

Molecular Modelling and Neutron Scattering Workshop: Techniques for Large-scale Systems

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This workshop sought to bring together two distinct groups of researchers with much in common but hitherto had not interacted particularly strongly. With the growing complexity of the systems in which both groups are currently interested, not least systems of increasing length scale, the time was ripe for a meeting of minds. It was hoped by the organisers that the experimentalists would leave the workshop better informed about the capabilities of molecular simulation, while the simulators would better appreciate the difficulties experimentalists face in interpreting the results of neutron scattering experiments. The meeting was sponsored by CCP5, the Institute of Physics and ISIS (the UK neutron scattering facility at Rutherford Appleton Laboratory) and took place in the pleasant surroundings of Cosener's House in Abingdon. The meeting was well attended by over fifty scientists from both academia and industry.

The first speaker was Prof. Dominic Tildesley (Imperial College), who described the molecular dynamics simulation of various air/water/oil/surfactant interfaces. Simulations of the air/water interface employed the SPC (simple point charge) model for the water molecule. A 2D periodic "slab" provided an acceptable description of the density profile, showing oscillatory behaviour near the interface at 277K (though capillary waves are dampened by the periodic boundary condition). The pressure tensor at the surface was very similar in 500 and 100 molecule simulations. The orientation of the water molecules at the surface was also investigated and attempts were made to reproduce the laser induced second harmonic generation. The results showed that water above and below the Gibbs dividing surface adopt slightly different orientations resulting in a switch of dipolar field on passing through the surface. The difficulty of interpreting the experimental result without the information gained through simulation was emphasised.

Simulations of phenol at the air-water interface showed that the orientation of phenol at the surface was unaffected by the degree of coverage, implying a dominance of the water-phenol interaction over the phenol-phenol interaction. The phenol was also observed to disrupt the structure of the water surface, changing the water dipole orientations at the surface significantly. Experimental confirmation of these observations was available from laser reflectometry.

Simulations were also undertaken to determine the microscopic origin of friction in the fabric softener dioctadecyl dimethyl ammonium chloride (DODAB). In these experiments DODAB molecules, arranged in layers attached to opposing surfaces, were slid past each other at the relatively high speed of 100 m/s (1 Å/ps) under a normal stress of 300Mpa and the friction coefficient calculated. It was observed that: the friction decreased with increasing normal force; increased with decreasing DODAB density; decreased with decreasing sliding velocity; and decreased with decreasing chain length. Some of these results were unexpected, and possible explanations were offered. For example decrease in friction with decreasing chain length may indicate the importance of the underlying surface roughness in experimental determinations of friction.

The final example of interface simulation presented was ongoing work of the DODAB/hexane interface to explore the penetration of oil into the DODAB matrix. Preliminary results showed that the hexane bulk was well accounted for and that the hexane molecules showed a tendency to align with the DODAB molecules as they penetrate the surfactant. The longer term objective was to reproduce the neutron reflectometry data for this system.

Prof. R.W. Richards (University of Durham) spoke on the subject of coarse-grain problems and asked "is there a fine grained solution?". Seeking to bridge the gap between atomistic descriptions of polymers and the large scale, Prof. Richards described a number of experimental studies in which the current theoretical models failed to provide adequate assistance.

Beginning with small angle scattering, the assumption of a Gaussian mass distribution for polymer chains leads to the Debye equation from which the radius of gyration of the polymer may be extracted. However in the case of syndiotactic polymethyl methacrylate (PMMA or perspex) the small angle x-ray scattering (SAXS) data is inconsistent with the Debye equation. The rotational isomeric state (RIS) model, which incorporates local conformations of the chains, gives a better description, indicating the importance of local structure. However neutron scattering experiments on a related polymer (PLMA), reveal that the main chain is consistent with a Gaussian model. There are also problems with describing the proportion of cis and trans conformations in such chains. Another problem in small angle scattering work was the verification of the stretching of the "arm" chains of star polymers, which is predicted theoretically. It proves to be extremely difficult to separate out the radius of gyration of a single arm without making additional assumptions.

Moving on to discuss polymers at fluid interfaces, modelling such systems was said to be in its infancy. The example presented was PMMA, with polyethylene oxide (PEO) grafts, at the air/water interface. These systems are studied by neutron reflectometry. The simplest models are used to account for experimental results. A two layer model appears to be adequate for low and intermediate surface concentrations and a three layer model is needed for high surface concentrations; the inference being that the polymer loops out of the surface with increasing concentration. However some important questions remain. It is unclear if the grafts are stretched or if they are at the excluded volume limit. Also of interest is the "wet brush" situation, where the theoretical scaling law for the brush height with surface concentration is only weakly confirmed by experiment. With regard to the dynamics of polymers at interfaces, the phenomenology is dominated by capillary waves of the order 30 to 1000 micrometres wavelength, which strongly scatter light. The capillary waves and dilational waves of the polymers at the surface represent coupled "lossy" oscillators. Light scattering experiments yield both dielectric and visco-elastic properties of the interface. However, the interpretation of these results is fraught with difficulty. The surface tension is obtained reasonably accurately, but observed resonances do not behave in the classical manner (the characteristic signals seen in the real and imaginary parts of resonances are not seen at the same frequency.) There is no satisfactory explanation for the dilational modulus or the dilational viscosity, for example and an unknown velocity coupling seems to be responsible.

In conclusion, it was stated that while the RIS model worked for homopolymers, it was not suitable for complex systems, where the random phase approximation was more successful if lacking

in fine detail. For interfaces, scaling laws and self consistent field models provide some explanation, but a deep theoretical understanding, particularly of dynamic phenomena is absent. There thus appears to be no fine grained solution as yet, but one is certainly required.

Dr G. Kneller (Aachen) sought to show how molecular dynamics (MD) simulation can be used to assist with the interpretation of neutron scattering experiments, with reference to some specific systems. The first example presented was myoglobin, which at temperatures below the glass transition shows a characteristic motion which is detectable by elastic neutron scattering experiments and is generally assigned to the “jump” rotational motion of methyl groups, since the corresponding jump distance accords with the 1.5 Å observed. However at the temperature concerned (< 200 K), there is unlikely to be sufficient thermal energy to account for the jump transition. It was shown how, in MD simulations, it is possible to isolate particular motions in a complex molecule - a video was shown of the motion of myoglobin with and without main chain motion. Computation of the elastic incoherent structure factor with these motions extracted revealed that the observed neutron scattering results could equally well be explained by liquid-like motion of the side chains, thus avoiding the jump model.

In a second example, MD simulation of crystalline polyacetylene was able to reproduce the frequency spectrum for the molecular motion, which compared well with experiment. The characteristic motion was shown to be rigid-body-like motion of the chains. The simulations incorporated the instrument resolution function and corrections for bending of the chains. The final example showed how constant pressure MD was used to examine the internal and global chain motion of alkyl chains in a matrix of TANO molecules ($C_9H_{16}NO_2$). The features of the inelastic structure factors were accounted for and shown to be due to translational motions of the chains. The angular distributions of the CH₂ groups revealed the stiffness of the chains.

Dr. T. Cosgrove (Bristol) explained how statistical mechanical models of polymer chains may be used to account for the experimental properties of real polymers. Beginning with the adsorption of chains on a surface it was shown that for small chains the free energy could be determined by “counting” the possible configurations on a cubic lattice (the self avoiding walk or SAW). By such methods it was possible to determine the value of the interaction parameter (the Flory surface parameter) for which adsorption at a surface occurs. For larger systems, Monte Carlo simulation (which introduces importance sampling) is used, which avoids the need to count all the possible configurations. The self consistent field theory (Scheutjens-Fleer model) may be used to calculate the adsorption isotherms. The form of chains attached to a surface may be described by the terms “pancake”, “mushroom”, “block” or “parabola” according to their appearance and represent subtle differences in behaviour.

Polymers at surfaces are studied by small angle neutron scattering. In general all components of the system contribute to the resulting scattering, though the different components can be extracted by modelling. An example system shown was the PEO chain at the water surface, the volume fraction profile was adequately described by a Gaussian model. Such models work well for single polymers, but not for mixtures or block copolymers, though in these cases it may be possible to obtain a fit to experimental data by adjusting the basic parameters. However it remains difficult

to deal with very large chains. Some outstanding challenges of these methods are: the effects of surface heterogeneity (the models assume perfect surfaces); surface charges and their effects; competitive adsorption; surface micellisation; the dynamics of chains; and the influence of head groups.

Dr D. Heyes (Surrey) provided an overview of molecular modelling techniques (principally MD) that have potential in modelling large scale structures. Large structures are characterised by large molecules and long relaxation times and include liquid crystals, colloids, polymers and Langmuir-Blodgett films. They can be monodisperse systems such as polystyrene latexes or polydisperse, such as colloids or clays, with a range of particle shapes as well as sizes. They may have chemical engineering interest, for example suspensions, damp powders and granular materials.

Conventional simulation methods can be extended to deal with such systems. Dr Heyes described such extensions, beginning with the smaller scale: clusters of atoms to represent colloidal particles, with a stochastic (collisional) solvent, where it is possible to examine the structure of the colloids and surrounding fluid, and dynamical properties such as velocity autocorrelation and orientational correlations. As an example of more detailed modelling, overbased detergents used in the petroleum industry to neutralise acidic combustion products were described. These are calcium carbonate nanoparticles with a surfactant “coat” to assist dissolution in oil. MD studies have addressed the nanoparticle structure and the adsorption of the surfactant.

On larger length scales the timescale becomes a limiting factor for full MD studies. The system relaxation times grow rapidly with system size. The strategy must then be to design interaction models that retain the essential physics on the length scale of interest, but abandon the microscopic complexity. As an example, the use of a simple “dumbbell” model of a surfactant in mixtures of spherical solvent molecules is able to show both discontinuous phases and micelles with a simple change in dumbbell particle sizes. Dr Heyes concluded with a description of Brownian dynamics, which allows the effects of a solvent to be modelled, without the molecular detail. The normal deterministic motion of the particles is augmented by random forces and balanced drag forces (Ermak’s algorithm). Such models have been used to model viscoelastic phenomena in colloidal systems and give the correct stretched exponential form for the correlation functions.

The final speaker was Dr D.J. Barlow (King’s College, London) who spoke about structure determination and modelling of surfactant aggregates. The interest here was pharmaceutical: surfactant vesicles encapsulating the active ingredients of pharmaceutical preparations have many advantages for storage and drug delivery. It is important to be able to design surfactants with the right characteristics, but to date a purely modelling approach is not capable enough. Neutron reflectometry studies of the surfactant structure at an interface offers some evidence of the ability of the surfactant to form vesicles, though this does not rule out them forming unwanted micelles.

Dr Barlow described methods for modelling reflectometry experiments using the optical matrix method. The results may be augmented by Langmuir trough experiments to obtain a broader understanding of the surfactant behaviour. However, while these experiments may show that a monolayer of surfactant cannot form a vesicle, a vesicle may be formed from a multilayer of surfactant molecules. Small angle neutron scattering can be used to examine the surface structure

of vesicles directly and it is possible to correlate vesicle thickness with surfactant molecular characteristics such as molecular weight, although no clear pattern has emerged from this. Isotopic substitution (selective deuteration) offers deeper insight into the surface structure, though the modelling of this is not particularly advanced. A program (SURFISS) has been developed to model the structure of surfactant monolayers and is yielding useful insights. Dr Barlow argued in favour of the greater availability of intelligent software to model surfactant systems, allowing greater ease in building the model system from a prescribed molecular structure.

The final event of the meeting was an open discussion chaired by Dr Jeff Penfold (RAL). In summarising the workshop he noted the great demand for reliable methods of scaling models up from atomistic to the mesoscale and larger, and the great complexity of the systems of interest. There was a strong need for more predictive capability in modelling polymers at interfaces, though the best way to feed in the chemical detail was unclear. An obvious role for simulation was to assist with the analysis of experiments, for example the detailed structure revealed by selective deuteration experiments.

In the subsequent discussion there was clear recognition that the time was ripe for closer collaboration between experimentalists and molecular modellers, particularly for mesoscale systems and small angle neutron scattering work. A role for CCP5 in developing suitable software was suggested, for which a project in modelling interfaces would be a suitable focus. With regard to computational methods, a role for reverse Monte Carlo methods was suggested as well as more conventional molecular dynamics (typified by the CCP5 simulation code DL_POLY) to assist with elastic and inelastic scattering work. A role for graphics based support software was also recommended.