetic field, (C) Inverted microscope (D) Linear photodiode array detector to detect the motion of the rod and the deformation of the interface (E) Surface pressure measurement (F) Flow geometry (G) Rod with a central magnetic part. Figure adapted from [4].

Colloid-laden interfaces

A vast body of research within Softcomp focuses on using colloidal particles and nanoparticles to modify the dynamics of interfaces. Compared to particles in bulk, the *rules of the game* that govern the interparticle interactions now change. The classical rules of colloid science are no longer obeyed when particles are pinned at an interface between two liquids or between liquid and air. In the first place, forces associated with the interfacial tension emerge. Researchers at CRPP in Bordeaux, K.U. Leuven and the University of Mainz have shown how these become extremely important when non-spherical particles are used. When particles with an ellipsoidal cross section are positioned at the interface, Young's equation requires that the angle between the interface and the colloid surface at the three-phase contact line is equal to the contact angle. This condition cannot be met when the interface remains flat, and hence an undulation of the contact line emerges, which entails a deformation of the interface. As a consequence, spatially anisotropic interface mediated capillary interactions are induced^[5,6]. Figure 2, from research at K.U. Leuven, shows how these attractive capillary forces lead to striking self-

assembled structures. Besides being beautiful, they are also useful because the structures are strong and present a very efficient way of controlling the surface rheological properties, which has been exploited to control the stability of emulsions^[7]. Much further work remains to be done, as other interactions forces are also affected in a nontrivial manner by the presence of the interface. In a Softcomp-inspired collaboration between the University of Delaware, the University of Mainz and K.U. Leuven, the effects of surfactants and electrolytes on the electrostatic interactions between particles at interfaces were directly measured using optical tweezers and compared to the theoretical models, revealing some unexpected features^[8]. Understanding these interactions further should enable a more rational design of solid stabilized emulsions and foams.

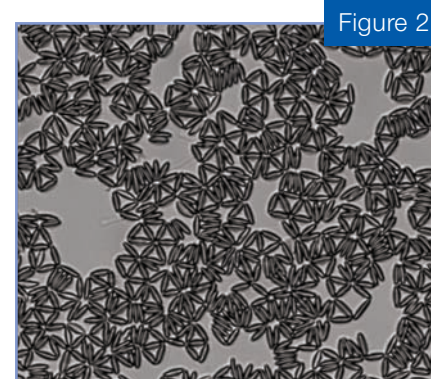


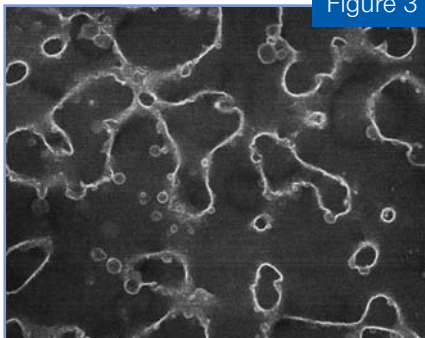
Figure 2
 Microscopy images of a monolayer of charged polystyrene spheroids with AR=5.5 at a planar water-decane interface, 360 hours after deposition at the interface. Image courtesy of Basavaraj Madivala at K.U. Leuven

Novel materials

Due to the fact that trapped particles and other ingredients can modify the viscoelastic properties of liquid-liquid interfaces, they can be used to assemble new materials. An interface that percolates through a predominantly fluid sample can be used to convey solidity to the sample. To this end, a novel material has been designed

by researchers at the University of Edinburgh, which exploits the properties of particle laden interfaces. It is called a bijel: a colloid stabilized emulsion with fundamentally new properties^[9]. To make a bijel, the researchers use particles with contact angles close to 90° and equal volumes of two phase-separating liquids that are similar.

Figure 3



Bijel structure stabilized using spherical colloids as seen using fluorescence confocal microscopy. Both fluids are dark with a bright interface. The slice is of a sample one week after formation. The samples are water-2,6-lutidine at critical composition with 2% volume fraction silica colloids quenched from room temperature to 313 K at 17 K/min. The scale bar is 100 μm. Image courtesy of Dr. P. Clegg at the University of Edinburgh.

Under suitable conditions, partially miscible liquids phase separate following a change in temperature or pressure via spinodal decomposition. Spinodal decomposition results in the formation of bicontinuous fluid domains characterized by a single length scale which increases as the phase separation proceeds. The first realisation of bijels made use of this kinetic pathway^[10]. Silica colloids were used, which were made neutrally wetting (wetting angle of 90°) for a partially miscible water and oil (2,6-lutidine) combination. The colloids were dispersed in the water and oil at room temperature when the liquids are miscible. When slowly warmed, the liquids begin to separate via spinodal decomposition. The colloids become adsorbed on the newly formed interfaces. As the fluid domains coarsen, the colloids are forced together. When the

particles are jammed into contact at the interface, the coarsening is arrested and the interfaces become increasingly solid-like. The bicontinuous structures, stabilized by interfacially jammed colloids, appear to be robust metastable states, contrary to bicontinuous microemulsions which are equilibrium structures. We are in the process of exploring how the unusual viscoelastic properties of the two-dimensional interfaces manifest themselves in three-dimensional samples of this kind.

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About SoftComp



SoftComp is a

Network of Excellence – a tool developed under the 6th Framework Programme of the European Commission dealing with the integration of European research, with the intention of strengthening scientific and technological excellence.

In particular, SoftComp aims to establish a knowledge base for an intelligent design of functional and nanoscale soft matter composites. It will do so by overcoming the present fragmentation of this important field for the development of new materials at the interface of non-living and living matter, where the delicate principles of self-assembly in polymeric, surfactant and colloidal matter prevail.

This Network of Excellence will create an integrated team that is able to activate the European potential in soft matter composite materials and thus disseminate excellence through extensive training and knowledge transfer schemes.

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Vacancies

Postdoc fellowship ...

... available at *Institut Curie-Paris*.

A post-doc fellowship is immediately available for an experimental study of lipid and protein diffusion in tubular structures (in vitro in membrane nanotubes or, in vivo, in axon dendrites). The project is a collaboration with J.F. Joanny, J.Prost of the Curie Institute for the theory, and A. Triller from the Neuroscience department of the Ecole Normale Supérieure. It is funded by the Fondation P.G. de Gennes.

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PhD position ...

... available in the Soft Condensed Matter group at *Utrecht University Soft Condensed Matter, Debye Institute Department of Physics and Astronomy* on static and sheared granular packings of deformable particles studied with confocal microscopy.

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CASE Studentship Phase behaviour and dynamics of lipid bilayer membranes ...

... available at *School of Physics and Astronomy University of Leeds, Leeds LS2 9JT*

A studentship is available for an experimental study of phase separation in lipid bilayer membranes using primarily AFM. Topics include the formation of stable liquid domains; the kinetics of domain formation and rules governing domain morphology; mechanical and rheological properties of supported membranes with nanometer spatial resolution; and how the introduction of detergents, proteins and drug molecules alters the membranes physical properties.

The project is a 3.5 year EPSRC-funded studentship appropriate for a student with UK status, and is part of a collaboration between the University of Leeds and Unilever. The student can begin immediately. It carries an enhanced stipend due to the industrial collaboration (CASE award).

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Coming Up...

SoftComp Conferences & Workshops Date

Julich Soft Matter Days 2008 Gustav-Stresemann-Institut Bonn, Germany www.fz-juelich.de/iff/jsmd2008 Jan Dhont: j.k.g.dhont@fz-juelich.de Gerhard Gompper: g.gompper@fz-juelich.de Dieter Richter: d.richter@fz-juelich.de	11-14 Nov 08
SoftComp Topical Meeting on Nanocomposites and Polymer Dynamics 2008 Montpellier, France www.lcvn.univ-montp2.fr/congres/ws_1108/Flyer.pdf J.Oberdisse: oberdisse@lcvn.univ-montp2.fr	27-28 Nov 08
British Society of Rheology Microstructure and Rheology Leeds, UK www.innfm.swan.ac.uk/bsr/conf/view_page.php?page_id=38&conf=35 Peter Olmsted: p.d.olmsted@leeds.ac.uk	15-16 Dec 08
SoftComp Topical Meeting on Colloidal and Polymer Synthesis Vigo, Spain www.eu-softcomp.net/meet/TM_v09 Luis Liz-Marzan: lmazan@uvigo.es	11-12 Mar 09
SoftComp Topical Meeting on Self-Assembly and Biomimetics 2009 Weizmann Institute, Israel www.eu-softcomp.net/meet/TM_w09 Nir Gov: Nir.Gov@weizmann.ac.il Samuel Safran: sam.safran@weizmann.ac.il	11-12 Mar 09
Workshop on Neutrons in Soft Matter Science Munich, Germany Dieter Richter: d.richter@fz-juelich.de	14-17 Apr 09

Coming Up (continued) ...

SoftComp Conferences & Workshops Date

Annual European Rheology Conference Cardiff, Wales www.rheology-esr.org/AERC/2009/	15-17 Apr 09
SoftComp Annual Meeting Venice, Italy www.eu-softcomp.net/meet/annual/am08 <ul style="list-style-type: none"> • NA Meetings • Work planning Meeting • NGB06 Meeting • NCC22 Meeting Dieter Richter: d.richter@fz-juelich.de	04-07 May 09
Course on Light Scattering and Microscopy Jülich, Germany Jan Dhont: j.k.g.dhont@fz-juelich.de	May 09
Mainz Materials Simulation Days 2009 Mainz, Germany www.mpip-mainz.mpg.de/mmsd W.Paul: wolfgang.paul@uni-mainz.de	03-05 Jun 09
13th Laboratory Course on Neutron Scattering Jülich/Garching, Germany www.neutronlab.de Reiner Zorn: r.zorn@fz-juelich.de	07-18 Sep 09

Personalia

Prof. Gerhard Gompper, Institut für Festkörperforschung Jülich, Germany, has been selected as an Outstanding Referee for the journals of the American Physical Society, 15th February 2008.

Prof. Christos N. Likos, Department of Physics, University of Duesseldorf, Germany, has been elected in July 2008 as member of the Advisory Board of the Journal "Soft Matter".

For more frequently updated information, please see also the SoftComp web pages...

Vacancies: www.eu-softcomp.net/news/jobs · SoftComp News: www.eu-softcomp.net/news/
 SoftComp Events: www.eu-softcomp.net/news/cal

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SIXTH FRAMEWORK
 PROGRAMME

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