

CCP5 Annual General Meeting

10 – 12 September 2018

The University of Manchester

Book of Abstracts



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ORAL CONTRIBUTIONS

Day 1

13.00 Registration opens

13.40 Welcome

Session 1

Chair: **Carlos Avendaño**, The University of Manchester

13.45 **Fernando Escobedo**, Cornell University
Optimizing the Ordered Self-Assembly of Soft and Hard Nanoscale Building Blocks: Pure Components and Alloys

14.30 **Massimiliano Chiappini**, Utrecht University
The role of particle curvature on twist, bend and splay deformations in nematic liquid crystals

14.50 **Dwaipayyan Chakrabarti**, University of Birmingham
Programming Hierarchical Self-Assembly of Patchy Particles into Colloidal Crystals via Colloidal Molecules

15.10 Coffee Break

Session 2

Chair: **Andrew Masters**, The University of Manchester

15.40 **Josep Bonet**, Rovira i Virgili University, Tarragona
Kinetic exchange of copolymer surfactants in micelles

16.10 **Pablo de Castro**, King's College London
Phase separation dynamics of polydisperse colloids: a mean-field lattice-gas theory

16.30 **David Quigley**, University of Warwick
Transport of Latent Heat in Seeded Nucleation Simulations

16.50 **Karl Fairhurst**, Imperial College London
SAFT association potentials for MD simulations

17.15 Poster Session and Drinks Reception

Day 2

Session 3

Chair: **Fernando Escobedo**, Cornell University

09.00 **Francesco Sciortino**, Sapienza University
Collective Behavior of DNA made nanoparticles

09.45 **Carlos Avendaño**, The University of Manchester
*Self-assembly of non-convex colloidal frames:
The formation of lacuna ordered structures*

10.05 **Daniel Corbett**, The University of Manchester
*Dynamic Monte Carlo simulations of
out-of-equilibrium colloidal liquid crystals*

10.25 Coffee + Posters

Session 4

Chair: **Karl Travis**, The University of Sheffield

10.55 **Carlos Nieto**, IFP Energies Nouvelles
*Coarse-grained modeling of complex fluids and electrolytes.
From parameterization to applications*

11.25 **Martin Trusler**, Imperial College London
*Thermophysical Properties and Phase Behaviour of Fluids
for Application in Geological Carbon Storage*

11.55 **Andrey Brukhno**, STFC, Daresbury Laboratory
*Simulation of surfactants and lipids in solution:
bridging between different scales and methods*

12.15 Lunch

Session 5

Chair: **Flor Siperstein**, The University of Manchester

13.15 **Peyman Moghadam**, University of Cambridge
*The Role of High-Throughput Computational Screening
in Materials Discovery*

13.45 **Miguel Jorge**, University of Strathclyde
*An accurate molecular model to predict adsorption of
polar adsorbates in metal organic frameworks with open metal*

- sites
- 14.05 **Karen Johnston**, University of Strathclyde
Evaluation and Optimisation of Interface Force Fields for Water on Gold Surfaces
- 14.25 **Giuliana Giunta**, The University of Manchester
A Novel Coarse-Grained Model to Simulate High Molecular Weight Polymers in Contact with Solid Surfaces
- 14.45 Coffee + Posters

Session 6

- Chair: **Francesco Sciortino**, Sapienza University
- 15.15 **Leo Lue**, University of Strathclyde
Structure and cluster formation in size asymmetric soft electrolyte systems
- 15.35 **Paola Carbone**, The University of Manchester
Atomic characterization of the electrolyte/graphene interface
- 15.55 **Simon Halstead**, The University of Manchester
The Effect of Halide Diffusion on the Liquid-Liquid Separation of Cobalt and Nickel Using Trihexyltetradecylphosphonium Halide Ionic Liquids
- 16.15 **Martin Horsch**, American University of Iraq
Multicriteria optimization of pair potentials for bulk fluid properties and the vapour-liquid surface tension
- 16.35 CCP5 Exec C/tee meeting
- 19.15 Conference Dinner at Christie's Bistro

Day 3

Session 7

- Chair: **Josep Bonet**, University Rovira i Virgili, Tarragona
- 09.00 **Andrei Zvelindovsky**, University of Lincoln
Block copolymers in confinements and under external fields
- 09.30 **Gerardo Campos**, The University of Manchester
Coarse-grained potential derivation for modelling the self-assembly of block-copolymers in binary solvents

- 09.50 **Matthias Nébouy**, University of Lyon
Coarse-grained modelling of semicrystalline thermoplastic elastomers
- 10.10 **Javier Burgos**, University of Liverpool
Coarse-graining polymer semiconductors
- 10.30 Coffee Break
- Session 8**
- Chair: **Carlos Nieto**, IFP Energies Nouvelles
- 10.50 **Zengqiang Zhai**, University of Lyon
Molecular topology of semicrystalline polymers: simulation of mono and polydisperse systems
- 11.10 **Achille Giacometti**, University Ca' Foscari, Venice
The elixir phase of chain molecules
- 11.30 **Kostya Trachenko**, Queen Mary University of London
New understanding of collective modes and thermodynamics of the liquid and supercritical states
- 11.50 **Ivan Scivetti**, STFC, Daresbury Laboratory
Reorganization energy upon charging a single molecule on an insulator measured by atomic force microscopy
- 12.10 **James Shaw**
Hierarchical self-assembly of triblock patchy particles into a tetrastack lattice
- 12.30 Closing Remarks

Optimizing the Ordered Self-Assembly of Soft and Hard Nanoscale Building Blocks: Pure Components and Alloys

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As meso-scale building blocks, oligomers, polymers, and nanoparticles can be tailored in ways that atomic or small-molecule building blocks cannot. Recent progress in synthesis and fabrication methods allow the creation of multi-block oligomers and nanoparticles that vary not only in size and chemical composition but also in shape, rigidity, branching topology, and spatial functionalization. A key challenge that such boundless possibilities present to modelers is the ability to predict the assembling patterns of novel building blocks, and thus potentially identify phases with desirable structures and physical, optical, electronic, catalytic or mechanical properties for emerging applications.

I will describe our efforts to optimize the formation of different types of colloidal alloys, which can be seen as the analog of strategies that have already developed to make useful salts or doped solids from inorganic elements or alloys and intermetallic compounds from metals, the goal is to advance general principles and approaches to design the inter-species interactions between nanoparticles that optimize the formation of either substitutionally disordered alloys or substitutionally ordered alloys. The work focuses on binary mixtures consisting of nanoparticle components whose interactions can be characterized by asymmetries in entropic and energetic characteristics. We have formulated variational principles for enhancing co-assembly behavior with the target type of substitutional order and tested those principles by application to mixtures containing components of diverse size and shape (including polyhedral) and selective interactions that mimic the hybridization of complementary short DNA strands grafted to the nanoparticle surfaces. Some of our specific predictions are consistent with results of nanoparticle alloys already realized.

I will also briefly describe our work on the phase behavior of polyphilic oligomers, i.e., molecules consisting of several block types, focusing on cases where a rigid core is one of the constituent blocks. We focus on architectures that can create complex bicontinuous structures, filling some of the gaps in the rich phase behavior that has already been mapped experimentally. As in the case of nanoparticles, we touch on the free-energy methods used to study some of these systems and how binary alloys provide a powerful means to access new phase behaviors.

Collective Behavior of DNA made nanoparticles

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DNA oligomers can nowadays be assembled to produce a large variety of nanometric constructs, via a cascade of self-assembly processes, each one guided by the length of complementary sequences of distinct DNA strands. In the lecture I will show that it is possible to build bulk quantities of DNA-made nanoparticles that closely match idealized colloids, transferring modern in-paper and in-silico intuitions into experimental realizations. I will show how unconventional collective behaviors, recently explored theoretically and numerically, can indeed be reproduced in the lab. Specifically I will discuss: (i) how to exploit limited valence interactions to suppress phase separation [1,2], enhancing the stability of the equilibrium gel phase [3-5]; (ii) how to exploit competing interactions to generate a material that is fluid both at high and at low temperatures and a solid-like disordered open network structure in between [6-8] and (iii) how to exploit bond-swap dynamics to create an all-DNA vitrimer [9-10].

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- [3] S. Biffi, R. Cerbino, F. Bomboi E. M. Paraboschi, R. Asselta, F. Sciortino and T. Bellini, Phase behavior and critical activated dynamics of limited-valence DNA nanostars, *Proc. Nat. Acad. Science*, **110** 15633-15(2013).
- [4] S. Biffi, R. Cerbino, G. Nava, F. Bomboi, F. Sciortino and T. Bellini, Equilibrium gels of low-valence DNA nanostars: a colloidal model for strong glass formers, *Soft Matter*, **11**, 3132 (2015).
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- [9] D. Montarnal, M. Capelot, F. Tournilhac, and L. Leibler, Silica-like malleable materials from permanent organic networks, *Science* **334**, 965 (2011).
- [10] F. Romano and F. Sciortino, Switching Bonds in a DNA Gel: An All-DNA Vitrimer, *Phys. Rev. Letts.* **114**, 078104 (2015).

Kinetic exchange of copolymer surfactants in micelles

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The exchange of surfactants in micelles with the bulk involves several processes which are difficult to characterize experimentally [1-4]. Microscopic simulations have the potential to reveal some of the key aspects that take place when a surfactant spontaneously exits a micelle. We present a study based on a dynamic version of a single-chain mean field theory [5] using a coarse-grained model for poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer systems [6]. The kinetics described in our simulations involves three different regimes which span over a large range of time [7]. After a fast initial rearrangement of the labeled chains, the system undergoes a logarithmic relaxation [8], which has been experimentally observed [1-2]. Contrary to what has been stated in previous analyses, this regime is caused by the intrinsic physical behaviour of the system, and not only due to the polydispersity of the samples. Finally, the terminal regime is characterized by an exponential decay. The exit rates predicted by our simulations are in good agreement with the ones experimentally reported. In addition, we find a subtle variation of the radius of gyration of the hydrophobic block while exiting the micelle, which challenges the vision of either a complete collapse or a full stretching commonly accepted in current theoretical and experimental literature [9].

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Coarse-grained modelling of complex fluids and electrolytes: From parameterization to applications

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Aqueous organic systems and electrolyte solutions are among the most important constituents of complex solutions involved in many industrial systems[1]. There is a need for accurate models able to both reproduce thermodynamic and transport properties of these systems[2]. Dissipative Particle Dynamics (DPD) seems to be a good alternative to standard atomistic simulations when dealing with large and complex systems. One of the key points in the accuracy of DPD simulations to reproduce thermo-physical properties is the availability of a thermodynamically consistent methodology to parameterize fluid-fluid interactions for different type of systems. Although several approaches have been proposed (Flory-Huggins c-parameter, Hildebrand solubility, etc.), they are not suitable for electrolytes or systems containing partially miscible molecules. We explore in this work several parameterization workflows able to address this problem. The obtained model will be illustrated through two examples: 1) the liquid-liquid equilibrium and interfacial tension of complex hydrocarbon systems, and 2) the osmotic coefficient for electrolyte solutions as a function of the salinity.

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Thermophysical Properties and Phase Behaviour of Fluids for Application in Geological Carbon Storage

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Deep saline aquifers and depleted oil & gas fields have been identified as promising sinks for the storage of large amounts of anthropogenic carbon dioxide. In order to design safe, effective and economic geological carbon storage projects, it is necessary to have a thorough understanding of the physical and chemical properties of mixtures of CO₂ and reservoir fluids, both brines and hydrocarbons, at reservoir conditions. This requires a combination of empirical data and well-founded models that can be applied in reservoir simulations.

In this work, a programme of experimental and modelling work has been undertaken with the objective of obtaining improved quantitative understanding the phase behaviour, interfacial properties and single-phase properties of systems containing carbon dioxide, water, salts, hydrocarbons and diluent gases. An overview of the outputs from this research will be presented. Examples include experimental measurements of the solubility of CO₂ in water and brines or various compositions, and measurements of the density, viscosity, *pH* and diffusion coefficients of the resulting solutions. Additionally, measurements have also been made of interfacial tension in CO₂-brine systems, both with and without diluent gases such as nitrogen or hydrogen that might be present in the CO₂ stream.

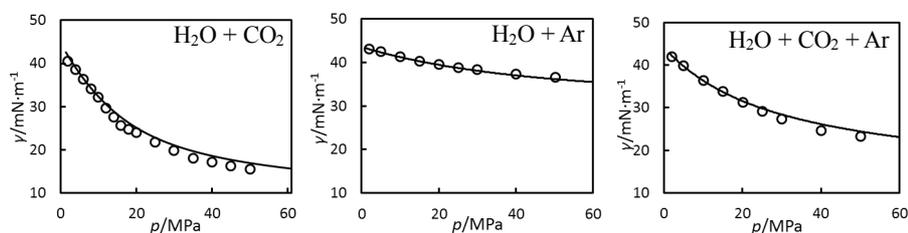


Fig. 1. Interfacial tension in binary and ternary mixtures of H₂O, CO₂ and Ar as a function of pressure at 448 K: ○, experiment; —, SAFT-VR Mie + Square-Gradient Theory

The results of the experimental programme will be compared with both established and recently-developed modelling approaches. For phase behaviour, these include traditional γ - ϕ approaches and also the SAFT approach. The latter has been successfully coupled with square-gradient theory to model interfacial tension (see Fig. 1). Conclusions will be presented concerning the current state of knowledge of phase behaviour, interfacial properties and single-phase properties of systems containing CO₂ with brine and/or hydrocarbon, with or without diluent gases, under conditions representative of geological carbon storage.

The Role of High-throughput Computational Screening in Materials Discovery

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Current advances in materials science have resulted in rapid emergence of thousands of functional adsorbent materials, including metal-organic frameworks (MOFs). This clearly creates multiple opportunities for their potential application, but it also creates the following challenge: *how does one identify the most promising structures, among the thousands of possibilities, for a particular application?* Due to practical constraints, experimental trial-and-error discovery is simply not fast enough and therefore more efficient alternatives must be developed to accelerate the discovery and deployment of new adsorbent materials. To tackle this problem our lab has first generated a curated database containing all the MOFs deposited in Cambridge Structural Database (CSD) – a database that is regularly updated by the Cambridge Crystallographic Database Centre with any new entries.¹ Using computational high-throughput screening (HTS) based on grand canonical Monte Carlo simulations and data mining methods we were capable of analyzing the results interactively and obtaining structure-property relationships through 5D visualisation techniques, thus providing invaluable insights to guide synthetic efforts and to reveal physical limits of performance.

We show key examples of computer-aided material discovery, in which we complete the full cycle from rapid HTS of MOF materials for methane and oxygen storage, to identification, synthesis and measurement of experimental adsorption in top-ranked structures. Our study delimits the relationships between structural properties and gas adsorption performance for up to 70,000 already-synthesized MOFs in dynamic 5D representations (Figure 1), allowing the final user to select the optimal material. We also used recent developments in advanced synthesis, engineering and densification of MOFs to produce pure monolithic structures of up to ca. 1 cm³ size without using high pressures or additional binders.² The resulting materials are able to reach, the DOE target for volumetric storage of methane, with a >50% improvement over any previously reported experimental value. They also report new world-record holding material for oxygen storage, which delivers 22.5% more oxygen than the best known material to date.^{3,4}

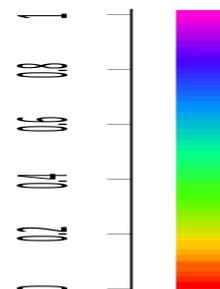


Fig.1. Structure-property relationships between oxygen deliverable capacity, heat of adsorption and void fraction for

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[3] T. Tian, Z. Zeng, D. Vulpe, M.E. Casco, G. Divitini, P. A. Midgley, J. Silvestre-Albero, J.-C. Tan, P. Z. Moghadam, and D. Fairen-Jimenez. *Nature Materials* **2018**, 17, 174–179.

[4] P.Z. Moghadam, T. Islamoglu, S. Goswami, J. Exley, M. Fantham, C.F. Kaminski, R.Q. Snurr, O.K. Farha, and D. Fairen-Jimenez. *Nature Communications* **2018**, Accepted.

Block copolymers in confinements and under external fields

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Block copolymers (BCPs) are long chain molecules consisting of several chemically different blocks. Due to the chemical nature of the bond between blocks they do not macrophase, but form various structures on the nano-scale. BCP systems can be used as templates for the energy materials, advances separation templates, catalysts and for nano-electronics devices. Modern materials science uses block copolymers in solutions and mixtures of several BPCs and BCPs and homopolymers. Due to the intrinsic complexity of the systems, which have a very large physical parameter space, their experimental study is a much elaborated task. With the advances of computers, computational methods become a crucial component in the BCP research and the advances materials design.

In our contribution we discuss computer simulation results for BCP systems and their relation to experimental data. Computer simulation results presented are based on two models: a Ginzburg-Landau type description and on self-consistent field theory (SCFT) for polymers. The Ginzburg-Landau model used is a basis for Cell Dynamics simulation (CDS) [1]. It is an extension of the square gradient model, which has proven to be very useful for polymer blends, while CDS is a powerful tool for BCP systems. In this talk we focus on two topics – confinements and external fields (electric, shear). In real practice BCP are often found in thin films (of the thickness of several structural domains), and most recently - in nano-pores. Confined structures are found to be very different from the bulk ones. We investigate various BCP systems: lamellae, cylindrical, spherical, and gyroid. Confinement has a profound influence on the BCP structure. In thin films non-bulk structures are formed in the layers next to the confining surfaces. In this way some such structures as perforated lamellae can be formed. In cylindrical pores helical and toroid structures are formed in various combinations. In spherical confinement the observed structures are reminiscent of knitting ball, onion, perforated spherical layer, virus-like morphology and others. Manipulation by the external electric or flow fields is a way of the nanostructure alignment. Kinetics of this process can be different depending on the field strength.

We observe various phase transformations in these two types of fields. Examples include: spheres-to-cylinders and giroid-to-cylinders, as well as orientation transitions, such as changing lamellae orientation. In the case of the electric field lamellae orientation is found to depend on the strength of the electric field and the temperature. Using CDS can serve as a first part of the simulation tandem together with SCFT in a computer-aided design of novel nanostructured materials [1].

1. Pinna M., Zvelindovsky A. V., *Eur. Phys. J. B*, **85**, 210 (2012)

The role of particle curvature on twist, bend and splay deformations in nematic liquid crystals

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In 1958, Frank derived in his seminal work [1] the free-energy cost of the three fundamental deformations (*splay, twist and bend*) of the nematic director field of uniaxial nematic liquid crystals, paving the way for the prediction of spatially modulated nematic phases. Building on Frank's theory, Meyer [2] and Dozov [3] realized that a bend deformation has to be accompanied by a complementary twist or splay deformation, postulating the existence of the *twist-bend* (N_{tb}) and the *splay-bend* (N_{sb}) nematic phases.

The N_{tb} phase – characterized by a heliconical winding of the particle axes and a consequent chiral symmetry breaking – has been found for systems of achiral *bent-core mesogens* both in experiments [4] and simulations [5], and the understanding of its formation mechanism may help to shed light on the long debated origin of the *chiral symmetry breaking* in suspensions of achiral colloids, such as fd-viruses. Vice versa, no evidences of a stable N_{sb} phase have been reported in literature.

To shed light on the formation mechanism of the N_{tb} phase and the elusiveness of the N_{sb} phase we perform an extensive computational and theoretical study of two models of bent-core mesogens. We demonstrate that the curvature of the particles plays a major role in the stabilization of the N_{tb} phase. We show that the pitch of the N_{tb} phase can be predicted from the microscopic details of the shape of the particles, in a *reverse-engineering* fashion. We report the first evidence of a stable N_{sb} phase since its prediction in 1976.

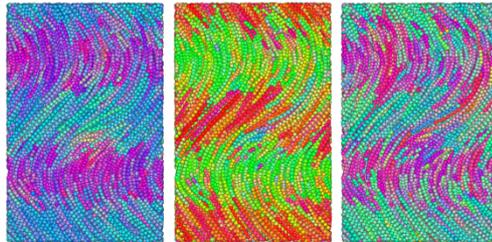


Figure 1. Twist-bend nematic phase. Mesogens are coloured according to the orientation of their prolate axis (left), polar axis (center) and oblate axis (right).

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Programming Hierarchical Self-Assembly of Patchy Particles into Colloidal Crystals *via* Colloidal Molecules

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Colloidal self-assembly is a promising bottom-up route to a wide variety of three-dimensional structures, from clusters to crystals [1]. Programming hierarchical self-assembly of colloidal building blocks, which can pave the way for structures ordered at multiple levels to rival biological complexity, poses a multiscale design problem [2]. In this presentation, I will demonstrate how a hierarchy of interaction strengths realised with triblock patchy particles can be exploited to address this multiscale design problem [3]. Our designer patchy particles are spherical in shape, having two asymmetric, attractive patches, at the poles across a charged middle band, resembling those synthesised recently [4].

We employed a variety of computer simulation techniques to show hierarchical self-assembly of our designer triblock patchy particles into colloidal crystals *via* small colloidal clusters, i.e. *colloidal molecules*, of uniform size and shape. In particular, we demonstrate the hierarchical self-assembly of triblock patchy particles into a cubic diamond lattice *via* tetrahedral clusters. Additionally, for a wider patch width and a longer patch–patch interaction range, we show that these triblock patchy particles self-assemble into a body-centered cubic crystal *via* octahedral clusters, thus lending generality to this design principle [3].

We also characterised dynamical pathways for crystallization, revealing that these crystals with a two-level structural hierarchy are indeed assembled stagewise *via* colloidal molecules [3]. Such a conceptual design framework opens up the prospects of reliably encoding hierarchical self-assembly of colloidal particles into an unprecedented level of sophistication. Moreover, the design framework underpins a novel bottom-up route to cubic diamond colloidal crystals, which have remained elusive despite being much sought-after for their attractive photonic applications.

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[3] D. Morphew, J. Shaw, C. Avins and D. Chakrabarti, *ACS Nano* **12**, 2355 (2018)

[4] Q. Chen, S. C. Bae and S. Granick, *J. Am. Chem. Soc.* **134**, 11080 (2012)

[5] A. van Blaaderen, *Science* **301**, 470 (2003)

Phase separation dynamics of polydisperse colloids: a mean-field lattice-gas theory

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New insights into phase separation in colloidal suspensions are provided *via* a dynamical theory based on the polydisperse lattice-gas model. The model gives a simplified description of polydisperse colloids, incorporating a hard-core repulsion combined with polydispersity in the strength of the attraction between neighbouring particles. Our mean-field equations describe the local concentration evolution for each of an arbitrary number of species, and for an arbitrary overall composition of the system. We focus on the predictions for the dynamics of colloidal gas–liquid phase separation after a quench into the coexistence region. The critical point and the relevant spinodal curves are determined analytically, with the latter depending only on three moments of the overall composition.

The results for the early-time spinodal dynamics show qualitative changes as one crosses a ‘quenched’ spinodal that excludes fractionation and so allows only density fluctuations at fixed composition. This effect occurs for dense systems, in agreement with a conjecture by Warren that, at high density, fractionation should be generically slow because it requires inter-diffusion of particles. We verify this conclusion by showing that the observed qualitative changes disappear when direct particle–particle swaps are allowed in the dynamics. Finally, the rich behaviour beyond the spinodal regime is examined, where we find that the evaporation of gas bubbles with strongly fractionated interfaces causes long-lived composition heterogeneities in the liquid phase; we introduce a two-dimensional density histogram method that allows such effects to be easily visualized for an arbitrary number of particle species.

[1] P. de Castro and P. Sollich, *Phys. Chem. Chem. Phys.*, 2017, **19**, 22509-22527

Transport of Latent Heat in Seeded Nucleation Simulations

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Accessing quantitative information on crystal nucleation rates remains a challenge. Such rates are a valuable input to solidification models with relevance to materials synthesis, fouling and pathogenic crystal formation in the body. Calculating these rates from molecular simulations is expensive, and prone to uncertainties which often reach several orders of magnitude. Nevertheless, progress has been made in extracting useful trends and comparisons when considering nucleation from the melt. These calculations use a variety of simulation & analysis techniques, many of which rely on the assumptions of classical nucleation theory (CNT) which can lead to systematic errors [1].

This presentation will compare two implementations of the seeding method [2,3] – a simulation protocol for fitting CNT parameters to simulations of a crystalline seed embedded in the parent phase. Practicalities and efficiencies of the two methods will be compared.

A particular issue is related to temperature control. Typical molecular simulations couple all degrees of freedom directly to a heat bath via one of the commonly used thermostats. In the context of a growing nucleus, instant dissipation of latent heat released on crystallisation is unphysical. Results will be presented from seeded simulations in which only the far-field is coupled to a thermostat, capturing physical transport of heat away from the growing nucleus. The impact on subsequently calculated nucleation rates will be assessed, and possible enhancements to the method postulated via coupling of CNT to simple diffusive models of heat transport.

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SAFT association potentials for MD simulations

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At the heart of many iterations of the statistical associating fluid theory (SAFT) equation of state (EoS) lies the first order thermodynamic perturbation theory (TPT1) of Wertheim, wherein anisotropic interactions, commonly hydrogen bonding, are treated using square-well (SW) potentials decorating a reference hard sphere [1], SW [2], Lennard-Jones [3], or Mie [4] fluid. By treating fluids in this way, the SAFT EoS maintains a close relationship with the underlying interaction potentials, which provides for molecular simulations to be run using the same force field. The results of these simulations can be used to fine-tune aspects of theory. However, the link between theory and simulations has been used more recently to parameterise coarse-grained (CG) molecular models [5].

The discontinuous geometry of a SW potential used to model the association means that these types of association models are not readily applicable to continuous molecular dynamics simulations, and as such the dynamic and transport properties of the models are difficult to evaluate. Geometrically different association potentials are not precluded within Wertheim theory and thus the substitution of a SW potential for smoothly-varying analogues can be done within the TPT1, and consequently within the SAFT framework, resulting in models more generally suitable for Molecular Dynamics (MD) simulation. These new models can then be utilised to evaluate properties conventionally inaccessible to the theory.

In this study, we present a formalism for the mapping of the SW potential onto smoothly varying alternatives, verifying the success of the procedure through a comparison of the MD simulations of the new models with Monte-Carlo (MC) simulations employing the traditional SW models and the SAFT- γ Mie [6,7] iteration of theory. The ultimate goal being to model associating molecules of interest in this way.

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Self-assembly of non-convex colloidal frames: The formation of lacuna ordered structures

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The design of macroporous structures have become increasingly important for applications in areas such as photonics, liquid phase catalysis, photocatalysis, design of ultrafast-charge battery electrodes, and drug delivery [1]. The typical approach for the fabrication of macroporous materials is using colloidal crystal templates where the interstices of the crystals are filled with a polymeric matrix [1]. This synthetic approach relies, however, on the availability of suitable templates with the desired structures. A different approach for the fabrication of macroporous materials is through the self-assembly of colloidal particles with complex non-convex shapes [2,3]. The shape of these particles is such that even in their most efficient packing attainable, they lead to the formation of highly open but ordered structures. In this work we discuss computer simulation results of systems comprising non-convex frame-like particles, such as colloidal rings (Figure 1a) and wireframe polyhedra (Figure 1b), interacting via repulsive interaction that exhibit the formation liquid crystals and crystal phases with unusual high free volumes [4-6]. We demonstrate that that the driven force towards the formation of these unusual macroporous structures is the partial interpenetration between the particles that act as *entropic bonds* that lock the particles into porous ordered microstructures. We also discuss the use of geometrical confinement to direct the formation of macroporous structures through the anchoring of the particles on the substrate [6].

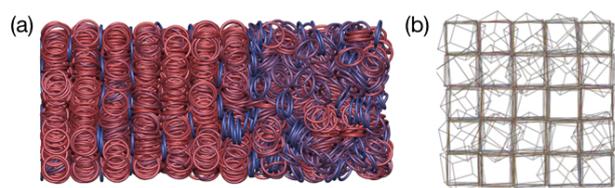


Figure 1. Formation of macroporous structures formed by (a) colloidal rings and (b) cubic wireframe particles.

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Dynamic Monte Carlos simulations of out-of-equilibrium colloidal liquid crystals.

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We have extended our Dynamic Monte Carlo (DMC) algorithm [1,2] to include the out-of-equilibrium dynamics induced by an external field. We have applied this method to colloidal dispersions of monodisperse and bidisperse rod-like particles. With our system initially in the isotropic phase we apply an external field and monitor the kinetics of the growth of nematic order along the direction of the field. We calculate the dependence of the characteristic reorientation (switching) time with the strength of the applied field. We also monitor the relaxation kinetics of the system once the external field is removed. Finally we compare our results with those achieved using traditional Brownian Dynamics (BD), and find excellent quantitative agreement.

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Simulation of surfactants and lipids in solution: bridging between scales and methods

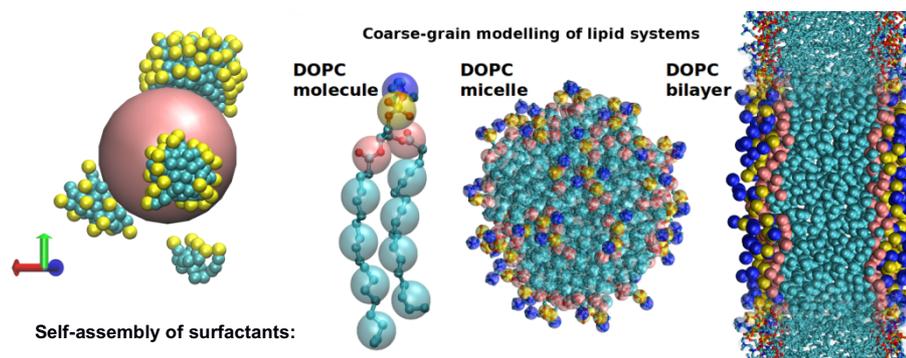
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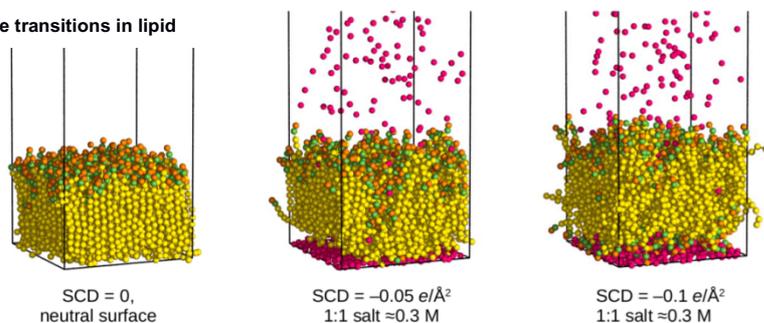
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The talk will explore the possibilities of bridging the gap between simulation of amphiphiles at different resolution and by employing a range of methodologies. In particular, case studies of well-known self-assembling surfactant and lipid systems in aqueous solution will be presented and the simulation results compared for the three major molecular simulation techniques implemented in the Daresbury software suite: Monte Carlo (DL_MONTE-2), molecular dynamics (DL_POLY), and dissipative particle dynamics (DL_MESO). The prominent case studies which have attracted great interest in both experiment and modelling, and hence can serve as reliable benchmarks for further model development (due to abundance of reported data in the literature), include:

1. Aggregation and dispersion of surfactants in solution at different concentrations;
 2. Phospholipid bilayer (membrane) properties modelled at different resolution;
 3. Interfacial behavior of amphiphiles and the related phase phenomena.
- Examples of such systems simulated on a coarse-grain level with the use of Martini (Dry) type models are given below.



Phase transitions in lipid



An accurate molecular model to predict adsorption of polar adsorbates in metal organic frameworks with open metal sites

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This work focuses on developing a fully transferable model to predict adsorption in Metal-Organic Frameworks (MOFs) with coordinatively unsaturated metal sites (CUS). MOFs are adsorbent materials of great interest within the research community due to their many desirable characteristics such as large surface areas, high porosity and high degree of tailorability. In particular, MOFs containing CUS have demonstrated highly selective adsorption by forming strong coordination bonds with specific adsorbates, which gives them great potential for challenging gas separations. The caveat of MOF variability is that this introduces an overly deep pool of potential MOFs to be assessed through purely experimental means.

As such, there is potential for computational modelling to play a pivotal role in adsorbent material design, e.g., through high-throughput screening of MOFs. However, accurate predictions of adsorption in MOFs by computer simulation require the development of realistic molecular models, which is especially difficult for CUS-containing MOFs. It has recently been demonstrated that conventional “off-the-shelf” molecular models are unable to correctly describe adsorption in CUS-containing MOFs.[1] In this work, we improve upon a recently proposed approach combining quantum mechanical (QM) calculations with classical Monte Carlo simulations. The specific interaction between gas molecules and the CUS is determined at the QM level using a density functional that accurately accounts for dispersion interactions.[2,3] The new model was first validated against ethylene adsorption in Cu-BTC and showed good agreement with experiment. Crucially, we demonstrate that the QM-derived potential parameters can also simulate polar adsorbates, such as carbon monoxide, which requires accounting for electrostatic interaction within the QM/GCMC combined method. Overall, our new model provides detailed insight into the molecular level adsorption mechanisms on MOFs with CUS, and constitutes a useful tool to design new materials for challenging separations.

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Evaluation and Optimisation of Interface Force Fields for Water on Gold Surfaces

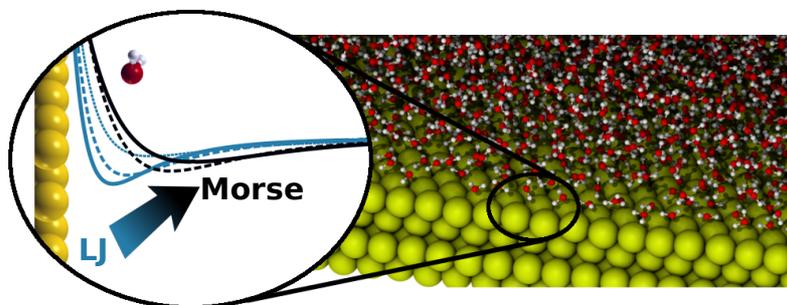
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The structure and dynamics of water at gold surfaces are important for a variety of applications, including lab on a chip and electrowetting. Classical molecular dynamics (MD) simulations are frequently used to investigate systems with water–gold interfaces, such as biomacromolecules in gold nanoparticle dispersions, but the accuracy of the simulations depends on the suitability of the force field. Density functional theory (DFT) calculations of a water molecule on gold were used as a benchmark to assess force field accuracy. It was found that Lennard-Jones potentials did not reproduce the DFT water–gold configurational energy landscape, whereas the softer Morse and Buckingham potentials allowed for a more accurate representation. MD simulations with different force fields exhibited rather different structural and dynamic properties of water on a gold surface. This emphasizes the need for experimental data and further effort on the validation of a realistic force field for water–gold interactions.



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A Novel Coarse-Grained Model to Simulate High Molecular Weight Polymers in Contact with Solid Surfaces

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The adsorption and dynamics of polymer chains in contact with solid surfaces plays an important role in many applications, especially in polymer nanocomposites, where inorganic fillers such as carbon black are embedded in the polymeric matrix with the aim of improving composite mechanical and rheological properties [1].

In order to predict the impact that the filler has on the final properties of the nanocomposites a detailed structural understanding of the polymer-filler interface is needed. It is indeed at the nanoscale that the adhesion between the polymer and the solid substrate is defined.

One of the major challenges in simulations of polymer nanocomposites is to model realistic molecular weight and surface roughness [2].

In this contribution we developed a new coarse-grained model that aims at simulating a realistic carbon black surface in contact with an entangled melt of polyisoprene. The first step involved a detailed structural understanding of the polymer in contact with graphite which is the main component of carbon black [3].

The roughness of the surface was imparted by the presence of different energy sites, where the energy values were experimentally calculated from the gas adsorption isotherms of ethene in contact with carbon black [3].

A bead-spring model for representing polymer chains in the melt state [4] was used since we demonstrated that this simple CG model is able to reproduce the structural features of polyisoprene.

Using this model we also investigate the behaviour of the adsorbed chains in the presence of small amount of low molecular weight diluents (plasticizers), which are added to modify the glass transition temperature of the polymer.

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Structure and cluster formation in size asymmetric soft electrolyte systems

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We examine the structure and thermodynamic properties of systems composed ions with rigid Gaussian charge distributions of differing widths that only interact electrostatically. These ultrasoft electrolytes [1,2] provide insight into the role of electrostatics in colloidal systems and have been observed to exhibit a liquid-vapor phase transition, as well as aggregation.

We perform molecular dynamics and Monte Carlo simulations over a broad range of ion densities and electrostatic coupling strengths for systems containing ions with different width charge distributions. Under certain conditions, these systems are observed to form large, finite sized clusters in an isotropic phase. The structure of these clusters, their charge and electrostatic potential distribution, and energetics of formation are analyzed in detail.

We compare and interpret the simulation results with a splitting field theory [3] framework that focuses on fluctuations in the electrostatic potential. Within this approach, the short wavelength and long wavelength fluctuations are treated within different approximation schemes. This theory can accurately describe the counterion mediated attractive interactions between like-charged plates [3,4] and the one-component plasma (OCP) [5] from the weak, intermediate, and strong coupling regimes. As the charge distribution of one of the ion species in the ultrasoft electrolyte broadens, the system more closely resembles the OCP, where the splitting theory is known to work well. We carefully examine the evolution of ultrasoft electrolyte as the width of one of the ions changes from being infinitely broad to smaller sizes. In particular, we present spatial correlations in the fluctuations of the electrostatic potential, decomposing them into short and long wavelength contributions. This information is used to extend the splitting theory to capture the region of cluster formation.

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Atomic characterization of the electrolyte/graphene interface

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The physics governing the adsorption of ions onto metallic or semimetallic surfaces underpins future technological developments in many areas. Specifically for graphene-based technology new emerging applications for example in energy storage or water filtration require a precise understanding of the relative stability of ions at the graphene surface and surface wetting properties. [1] However, many questions about the atomic structure of the electrolyte/graphene interface remain challenging to answer since the characterization of the interface proved to be elusive largely because the experimental techniques have not allowed direct observation of the behaviour of the ions. [2]

The driving force for the ion interfacial adsorption is a complex mix of enthalpic and entropic contributions, but molecular dynamics (MD) simulations of the electrolyte interface with both air and unstructured hydrophobic surfaces have demonstrated that it is mainly related to the stability of the ion's solvation shell and its propensity to dehydrate. [3] For a semi-metallic surface, such as graphene, the proximity of an ion induces a further effect associated with polarization of the surface itself, which strongly affects the interfacial attraction/repulsion of the ions. In order to capture these important phenomena, we recently developed a novel molecular model that can include the polarizability of all the species involved and allow the prediction of the specific relative adsorption of ions on the graphene surface for electrolyte concentrations comparable to the experimental ones. [4]

In this talk we will show that this new model predicts that in a 1 M electrolyte solutions, cations are adsorbed onto the graphene surface with a trend ($\text{Li}^+ < \text{Na}^+ < \text{K}^+$) opposite to that predicted by the gas-phase calculations and different than from that obtained from the single-ion simulations and with an energy of adsorption now validated by microscopy and electrochemistry experiments. [5] We will discuss how these findings are relevant for the graphene exfoliation process and wetting properties of the surface.

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The Effect of Halide Diffusion on the Liquid-Liquid Separation of Cobalt and Nickel Using Trihexyltetradecylphosphonium Halide Ionic Liquids

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Cobalt and nickel are ubiquitous materials in the modern world, being utilised in various applications such as batteries or high-strength machine components. These materials are often found together both in natural mineral deposits and in many applications, but separating them can be challenging. Due to their tuneable properties and limited miscibility with water, ionic liquids are ideal for liquid-liquid separations. Experiments have shown that dilute trihexyltetradecylphosphonium chloride is able to selectively extract cobalt from an acidic aqueous phase containing a mixture of Ni(II)Cl₂ and Co(II)Cl₂ [1, 2].

In this work, quantum mechanical (QM) and molecular dynamics simulations have been used to investigate the thermodynamic driving forces for this separation process. Different candidates for the solute species present were examined using a combination of QM calculations and thermodynamic modelling. The excess chemical potential of each species was then determined in both aqueous and dilute ionic liquid phase using the Bennett Acceptance Ratio method. The results showed that anionic species preferentially transferred to the ionic liquid phase and, in the presence of concentrated HCl in the aqueous phase, cobalt formed [CoCl₄]²⁻ whereas nickel formed either [NiCl(H₂O)₅]⁺ or [Ni(H₂O)₆]²⁺. Interestingly, the overall transfer process was driven by the back diffusion of chloride anions to balance the charge and, without this, the process was unfavourable. It is thought that the driving force for the transfer of chloride to the aqueous phase is that, in the ionic liquid phase, the chloride possesses an incomplete solvation shell. Thus, in the aqueous phase the chloride is thermodynamically more stable.

In order to build on this work and gain some insight in to optimising the extraction process, further calculations have been carried out replacing all chloride ions with either fluoride or bromide.

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Multicriteria optimization of pair potentials for bulk fluid properties and the vapour-liquid surface tension

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To reach the precision required by engineering applications, molecular models need to be adjusted to a variety of thermodynamic properties. This implies the presence of multiple conflicting objectives. Here, it is discussed how models can be developed which yield good compromises between quantitative agreement for bulk properties as well as the vapour-liquid surface tension.

The progress and the remaining limitations of the application of molecular modelling and simulation to vapour-liquid coexistence are analysed, concerning the accuracy of model predictions for the vapour-liquid surface tension and the potential for a further improvement by multicriteria optimization of the force-field parameters [1]. In the present work, the two-centre Lennard-Jones plus point quadrupole (2CLJQ), two-centre Lennard-Jones plus point dipole (2CLJD), and Mie-6 model classes are considered [2, 3], and a long-range correction scheme is applied to compute long-range interactions for multi-site molecular force-field models in systems with planar symmetry, combining the Janeček method with angle-averaging [4]. In this way, the vapour-liquid surface tension of the molecular models can be computed efficiently.

The multicriteria optimization problem is addressed by constructing the Pareto front, i.e., the set of rational compromises, from which models tailored to special needs can subsequently be chosen consciously by individual users or automatically, e.g., by thermodynamic property databases and simulation software. Three optimization criteria are defined by the root mean square deviation for the saturated liquid density, the saturated vapour pressure, and the vapour-liquid surface tension. An approach based on self-organizing patch plots is used to visualize the Pareto front [1]. The Pareto knee region is investigated to identify concrete model parameterizations which constitute an overall compromise between interfacial and bulk properties [2].

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Coarse-Grained Potential Derivation for Modelling the Self-Assembly of Block-Copolymers in Binary Solvents

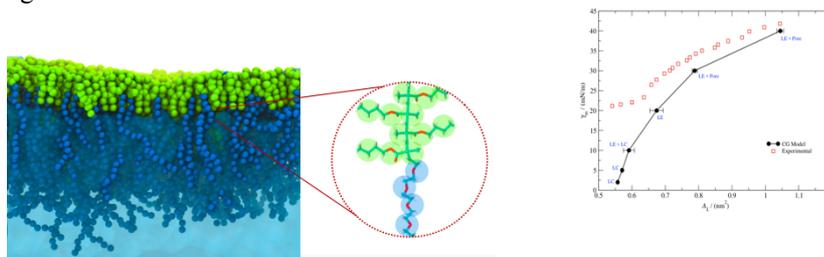
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Amphiphilic block copolymers in mixtures of selective and common solvents are able to self-assemble into colloidal size aggregates such as vesicles or more complex mesophases including polymeric nanospheres with bicontinuous internal structure (BPNs)[1], which have been recognised as excellent templates for the synthesis of nano-structured porous materials[2]. Motivated by their essential role in the preparation of complex self-assembled morphologies, we herein develop new computationally efficient coarse-grained models for studying by means of molecular dynamics simulations the phase and aggregation behaviour of methacrylate-based copolymers in mixtures of THF and water (common and selective solvents, respectively). The CG potential derivation is based on a hybrid thermodynamic-structural approach which incorporates macroscopic and atomistic-level information, more specifically, the target properties in the parameterisation are those that govern the self-association mechanism (i.e. interfacial tension, chain conformational entropy and excluded volume repulsive interactions [3]). The resulting transferable model allow for the reproduction of the behaviour of copolymers in aqueous and organic solutions, melts and interfaces.

In particular we focus on mapping phase diagrams of these copolymers in binary solvents with emphasis on the morphological transformations of self-assembled aggregates as a function of the selective/common solvent ratio, polymer concentration and chain architecture. Our ultimate aim is to contribute to the development of the computer-based design of nanostructured materials.



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Coarse-grained modelling of semicrystalline thermoplastic elastomers

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Semicrystalline thermoplastic elastomers (TPEs) consisting of segmented block copolymers made of hard and soft segments (HS/SS) are widely used in the industry. However, their structure-properties relationship and especially the link between the SS conformations and the mechanical behaviour still remains elusive [1].

In order to get a better understanding on the structure of these materials, we propose a simple coarse-grained finite-extensible nonlinear elastic (FENE) Lennard-Jones (LJ) model implemented by Molecular Dynamics simulations. We investigate the ability of the copolymer to form multiphase structure with crystalline HS so as to mimic the real structure. Two strategies have been tested to induce crystallisation. In the first, the HS are modelled as chains of tangent hard spheres as it is usually done for crystallization of soft colloidal polymers [2]. The second one is based on recent results concerning the crystallisation of a simple coarse-grained homopolymer and consists in rigidifying the chains by modifying the LJ potential [3].

Starting from an equilibrated melt, isothermal treatment leads to the formation of HS ribbons in a matrix of SS behaving as tie molecules between the crystallites. However, the structure of the crystallites highly differs depending on the method chosen to induce crystallisation. While the first one reveals a coarse crystallisation (figure a), the second one comes to well-defined ribbons with HS perpendicular to the growth axis (figure b), which is closer to the real structure. The outcome of these MD simulations can serve as input for analytical models [4].

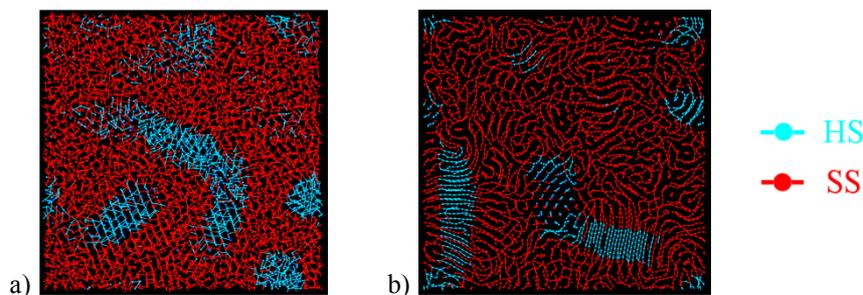


Figure: Slices of box simulation: ribbon structure for first a) and second b) methods.

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Coarse-graining polymer semiconductors

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Conjugated polymers are organic materials displaying a semiconducting behaviour due to their electronic band structure and, more specifically, their typically low energy band gap. Some studies on charge transport have reported mobilities as high as $\mu_h \sim 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for these materials [1], making them as efficient as some inorganic semiconductors such as amorphous silicon [2], and providing the possibility of using them in electronic and photovoltaic devices. In addition to their specific semiconducting and optoelectronic behaviour [3], other properties such as flexibility, solubility, self-assembly and cheap manufacturing, make these materials of interest for a number of industrial applications such as organic photovoltaic cells, field-effect transistor and flexible displays. As far as their structure is concerned, previous studies have shown that structural properties of organic polymers can affect their electronic behaviour [4]. However, although a correlation between high crystalline order and electronic efficiency has been suggested by some studies [5], more recent results on polymers with no crystalline order like those containing the dyketopyrrolopyrrole (DPP) group have challenged this view [6]. In this work, we aim to design a coarse-grained model to study the structure of organic polymers containing DPP groups in order to use these results in the future determination of the electronic structure.

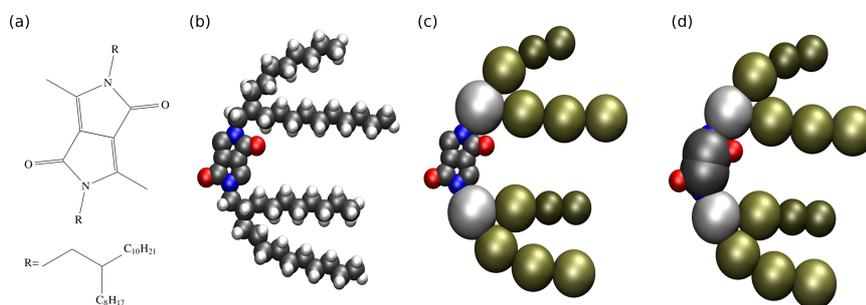


Figure 1. Dyketopyrrolopyrrole group as shown by (a) the chemical structure, (b) an all-atomistic model, (c) a hybrid all-atomistic/coarse-grained model, and (d) a fully coarse-grained model.

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Molecular Topology Of Semicrystalline Polymers: Simulation Of Mono And Polydisperse Systems

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Semicrystalline polymers are used in a broad range of applications. It is largely agreed [1, 2] that the mechanical properties of semicrystalline polymers are mainly governed by the presence of molecular connections between the crystallites, namely, chain entanglements and tie molecules (TMs). However, due to the experimental limitation, no quantitative data for the TM concentration has been reported [3]. It is known that both crystallization conditions as well as polydispersity strongly influence the concentration of tie molecules, but no direct experimental observation is available. Molecular Dynamics (MD) simulation is an excellent tool to overcome the difficulties of experimental measurements and can be used to study the non-equilibrium process of crystallization at the nanoscale. A great deal of efforts have been made both experimentally and theoretically to explore the crystallization mechanism of polymers, however, very few of which involved polydispersity [4, 5]. As a matter of fact, the occurrence of polydisperse aggregates is much more common than the existence of pure compounds in a broad spectrum of natural products.

In this work, we performed massive MD simulation of seven bidisperse polymer systems with various PDI (polydispersity index), which consist of the same total number of beads (i.e. 100,000), using the algorithm of radical-like polymerization (RLP) [6]. We used a coarse-grained polymer model where polymer chains consist of “beads” representing few structural units, around five to ten carbon groups. The model is based on two potentials: Intra-chain interactions of bonded beads are given by a Finite-Extensible Non-linear Elastic (FENE) potential, all other interactions are modelled by a simple Lennard-Jones (LJ) potential. Isothermal crystallization has been employed, and the mechanism of crystallization has been investigated. We developed a tool to access quantitative analysis of molecular topology.

It has been found that the PDI influences the nucleation and growth of crystallites, and then would determine the rate of crystallization and crystallinity. Moreover, the molecular topology also exhibits a dependence on the composition of the disperse systems. Figure 1 shows a snap shot of one of the systems, which looks very much like lamellae.

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The elixir phase of chain molecules

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A phase of matter is a familiar notion for inanimate physical matter. The nature of a phase of matter transcends the microscopic material properties. For example, materials in the liquid phase have certain common properties independent of the chemistry of the constituents: liquids take the shape of the container; they flow; and they can be poured – alcohol, oil and water as well as a Lennard-Jones computer model exhibit similar behavior when poised in the liquid phase. Here we identify a hitherto unstudied ‘phase’ of matter, the elixir phase, in a simple model of relatively short polymers whose backbone has the correct local cylindrical symmetry induced by the tangent to the chain. The elixir phase appears on breaking the cylindrical symmetry by adding side spheres along the negative normal direction, as in proteins. This phase, nestled between other phases, has multiple ground states made up of building blocks of helices and almost planar sheets akin to protein native folds. We discuss the similarities of this ‘phase’ of a finite size system to the liquid crystal and spin glass phases. Our findings are relevant for understanding proteins; the creation of novel bio-inspired nano-machines; and also may have implications for life elsewhere in the cosmos.

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New understanding of collective modes and thermodynamics of the liquid and supercritical states

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A theory of liquids liquid-glass transition requires understanding most basic thermodynamic properties of the liquid state such as energy and heat capacity. This has turned out to be a long-standing problem in physics [1]. Landau&Lifshitz textbook states that no general formulas can be derived for liquid thermodynamic functions because the interactions are both strong and system-specific. Phrased differently, liquids have no small parameter.

Recent experimental and theoretical results open a new way to understand liquid thermodynamics on the basis of collective modes (phonons) as is done in the solid state theory. There are important differences between phonons in solids and liquids, and we have recently started to understand and quantify this difference. I will review collective modes in liquids including high-frequency solid-like transverse modes and will discuss how a gap in the reciprocal space emerges and develops in their spectrum [2]. This reduces the number of phonons with temperature, consistent with the experimental decrease of constant-volume specific heat with temperature [1]. I will discuss the implication of the above theory for fundamental understanding of liquids. I will also mention how this picture can be extended above the critical point where the recently proposed Frenkel line on the phase diagram separates liquid-like and gas-like states of supercritical dynamics [1,3-5].

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Reorganization energy upon charging a single molecule on an insulator measured by atomic force microscopy

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We have recently presented a novel approach that allows for direct measurements of the reorganization energy of single molecules adsorbed on an insulating film supported by a metal substrate [1]. The reorganization energy, defined as the energy released from the geometry distortion upon changes in the charge state, is a key fundamental quantity in the description of electron transfer [2] and, therefore, it plays a decisive role in many fundamental processes at the nano-scale level [3,4].

In this presentation, we will focus in the theoretical aspects for the computation of reorganization energies via Density Functional Theory (DFT). We show that the well-known limitations to describe charge transfer phenomena at surfaces can be circumvented if we use the classical perfect conductor approximation for the metal substrate and treat the insulating film and the adsorbed molecule fully within the framework of DFT [5]. Results for the redox reaction of naphthalocyanine (NPc) molecules on multilayered NaCl films demonstrate the capability of this computational method not only to provide fundamental insight of the relaxation mechanisms for different molecular charge states, but also to guide experimentalists towards the ultimate goal of tuneable single-electron intermolecular transport.

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Hierarchical Self-Assembly of Triblock Patchy Particles into a Tetrastack Lattice

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The photonic properties of colloidal crystals have attracted a great deal of attention for their applications, arising largely from band gaps restricting propagation of photons of certain frequencies within the crystals [1]. In this context, diamond and tetrastack lattices are especially sought-after [2,3]. Here we demonstrate the self-assembly of triblock patchy particles into a tetrastack lattice *via* tetrahedral clusters, as shown in Figure 1. Our designer patchy particles are spherical in shape, having two circular attractive patches, A and B, at the poles across a charged band in the middle. Certain variants of these particles resemble closely those synthesised recently [4], and are shown to undergo hierarchical self-assembly into a cubic diamond lattice [5]. Using a variety of computational techniques, namely a global optimisation technique, virtual-move Monte Carlo method and Brownian Dynamics simulation, we show that a hierarchical self-assembly pathway facilitates the formation of a tetrastack lattice, by negotiating “kinetic traps” more effectively. We present a detailed analysis of such a pathway.

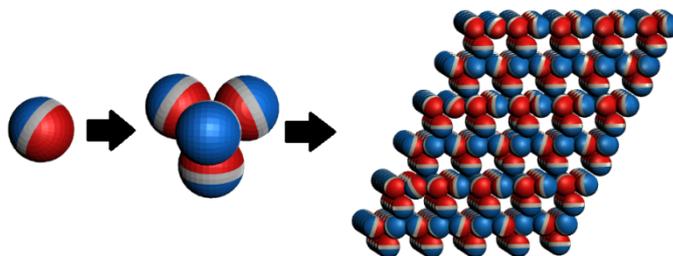


Figure 1: Hierarchical self-assembly of triblock patchy particles into a tetrastack lattice *via* tetrahedral clusters.

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POSTERS

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Computational modelling of the effect of surfaces on polyvinylidene difluoride
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Rejection-free Markov-chain Monte Carlo in liquid water

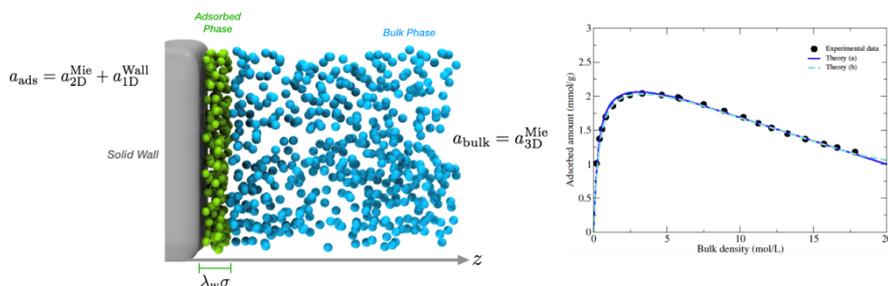
Molecular Thermodynamics of Adsorption Using a 2D-SAFT-VR-Mie Approach

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We present a Molecular-Thermodynamic theory to describe adsorption isotherms of complex fluids based on the 2D SAFT-VR approach [1] applied to the Mie potential. Adsorption is represented in terms of two different subsystems, the bulk and adsorbed phases, each one described in terms of particles interacting via a Mie potential. Adsorbed particles are modelled through a SW surface-particle pair interaction. The 2D theory gives an analytical expression for the first-order perturbation term of the adsorbed fluid, which is shown to perform well in comparison with computer-simulation results for different Mie fluids. The thermodynamic properties of the bulk fluid are obtained with the SAFT-VR-Mie approach [2]. The combined 2D-3D theory is applied to the description of adsorption isotherms of carbon dioxide on dry coal.



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Towards the coarse-grained modelling of dimethacrylate-based biomaterials

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Dimethacrylate-based biomaterials became a prominent class of filling materials in dentistry and surgery. They offer a comparably easy processability and superior aesthetic properties in contrast to conventional materials. *In vivo* polymerisation, initiated via light irradiation, requires a reduction of polymerisation shrinkage to eliminate the risk of secondary caries at the tooth-compound interface due to formation of small cracks. This can be accomplished either by addition of filler particles or tuning of the steric hindrance of the monomers.

In molecular dynamics of polymers, large simulation cells limit the applicable time scale. In addition, equilibration time increases with the degree of polymerisation. To overcome this limitation in polymer dynamics so-called coarse-grained (CG) models are used, where multiple atoms are combined to form superatoms (so-called beads), reducing the degrees of freedom and thus the computational effort (cf. Figure 1). To parameterise these simplified models, the iterative Boltzmann inversion approach is applied, where the initial parameters are generated by inverting target distributions of local structures. [1] Subsequent optimisation is performed to match distributions of the CG model to those of the atomistic model. As a model system, urethane dimethacrylate (UDMA) was chosen, which is one of the most commonly used polymer resins in dentistry nowadays.

Utilising the generated parameters, we aim for elucidation of the structure formation during polymerisation with respect to the shrinkage. In future the focus will also be on polymer mixtures as well as cavity formation, while the latter will require a suitable backmapping scheme. [2]

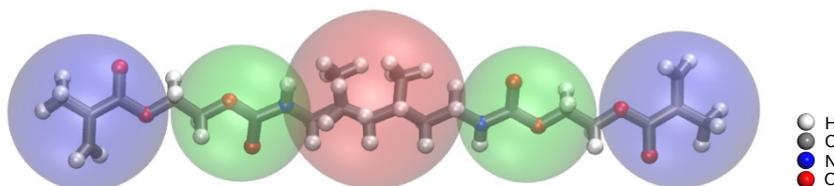


Fig. 1: Structure of a UDMA molecule in atomistic and CG resolution, colours of the large spheres indicate the different bead-types.

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Computational adaptation of metal-organic frameworks for highly selective sensor materials

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Most sensors, in everyday life as well as in science, show good sensitivity, but disregard selectivity. One way to generate a sensor material that offers high selectivity is the utilization of metal-organic framework (MOFs).^[1] In this work the Zr-based MOF UiO-66 is used as a model system.^[2] It consists of an inorganic building unit and terephthalate as organic linker.

MOFs can be designed for desired applications by a sophisticated selection of synthesis parameters. This can be done, for example, by varying the linker molecule. In our study, this is done first by functionalising the linker molecule to examine the change of the properties.

By usage of molecular modelling methods, a porous solid containing a cavity specifically suited for the adsorption of the small ethanolamine molecules, can be identified and preferred sorption sites can be simulated. The calculated interaction energy correlates supposedly with the selectivity of the adsorption. By maximizing the amount of this energy, a highly selective sensor material might be predicted.

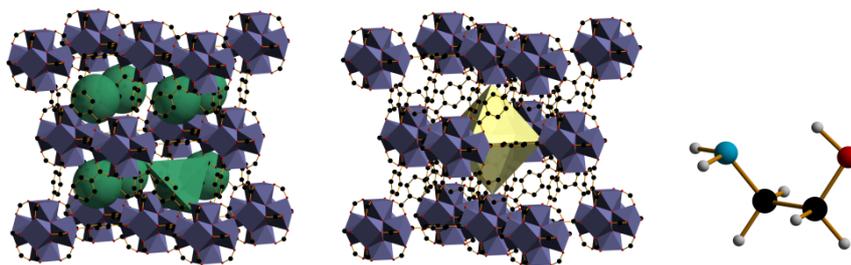


Figure 1: Construction principle of UiO-66 with indicated pore (tetrahedrally shaped pore left, octahedrally shaped pore middle) and ball and stick model of ethanolamine (right).

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Modelling the kinetics of silica polymerization

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Templated synthesis refers to the technique where the synthesis process can be designed according to specific applications. This is particularly relevant to periodic porous materials (ppm) which have various industrial applications depending on their diverse functionalisations.

Here, we are interested in a specific member of the ppm - bicontinuous porous materials [1] which are formed as a result of self-assembly of amphiphilic copolymers. This self-assembly is affected by different factors, such as, the presence of silicates, solvent, cosolvent, pH. In this work, we investigate how the presence of silica affect the self-assembly of these block copolymers. We study the mechanism of self-assembly [2] and the interactions between polymer and silicates.

We employ molecular dynamics simulations of coarse-grained models of amphiphilic diblock copolymer PEO-b-PBMA with silicates in water and cosolvent system, where PEO represents the hydrophilic block and PBMA, the hydrophobic block.

The existent coarse-grained silica model [3] was tested but it could not reproduce the expected experimental behaviour. Hence, a new silica coarse-grained model is being developed by comparing the solvation free energy of monosilicic acid in solvent with the values obtained from DFT calculations. The details of the model development are presented here.

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Modelling of Electrowetting and Other Interfacial Properties of Liquids on Graphene

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The project focus is on using molecular simulations to analyse interfacial properties of electrolyte solutions in contact with graphene flakes.

In particular it is of interest the variation of contact angle of micro- and nano-sized droplets with the application of an electric field: a phenomenon called electrowetting. The initial stages involved the study of the wetting properties of water on graphene, which yield a contact angle of $67^\circ \pm 2^\circ$, which is in agreement with experimental values¹. Concurrently, aqueous salt solutions (KCl, LiCl, NaCl all at 1M) in contact with graphene were studied in bulk systems and in droplet configurations. This involved an analysis of the double layer created on graphene and the use of DLVO theory to model the dispersion of graphene flakes in these solutions. Novel parameters^[1] were used to appropriately model the polarizability of water and graphene. During the project the simulation results are compared with concurrent experiments^[2,3] to provide the opportunity to confirm the validity of the models created.

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Predicting phase separation in polymer blends that contain branched molecules

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High performance polymer composites containing a blend of thermosets and thermoplastics are becoming widely used as a replacement for metals in a range of industries, particularly in aerospace, where weight reduction drastically increases fuel efficiency. Such blends phase separate during the curing process of the thermosetting network, and the final morphology of the material determines its mechanical properties. Network-rich regions provide strength, and thermoplastic-rich regions allow energy dispersion to prevent crack propagation. Therefore, it is important to understand the relationship between phase separation and structure.

The Flory-Huggins model is usually used to predict the occurrence of phase separation via free energy calculations, but it does not adequately describe blends of branched thermosets and linear thermoplastics. As a mean field theory, it ignores the local conditions of the system, and therefore overlooks the conformational restrictions of the branched component. It also neglects the interplay between entropy and energy, when in reality energetic interactions greatly impact on the conformation of the polymer and therefore affect the entropy.

Our work uses simulation to improve free energy calculation for branched polymers. We describe the polymers as self-avoiding walks on a lattice, as in the Flory-Huggins model. This time, however, the exact positions and interactions of other polymer segments are taken into account, meaning that both the local conditions and the interplay between energy and entropy are considered. This is an extension of Meirovitch's 'Hypothetical Scanning' and 'Hypothetical Scanning Monte Carlo' methods [1]. The previous work considered the entropy of linear polymers, and we have improved the model to cover free energy and branched polymers.

Currently we are using Monte Carlo methods to directly simulate systems containing various proportions of branched and linear polymer, and various configurations of branched polymer. By comparing the radial distribution functions of the different components, we are able to gain insight into the morphology and how the phase separation varies as a function of cross-linking extent.

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Structure and Dynamics of Li-rich $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (LATP), where $0.3 < x < 0.5$: A Combined Computational and Experimental Study

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The importance of understanding Li ion diffusion mechanisms in ceramic materials is key when developing solid state Li batteries.

LISICON materials, such as LATP, have been studied to include nudged elastic band calculations with DFT [1], diffraction experiments [2] and molecular dynamics calculations [3].

In this work, we report molecular dynamics simulations on a much larger scale at a range of temperatures, over nanosecond timescales, with activation barriers of 0.3 eV in accordance with experimental data. The elucidated migration pathway suggests a vacancy migration involving M1 (6b) and M2 (18e) sites suggesting that the M'1 (6a) site is only a metastable site and disappears at higher temperatures. Furthermore, the Al doped dynamic simulations suggest Li trapping.

Acknowledgements

The authors acknowledge the use of the Archer national supercomputer service, and the Hydra machine at Loughborough university.

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The Effect of Atomic Point Charges on Adsorption Isotherms of Metal Organic Frameworks

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Metal-organic frameworks (MOFs) are crystalline and porous materials consisting of coordination bonds between transition-metal cations and organic ligands. [1] The intrinsic ability of MOFs to adsorb molecular fluids is one of their most studied and promising properties. MOFs exhibit many characteristic physical attributes including high pore volume, large surface area and well-defined crystalline structure which make them suitable for adsorption-based applications such as gas storage, purification, sensing devices and drug delivery. [2] The interactions between MOFs and adsorbates have been increasingly predicted and studied by computer simulations, particularly by Grand-Canonical Monte Carlo (GCMC), as this method enables comparing the results with experimental data and also provides a degree of molecular level detail that is difficult to obtain in experiments. The assignment of atomic point charges to each atom of the framework is essential for modelling Coulombic interactions between atoms in the MOF and between the MOF and the adsorbate. Such interactions are important in adsorption of polar gases like water or carbon dioxide. The aim of this work is to investigate the effect of varying atomic point charges on adsorption isotherm predictions, identify the underlying trends, and based on this knowledge to improve existing models in order to increase the accuracy of gas adsorption prediction in MOFs. Multiple methods have been developed to assign atomic point charges in MOFs. [3] Adsorption isotherms for CO₂ and water in several MOFs were generated with GCMC by using point charge sets obtained by methods including ChelpG, DDEC and REPEAT, among others. [4, 5, 6] We carried out this work for 5 widely studied MOFs; CuBTC, IRMOF-1, UiO-66, MIL-47 and CoMOF-74. We included both MOFs with and without open metal sites (OMS), specifically to investigate whether this property affects the predicted adsorption behaviour. [7] Our results show that MOFs without OMS or polar functional groups show very little sensitivity to the nature of the point charges. In contrast, adsorption in MOFs that contain OMS is much more sensitive to the point charge values, with particularly large variability being observed for water adsorption in such MOFs. This suggests that particular care must be taken when simulating adsorption of polar molecules in MOFs with open metal sites to ensure that accurate results are obtained.

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Rheological consequences of the addition of Janus nanodimers to a lamellar phase

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Polymer nanocomposites (PNCs) are materials made of a polymer matrix incorporating fillers with at least one of their dimensions in the nanometric scale. These nanofillers can significantly modify the mechanical, thermal and rheological properties of the matrix, making these materials of great interest for industry. In particular, lamellar systems are of strategic importance due to their applicability as coats and thin films [1,2]. In this work, we aim to study the possibility of precisely controlling the viscosity of a lamellar phase of di-block copolymers (Fig. 1) by loading it with a fixed volume fraction of Janus nanodimers (JNDs), which are particles with two chemically different spherical moieties (Fig. 2). To this end, a number of systems containing JNDs at different nanofiller-matrix interactions have been studied with two different computational approaches, namely Molecular Dynamics and Dissipative Particle Dynamics simulations.

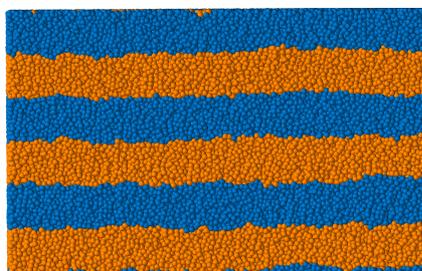


Figure 1: Lamellar phase of coarse-grained diblock copolymer containing no JNDs.

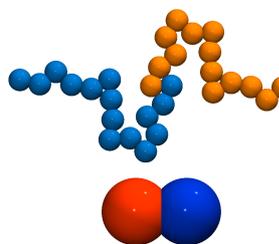


Figure 2: Coarse-grained model of the polymer (top) and JND (bottom).

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Development of the ReaxFF Reactive Force-Field Description of Gold Oxides

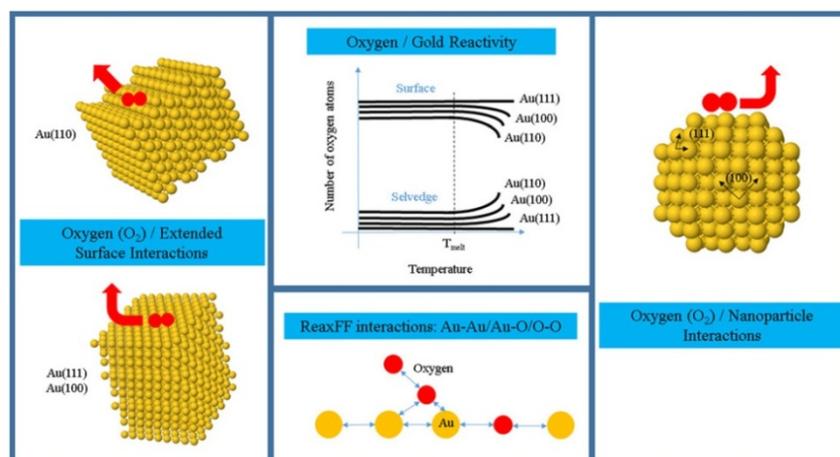
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A new reactive force-field (ReaxFF) interatomic potential has been derived for the Au/O system [1]. The potential has been trained across an extensive set of bulk and surface Au and Au/O systems, and describes both the bulk systems and gas-surface interfaces. The potential is shown to be able to simulate the interactions between oxygen molecules and the low-index Au(111), missing-, pairing-row and trench reconstructed Au(110), and the added-row Au(100) facets. Both relativistic and non-relativistic pseudo-potentials were used to generate distinct training sets, and the quantitative differences between the training sets as well as the quantitative and qualitative differences between the predictions of the two derived force-fields are discussed.

The potential has also been shown to predict, in turn, surface and bulk oxide phase formation using both molecular dynamics (MD) and Grand Canonical Monte Carlo (GCMC) simulations. The generic behaviour of the potential is discussed by comparing ReaxFF predictions for the Au/O system presented in this work in the light of recent developments within the field of gold-catalysed surface processes and the behaviour of transition metal surfaces under strain [2].



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Interactions of terpenes in water and aqueous alcohol solutions

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Terpenes are primary components of essential oils produced by some plants and insects. They are natural antimicrobial agents and also known for their ability to promote penetration of drugs through biological membranes [1]. From experimental observations, terpenes are insoluble in water but soluble in alcohol solutions. Understanding the interactions between terpenes and organic solvents at the molecular level is of key importance for future research in drug delivery.

Two different computational methods are used in this study: atomistic molecular dynamics (MD) using OPLS-AA force-field and Dissipative Particle Dynamics (DPD) [2,3]. The DPD model for terpenes is developed in the framework of this project and validated by MD simulations.

This study is focused on the two terpenes, menthol and limonene, and two alcohols, ethanol and isopropyl alcohol. The results show that the solubility of the terpenes strongly depends on the system size and concentration. In water, both terpenes self-assembled into a clusters but the aggregation is found to be stronger in the case of (more hydrophobic) limonene. It was also found that in the case of limonene a more concentrated alcohol solutions are required to dissolve the aggregates. Evaluation of the free energy of interaction between these terpenes molecules in water and alcohol solution will also be presented.

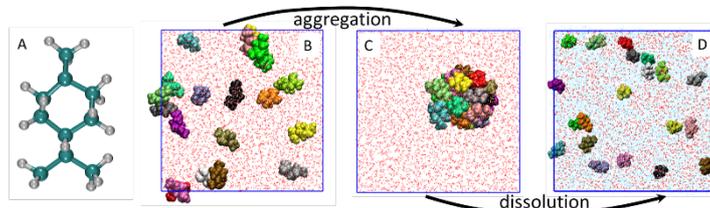


Figure 1. (A) Limonene; (B) starting configuration of limonene in water, (C) self-assembly of limonene and (D) dissolution of limonene aggregate with ethanol.

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Modeling the Effect of Polymer Chain Stiffness on the Behavior of Polymer Nanocomposites

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Due to their central role in industrial formulations spanning from food packaging to smart coatings, polymer nanocomposites have been the object of a remarkable attention over the last two decades. Incorporating nanoparticles (NPs) to a polymer matrix modifies the conformation and mobility of the polymer chains at the NP-polymer interface and can potentially provide materials with enhanced properties as compared to pristine polymers. To this end, it is crucial to predict and control the ability of NPs to diffuse and achieve a good dispersion in the polymer matrix. Understanding how to control the NPs' dispersion is a challenging task controlled by the delicate balance between enthalpic and entropic contributions, such as NP-polymer interaction, NP size and shape, and polymer chain conformation.

By performing Molecular Dynamics (MD) simulations, we investigate the effect of polymer chains' stiffness on the mobility of spherical NPs that establish weak or strong interactions with the polymer. Our results show a sound dependence of the NPs' diffusivity on the long-range order of the polymer melt, which undergoes an isotropic-to-nematic phase transition upon increasing chain stiffness. This phase transition induces a dynamical anisotropy in the nematic phase, with the NPs preferentially diffusing along the nematic director rather than in the directions perpendicular to it.

Not only does this tendency determine the NPs' mobility and degree of dispersion in the polymer matrix, but it also influences the resistance to flow of the polymer nanocomposite when a shear is applied. In particular, to assess the role of the chains' conformation on the macroscopic response of our model PNC, we employ reverse non-equilibrium MD to calculate the zero-shear viscosity in both the isotropic and nematic phases, and unveil a plasticizing effect at increasing chain stiffness when the shear is applied along the nematic axis.

Calculating the scission free energy of worm-like micelles using dissipative particle dynamics simulations

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Worm-like micelles (WLM) are long, self-assembled structures formed by surfactants at high concentrations. Due to the threadlike structure these micelles share many features in common with polymeric systems with an additional relaxation process of micelle breaking/forming. Thus, they are often thought of as ‘living’ polymers. These WLM systems demonstrate complex rheological behaviour that is heavily dependent on many factors, including the surfactant composition and temperature. In addition, the salt concentration is particularly important for ionic surfactants that are common in industrial applications, such as oil recovery, detergents and personal care products.

There is a well-established theory developed by Cates and co-workers [1] that relates the microscale structure to the macroscopic properties of these complex fluids. One key parameter is the scission free energy (E_{sci}), that is, the change in free energy upon breaking a cylindrical micelle into two hemispherical caps (see Figure 1). This can be directly related to the mean micelle length and mean aggregation number.

Here we use Dissipative Particle Dynamics simulations (DPD) to calculate the scission free energy. We employ a simulation protocol developed by Wang *et al* [2]. Briefly, we simulate an infinitely long micelle composed of SLES and CAPB surfactants and calculate the scission free energy using umbrella sampling and the weighted histogram analysis method (WHAM). The reaction coordinate chosen is the number of tail beads in a denoted scission region which has been shown to give a robust calculation of the scission free energy. From these simulations, we are investigating the how the DPD model employed and salt concentration affect the scission free energy.

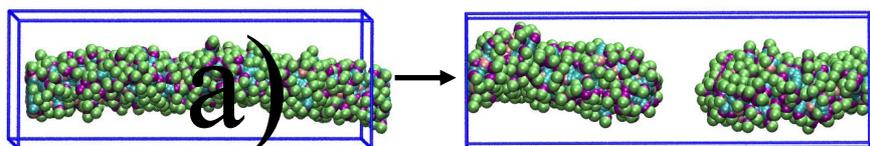


Figure 2 The scission free energy (E_{sci}) is the change in energy from breaking a wormlike micelle (a) into two hemispherical caps (b).

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Assessing coarse-grained models for the self-assembly of block copolymers

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Block copolymers find applications in many fields, including adhesives, plastics, drug delivery and photonics. Several of these rely on the ability of block copolymers to self-assemble into ordered mesophases in solution. One such application of particular interest to our research group is their use as templates in the synthesis of porous silica materials, such as SBA-15 [1]. Because of their highly ordered pores, high surface areas, high functionality and low cost, mesoporous silicas have been of great interest for an increasing variety of applications and research. Understanding the synthesis mechanism for this class of materials, however, models that can predict how block copolymer templates self-assemble in aqueous solution. This study aims to produce an accurate coarse-grained (CG) model of self-assembling block copolymers, including those used in the synthesis of SBA-15 mesoporous silica (i.e., Pluronic surfactants). Such a model will enable us to probe the large time and length scales that are needed to describe the mesostructure formation from solution, thus clarifying the mechanisms by which these materials are formed.

Our approach is based on the established Martini CG force field [2], which has been previously applied to model these systems [3,4]. We have found that existing models are unable to accurately describe micelle aggregation self-assembly of Pluronic surfactants, although they are designed to match single-chain properties. We have thus systematically tested the existing MARTINI parameters for the alkane solvent basis of these systems against experimental values such as Gibbs free energies of solvation, enthalpies of vaporisation, self-diffusion coefficients, and radii of gyration. This has led to improved mapping schemes and adjusted parameters for solvents, and for early polymer simulation in those solvents. In the future, we will test these improved parameters against the phase diagram of more elaborate block copolymer surfactants, in order to effectively replicate the micelle aggregation and formation processes.

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Bridging the gap between *in-silico* and experimental chemistry – a close view into the formulation world

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The chemical industry manufactures a wide variety of complex formulations that exhibit a range of soft matter phenomena depending on the specific chemical contributions. For example, liquid based surfactants can display various micellar states (e.g. isotropic, hexagonal, lamellar, bicontinuous), phase separations or sublimation depending on concentration. The microstructure of the liquid significantly impacts the performances of the final product. Quantitatively comparable models demonstrating real-like aggregative behaviour are the key to successfully employing *in silico* techniques within the R&D process.

Our work focuses on the development of simulation and analytical methods for formulation science. We present a top-down dissipative particle dynamics (DPD) parametrisation protocol [1] which utilises experimental densities and partition coefficients (logP) to determine the interactions between beads of different nature. Our parameter set was validated against a variety of different liquid molecules, showing excellent agreement between experimental and simulated logP.

The parameter set was then used to investigate the aggregative behaviour of families of industrially relevant surfactants, including non-ionic (NI) and sulfonated surfactants (SDS and SLES) [2].

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Phase behaviour of self-assembled monolayers controlled by tuning physisorbed and chemisorbed states

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The self-assembly of molecules on surfaces into 2D structures is important for the bottom-up fabrication of functional nanomaterials, and the self-assembled structure depends on the interplay between molecule-molecule interactions and molecule-surface interactions. Halogenated benzene derivatives on platinum have been shown to have two distinct adsorption states: a physisorbed state and a chemisorbed state [1], and the interplay between the two can be expected to have a profound effect on the self-assembly and phase behaviour of these systems. We developed a lattice model that explicitly includes both adsorption states, with representative interactions parameterised using density functional theory calculations. This model was used in Monte Carlo simulations to investigate pattern formation of hexahalogenated benzene molecules on the platinum surface [2,3]. Molecules that prefer the physisorbed state were found to self-assemble with ease, depending on the interactions between physisorbed molecules. In contrast, molecules that preferentially chemisorb tend to get arrested in disordered phases. However, changing the interactions between chemisorbed and physisorbed molecules affects the phase behaviour. We propose functionalising molecules in order to tune their adsorption states, as an innovative way to control monolayer structure, leading to a promising avenue for directed assembly of novel 2D structures.

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Dissolution of Surfactant Lamellar Phases

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Formulated products are everywhere we look, from toothpaste to motor oil and from salad dressings to make up, they are an essential part of everyday life. As different as all these products seem, they all contain mixtures of surfactants, oil, water, particles, and even air prepared in such a way to produce the desired properties.

Surfactants are used to stabilise emulsions and foams, add lubricacy to surfaces, induce deterging properties, and act as antibacterial agents along with other applications. Therefore, surfactant dissolution is an important part of formulated product preparation as well as formulated product use.

In this work we are interested in understanding the effect on the dissolution process of the strength of the solvophobic tail of lamellar liquid crystals. We start by modelling the dissolution process of a surfactant/solvent lamellar liquid crystal with dissipative particle dynamics, as shown in Figure 1. The dissolution of this system is then compared with modified solvophobic tail parameters.

The dissolution rate is tracked by examining the variation of the surface tension and the variation of the local concentration with time in the simulations.

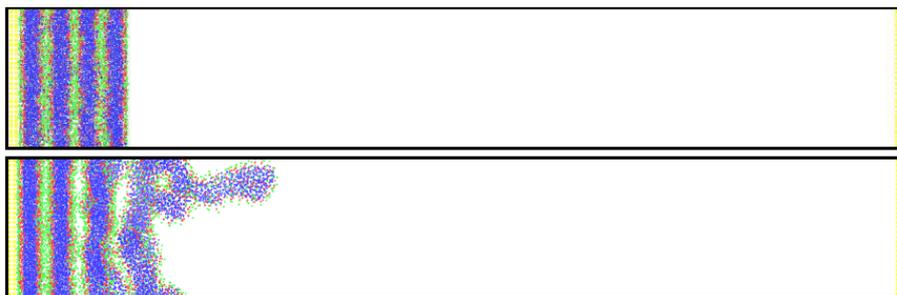


Figure 1. Initial dissolution steps of a lamellar phase dissolving in a box of water (water beads not shown for clarity).

From single-chain nanoparticles to gels: Computational study of the competition between intra- and inter-molecular bonding of polymers in solution

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By means of molecular dynamics simulation, we investigate the phase behaviour of solutions of functionalized polymers with the ability to form both intra- and inter-molecular bonds. Under highly dilute conditions, these polymers form soft nano-objects - so-called single-chain nanoparticles - of molecular size between 5 and 20 nm, resulting from the purely intra-molecular cross-linking of the reactive functional groups. Upon increasing the density of the system, the competition between intra- and inter-molecular bonds leads to the formation of physical gels. We systematically characterize the formation of single-chain nanoparticles, clusters, and percolating networks as a function of concentration, bond strength and polymer architecture. We find that intra-molecular bond formation is favoured over a wide range of densities, which leads to similarities with low-valence colloidal gels. Aside from the simulations, we try to model the system in a way such that it can be treated by Wertheim theory. To this end, we treat the reactive functional groups as belonging to either of two distinct species A and B , depending on whether they are intra- or inter-molecularly bonded. As such, we are able to assign a fixed valence to the interacting species and we can explicitly write down the free energy of the system as a function of density and fraction of species A , x . Minimizing this free energy with respect to x , we hope to be able to predict the phase diagram of the semidilute solution.

Computational modelling of the effect of surfaces on polyvinylidenedifluoride

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In modern computer technology the realisation of flexible electronics materials, has great potential in developing new flexible electronics devices, such as energy harvester and wearable computers for space foundation applications. As flexible materials suitable for electronics devices is very limited, the choice of which material to use is limited to the few which possesses all the relevant properties needed in computer technology such as (*e.g.* Coercive field, Curie Temperature and spontaneous polarisation).

The physical properties of polyvinylidenedifluoride (PVDF) is a highly promising semi-crystalline polymer, which has the properties needed for being applied in modern electronics, but still presents crystalline issues in preparing high-quality ferroelectric samples. PVDF has been approached in a computational study using density functional theory (DFT) and molecular dynamics (MD) to determine the fundamental properties of the ground states of PVDF polymorphs and to predict the behaviour of PVDF chains in contact with surfaces. Surfaces are indeed able to affect properties of materials thank to the special condition verified at the interface surface/polymer interaction. Confinement and electrostatics effects as properties of modelled graphene sheets have been investigated for the ability of changing PVDF chains dispositions improving crystal phase formation.

Results of the computational investigation verified the importance of electrostatics charges in driving PVDF chains towards a linear and ordered disposition on the surface sheet, with increase crystallinity grade.

Rejection-free Markov-chain Monte Carlo in liquid water

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Markov-chain Monte Carlo methods are used throughout the statistical sciences. The majority of algorithms are (time) reversible and therefore satisfy the detailed-balance condition, which ensure convergence to the correct probability distribution. However, reversible Markov processes often lead to slow, diffusive behaviour on the configuration space. The event-chain Monte Carlo (ECMC) algorithm [1] circumvents this by augmenting the configuration space with a lifting variable [2] to connect two nonreversible Markov sub-processes that strictly evolve in opposite directions on the original configuration space. This is the case for two-particle interactions in one spatial dimension, but generalizes to multiple particles and interactions in higher dimensions. Nonreversibility effectively drives the system through the original configuration space, rather than leaving it to meander through diffusively, resulting in shorter ECMC mixing times than those of reversible Markov processes [3]. This lifted Markov process is formally rejection free and satisfies skew detailed balance on the augmented space, the latter of which ensures convergence to the correct distribution.

In this presentation, I will introduce nonreversible Markov processes and skew detailed balance, before outlining rejection-free ECMC. I will then present the application to all-atom models of liquid water [4]. This uses the locally charge-neutral property of water molecules to reduce the Coulomb scaling to $O[N \ln(N)]$ (N the number of water molecules) with neither an interpolating mesh, nor a thermostat, nor spatial cut-offs on the lengthscale of the interaction potentials.

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