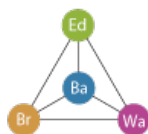


Soft Materials and Slow Dynamics: Challenges for Mathematical and Computational Modelling

Bath Royal Literary and Scientific Institution
1-2 November 2010



Organizers:
Rob Jack and Nigel Wilding
University of Bath



**Mathematical Challenges
of Molecular Dynamics**
A Mathematical-Chemical Network



IOP Institute of Physics

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Engineering and Physical Sciences
Research Council

Workshop Programme

Monday 1st November

09.00-09.30	Arrival.
09.30-09.40	Welcome and introductory remarks.
09.40-10.30	P. Camp: Adsorption and tribology of molecules on and between surfaces.
10.30-11:00	A. Likhtman: Multiscale modelling of entangled polymers.
11.00-11.20	Refreshments
11.20-12.10	C. Likos: Glass transition in polymer mixtures.
12.10-13.00	J. Garrahan: Molecular random tilings.
13.00-14.10	Buffet Lunch
14.10-15.00	P. Sollich: Crystalline phases of polydisperse spheres.
15.00-15.30	D. Ashton: Exploring particle size and shape effects in highly size-asymmetric binary mixtures.
15.30-15.50	Refreshments
15.50-16.40	L. Berthier: When glasses jam: Equilibrium statistical mechanics description of the jamming transition.
16.40-17.10	P. Royall: Newtonian dynamics in gelation: can C60 form the first one-component gel?
17.10-17.40	R. Evans: Solvation forces and phase transitions of fluids confined between opposing (solvophobic and solvophilic) walls.

Tuesday 2nd November

09.10-10.00	G. Kahl: Obstacles and confinement: slow dynamics of colloids in porous confinement.
10.00-10.50	G. Biroli: Do solids flow?
10.50-11.10	Refreshments
11.10-11.40	A. Zaccone: The nonaffinity and the rigidity of amorphous solids.
11.40-12.10	J. Tavaoli: The POD.
12.10-13.00	H. Löwen: Nonequilibrium phenomena in colloids and complex plasmas.
13.00-14.20	Buffet Lunch
14.20-14.50	A. Archer: Model colloidal suspensions with competing interactions exhibiting phase transitions to modulated phases.
14.50-15.20	R. Henchman: Navigating the potential energy surface of liquid water.
15.20-15.50	M. Wilson: Structure and dynamics of network-forming liquids.
15.50-16.00	Closing remarks
16.00	End

Abstracts of talks

Philip Camp

Title: Adsorption and tribology of molecules on and between surfaces

Recent coarse-grained simulation studies of various aspects of molecular adsorption and tribology will be reported. The physisorption of linear and star polymers on smooth surfaces will be discussed. Emphasis will be placed on the comparison between simulation results and the predictions of scaling theories for the structures of the adsorbed layers [1,2]. The kinetic friction arising from an oil-like fluid layer confined between sheared parallel surfaces will be considered next. Of particular note is an observed logarithmic dependence of the kinetic-friction coefficient on shear rate. The effects of small concentrations of amphiphilic additives on the kinetic friction will be described and correlated with the steady-state distribution of additive molecules throughout the fluid layer [3]. Finally, some outstanding problems and ongoing work in this broad area will be outlined.

[1] "Adsorption and self-assembly of linear polymers on surfaces: A computer simulation study", A. Chremos, E. Glynos, V. Koutsos, and P. J. Camp, *Soft Matter* 5, 637-645 (2009).

[2] "Adsorption of star polymers: computer simulations", A. Chremos, P. J. Camp, E. Glynos, and V. Koutsos, *Soft Matter* 6, 1483-1493 (2010).

[3] "Molecular simulations of kinetic-friction modification in nanoscale fluid layers", M. R. Farrow, A. Chremos, P. J. Camp, S. G. Harris, and R. F. Watts (submitted).

Alexei Likhtman

Title: Multiscale modelling of entangled polymers.

I will briefly review multiscale approach to modelling of entangled polymers, which includes molecular dynamics (MD), single chain stochastic models (slip-springs) and the tube model. After that I will concentrate on the link between many chain (MD) and single chain models. I will report results from molecular dynamics simulations on stress relaxation and show the detailed comparison with slip-spring model. In the second part of the talk I will turn to the issue of microscopic definition of entanglement in molecular dynamics. We propose to define entanglement as a long-lived contact between mean paths of the two chains. Using this definition, we present empirical evidence and statistical properties of such entanglements, and discuss the implications for the tube theory and the slip-spring model.

Christos Likos

Title: Glass transitions in polymer mixtures

Soft composite materials consisting of mixtures of polymers with different sizes and/or architectures provide possibilities to tune the rheology and dynamical response that are much richer than those known for hard interactions. This flexibility stems from the penetrability of the particles involved, as well as from the ability to influence physical parameters of the models within a vast range. In this talk, we will present a combination of recent theoretical and experimental results, demonstrating the existence of multiple glass states in soft mixtures, applying tools that stem from coarse-graining techniques, Mode-Coupling Theory and computer simulations. A critical assessment of the applicability of coarse-graining approaches will also be discussed, in light of recent experimental results.

Juan Garrahan

Title: Molecular Random Tilings

We have recently shown that a small organic molecule, p-terphenyl-3,5,3',5'-tetracarboxylic acid, when adsorbed on graphite self-assembles into a two-dimensional rhombus random tiling. This tiling is close to ideal, with long range correlations punctuated by sparse localised tiling defects. This is a rare example of a molecular system displaying "Coulomb" phase behaviour and fractional excitations. I will discuss the static and dynamic properties of these kind of random tilings, and explore analogies with other dynamically arrested systems. I will also discuss connections to the theoretically predicted phase behaviour of interacting planar tilings and dimer coverings.

Peter Sollich

Title: Crystalline phases of polydisperse spheres

We use specialized Monte Carlo simulation methods and moment free energy calculations to provide conclusive evidence that dense polydisperse spheres at equilibrium demix into coexisting fcc phases, with more phases appearing as the spread of diameters increases. We manage to track up to four coexisting phases. Each of these is fractionated: it contains a narrower distribution of particle sizes than is present in the system overall. We also demonstrate that, surprisingly, demixing transitions can be nearly continuous, accompanied by fluctuations in local particle size correlated over many lattice spacings.

Douglas Ashton

Title: Exploring particle size and shape effects in highly size-asymmetric binary mixtures

The statistical mechanics of binary fluid mixtures whose components have a large disparity in their sizes is rich in features and has wide applications from protein solutions to synthetic colloids. Through careful selection of the smaller species one can alter the effective interactions between the large species, and dramatically change the bulk phase behaviour and microscopic structure. However, from a computer simulation perspective, large size-asymmetries are difficult to handle due to the large particles being jammed by the small ones. Here we show how specialised Monte Carlo techniques can overcome the principal bottleneck to not only permit study of the effective interactions, but also the full phase behaviour of such systems. The results reveal that small changes to the properties of the small particles can lead to qualitative deviations from the standard depletion picture of colloidal interactions[1].

Going beyond isotropic interactions, we consider the effect of altering the shape of the large particles to create depletion driven directional bonds, as is the case in the "lock and key" colloids recently proposed by Sacanna et. al.[2] For such a system we report a preliminary study of the effect of the interplay between size and shape of the large particles on the effective interactions. We argue that lock and key colloids offer exciting new possibilities for the self assembly of colloidal molecules and nano-structures.

[1] Ashton et al arXiv:1007.3686 (2010)

[2] Sacanna et al. Nature, 464, 575 (2010)

Ludovic Berthier

Title: When glasses jam: Equilibrium statistical mechanics description of the jamming transition

About 50 years ago, J.D. Bernal introduced the idea that random assemblies of spheres represent a valuable model to understand the liquid state. Connections between purely geometric approaches (how to pack particles in three dimensions?), and statistical mechanics theories of the liquid state (how to describe dense fluids?) are still actively sought. In this talk, I will discuss a variety of phase transitions occurring when random configurations of spheres are compressed, described as 'glass' or 'jamming' transitions for thermal and athermal systems, respectively, and the unexpected connections between them. In particular, I will show that it is possible to describe theoretically the nonequilibrium jamming transition occurring in athermal disordered packings of soft repulsive particles using equilibrium statistical mechanics concepts, showing that Bernal's insight successfully works backwards.

Paddy Royall

Title: Newtonian dynamics in gelation: can C60 form the first one-component gel?

Until now, gels have typically been formed in multicomponent soft matter systems, consisting of a solvent and one or more macromolecular or colloidal species in which the dynamics of the larger species is typically Brownian. Gelation in such systems is often associated with arrested liquid-gas phase separation, the gels formed are consequently far from equilibrium. Molecular systems can relax on much shorter timescales: to date no gel has been formed in a one component molecular system.

Using molecular dynamics simulations, we show that, for sufficient quench rates, the Girifalco model of C60 can form gels which we identify by their slow dynamics and long-lived network structure. These gels are stable at room temperature, at least on the simulation timescale of 10 ns. At moderate temperatures around 1000 K, below the bulk glass transition temperature, C60 exhibits crystallisation and phase separation proceeds without the dynamical arrest associated with gelation, in contrast to many colloidal and soft matter systems.

R. Evans

Title: Solvation forces and phase transitions of fluids confined between opposing (solvophobic and solvophilic) walls

We consider a simple fluid confined between two parallel walls that are either (i) identical or (ii) exert different external fields so that one wall is attractive and is wet by liquid (solvophilic) while the other is repulsive and may be wet by the gas phase (solvophobic). Case (i) is well-studied: below the bulk critical temperature T_{cb} capillary condensation gives rise to a discontinuous jump in the solvation force (the excess pressure arising from fluid confinement) as a function of wall separation L or chemical potential. In case (ii) a 'delocalized interface phase' may form in the range $T_{cb} > T > T_w$, the wetting transition temperature. This phase exhibits a liquid-gas interface near $L/2$ with pronounced thermal fluctuations. We investigate the properties of this unusual phase using an effective interfacial Hamiltonian approach and a fully microscopic classical density

functional theory. For the physically relevant case of a Lennard-Jones fluid, with r^{-6} interatomic attraction, we determine the scaling functions of the solvation force f_s , the adsorption and the correlation length of interfacial fluctuations for temperatures removed from T_{cb} . We argue that these results remain valid beyond the mean-field treatment. In this temperature range, and for large separations, f_s is repulsive and decays as L^{-3} -the same power law as the critical Casimir force. We discuss the rich phase behaviour that occurs for smaller separations L .

Gerhard Kahl

Title: Obstacles and confinement: slow dynamics of colloids in porous confinement

Using molecular dynamics simulations we have studied the slow dynamics of a hard-sphere fluid confined in a matrix quenched from an equilibrated hard-sphere fluid [1], resembling the movement of hard colloids in disordered porous environments. We have observed the presence of both discontinuous and continuous glass transitions, anomalous diffusion, and de-coupling of the time scales for the relaxation of the single-particle and the collective correlators. On one side, our observations are to a great extent consistent with the predictions of a recent extension of mode-coupling theory for so-called "quenched-annealed" systems [2]; only the subtle re-entrant behavior predicted by the theory has not been confirmed, yet. On the other side, our simulations are able to provide a more profound insight into the microscopic details than a theoretical approach can possibly do: we have made a detailed analysis of the properties of the voids of the porous matrix and we have calculated the quantities of interest separately for particles trapped in voids formed by the matrix and for particles that unrestrictedly move through the entire system.

[1] J. Kurzidim, D. Coslovich, and G. Kahl, Phys. Rev. Lett. 103, 138303 (2009); Phys. Rev. E (in press; arXiv:1007.0429).

[2] V. Krakoviack, Phys. Rev. E 75, 031503 (2007); Phys. Rev. E 79, 061501 (2009)

Giulio Biroli

Title: Do solids flow?

Are solids intrinsically different from liquids? Must a finite (yield) stress be applied in order to induce flow? Or, instead, do all solids only look rigid on some finite timescales and eventually flow if an infinitesimal shear stress is applied? Surprisingly, the answers to these simple questions are still lacking and matter of debate. In this talk we will show using very simple nucleation arguments that solids like crystal and glasses indeed flow. However, they do so in a way inherently different from liquids: their macroscopic shear modulus is always zero but their viscosity diverges for vanishing shear stress with an essential singularity. We find an ultra-slow decrease of the shear stress as a function of the shear rate, which explains the apparent yield stress identified in rheological flow curves for solids.

Alessio Zaccone

Title: The nonaffinity and the rigidity of amorphous solids

We propose a novel approximation for the dynamical matrix of model disordered solids which, for the first time, enables the analytical calculation of the elastic constants. The theory, by fully accounting for the nonaffinity of the displacement field, is in quantitative agreement with simulations and predicts the vanishing of the shear modulus at the isostatic point with a linear dependence upon the distance from the isostatic point (i.e. proportional to $z-2d$ where z is the coordination number and d is the space dimension). The vanishing of rigidity is shown to be a consequence of the exact balancing, at the isostatic point, of positive affine and negative nonaffine terms.

Joeseeph Tavacoli

Title: The POD

We present a partially covered Pickering drop that climbs and dives in response to a positive temperature gradient running from top to bottom within a continuous phase. Our diver is formed by pouring glass-micro beads through a top layer of pentane into a bottom ethanediol layer. The glass beads trap air and pentane in this procedure and as the beads sediment, the trapped pentane rises through the beads to self assemble into a partially covered Pickering droplet of air, pentane and pentane vapour within a continuous phase of ethanediol. We name this self-assembled-mobile drop the particle-stabilised oscillation diver (the POD). The interfacially trapped beads are essential to POD formation as they act as a ballast to produce a near neutrally buoyant species and due to its air-vapour bubble, which expands and contracts accordingly with changes in temperature, the POD is able to both climb and dive within a narrow temperature window. Oscillation occurs because the temperatures of the bubble and the background gradient, which is provided in-situ by evaporation of the overlying pentane layer, are out of phase and thermal equilibrium is never reached. These features are common to automatic Cartesian divers [1] of which the POD is the first self-assembled example. The POD can be likened to an electronic relaxation oscillator with vertical oscillation analogous to voltage, thermal resistance to electrical resistance and bubble size to capacity.

[1] R. Stuart Mackay, Am. J. Phys. 26, 60 (1958). *ibid* 26, 403 (1958).

Hartmut Löwen

Title: Nonequilibrium phenomena in colloids and complex plasmas

Colloidal dispersions and complex plasmas are ideal model systems to study nonequilibrium phenomena on the fundamental particle-scale. These two systems share the classical many-body character of strongly coupled systems but differ in their dynamics which is overdamped in the colloidal and almost ballistic in the complex plasma case. In the talk, lane formation in oppositely driven binary mixtures [1,2] will be discussed as well as the kinetics of fluid demixing [3].

[1] K. R. Sutterlin, A. Wysocki, A. V. Ivlev, C. Rath, H. M. Thomas, M. Rubin-Zuzic, W. J. Goedheer, V. E. Fortov, A. M. Lipaev, V. I. Molotkov, O. F. Petrov, G. E. Morfill, H. Lowen, Phys. Rev. Letters 102, 085003 (2009).

[2] T. Vissers, A. Wysocki, M. Rex, H. Löwen, C. P. Royall, A. Imhof, A. van Blaaderen, Lane formation in driven colloidal mixtures, to be published.

[3] A. Wysocki, C. Rath, A. V. Ivlev, K. R. Sutterlin, H. M. Thomas, S. Khrapak, S. Zhdanov, V. E. Fortov, A. M. Lipaev, V. I. Molotkov, O. F. Petrov, H. Lowen, G. E. Morfill, Phys. Rev. Letters 105, 045001 (2010).

Andrew Archer

Title: Model colloidal suspensions with competing interactions exhibiting phase transitions to modulated phases

Certain colloidal fluids have been observed to spontaneously form cluster, stripe and other patterned morphologies in both two and three dimensional colloidal suspensions [1]. In these systems, the effective pair potentials between the particles are isotropic and the structuring stems from the fact that the pair interaction between particles has competing attraction and repulsion over different length scales. Using a simple mean-field density functional theory (DFT) and Monte-Carlo computer simulations, we investigate the structure and phase behaviour of a model fluid composed of particles interacting via a pair potential which has a hard core, is attractive at intermediate separations and repulsive at large separations. We investigate the nature of the phase transition between the uniform and modulated phases and find that the transition can be either continuous or first order. On changing the various system parameters we find that the phase diagram can exhibit a pair of tricritical points and/or a Lifshitz point. Our simple DFT proves to be a valuable tool in understanding the phase behaviour of these systems and is able to predict the various modulated phases and the nature of the phase transitions between them.

[1] See for example, R.P. Sear, S.-W. Chung, G. Markovich, W.M. Gelbart and J.R. Heath, Phys. Rev. E 59, R6255 (1999); A. Stradner, H. Sedgwick, F. Cardinaux, W.C.K. Poon, S.U. Egelhaaf and P. Schurtenberger, Nature 432, 492 (2004); H. Sedgwick, S.U. Egelhaaf, and W.C.K. Poon, J. Phys.: Condens. Matter 16, S4913 (2004); A.I. Campbell, V.J. Anderson, J.S. van Duijneveldt, and P. Bartlett, Phys. Rev. Lett. 94, 208301 (2005).

Richard Henchman

Title: Navigating the Potential Energy Surface of Liquid Water

A new definition for a hydrogen bond is applied to give a detailed characterisation of the structure and dynamics of liquid water. The definition avoids the use of arbitrary parameters, gives the hydrogen bond a conceptual basis by equating it with a local energy well in the potential energy surface, and sharply resolves transition states in hydrogen-bond switching. The definition distinctly shows that the dominant hydrogen-bond coordination is tetrahedral, that there are smaller proportions of trigonal and trigonal bipyramidal, and that there are very few broken hydrogen bonds. Each of these components is characterised in terms of structure, enthalpy, entropy, density and dynamics to show how they are consistent with water's properties. The hydrogen-bond definition also resolves three main types of hydrogen-bond switching depending on whether the donor and the new acceptor already share a hydrogen bond. These switch-types further contribute to water's dynamical properties.

Mark Wilson

Title: Structure and dynamics of network-forming liquids.

Intermediate-range order (IRO), in which systems exhibit structural ordering on length-scales beyond the nearest-neighbour (short-range), has been identified in a wide range of materials and is characterised by the appearance of the so-called first sharp diffraction peak (FSDP) at low scattering angles. The precise structural origin of such ordering remains contentious and a full understanding of the factors underlying this order is vital if such materials (many of which are technologically significant) are to be produced in a controlled manner.

Simulation models, in which the ion-ion interactions are represented by relatively simple potential functions which incorporate (many-body) polarization and which are parameterised by reference to well-directed electronic structure calculations, have been shown to reproduce such IRO and allow the precise structural origin of the IRO to be identified. Furthermore, the use of relatively simple (and hence computationally tractable) models allows for the study of the relatively long length- and time-scales required. Two typical systems, zinc chloride (which is usually considered as 'ionic') and germanium selenide (considered as having 'covalent' character) have been recently modelled as key target systems deliberately chosen so as to potentially represent two different bonding 'types' whilst both displaying FSDPs at $\sim 1\text{\AA}^{-1}$. Both have received recent significant experimental and computational (electronic structure) attention. The underlying structures are analysed with reference to both recent (neutron scattering) experimental results and high level electronic structure calculations and the origin of the FSDP in the Bhatia-Thornton $S_{CC}(k)$ function discussed. The role of key structural units (corner and edge sharing polyhedra) in determining the network topology is investigated in terms of the underlying dynamics and the relationship to the glass transition considered.

List of participants

Surname	First Name	Email	Institution
Archer	Andrew	A.J.Archer@lboro.ac.uk	University of Loughborough
Ashton	Douglas	d.ashton@bath.ac.uk	University of Bath
Bartlett	Paul	p.bartlett@bristol.ac.uk	University of Bristol
Berthier	Ludovic	berthier@lcvn.univ-montp2.fr	Universite Montpellier
Biroli	Giulio	giulio.biroli@cea.fr	CEA-Saclay
Camp	Philip	philip.camp@ed.ac.uk	University of Edinburgh
Cao	Jung	jing.cao@reading.ac.uk	University of Reading
Cheung	David	david.cheung@warwick.ac.uk	University of Warwick
Chirawatkul	Prae	Pc249@bath.ac.uk	University of Bath
Dunleavy	Andrew	ad9111@bristol.ac.uk	University of Bristol
Evans	Mike	r.m.l.evans@leeds.ac.uk	University of Leeds
Evans	Robert	bob.evans@bristol.ac.uk	University of Bristol
Farrow	Matthew	matthew.farrow@ed.ac.uk	University of Edinburgh
Fullerton	Christopher	christopher.fullerton@postgrad.man.ac.uk	University of Manchester
Garrahan	Juan	juan.garrahan@nottingham.ac.uk	University of Nottingham
Grant	James	rjg20@bath.ac.uk	University of Bath
Henchman	Richard	henchman@manchester.ac.uk	University of Manchester
Jack	Robert	r.jack@bath.ac.uk	University of Bath
Kahl	Gerhard	gkahl@tph.tuwien.ac.at	T.U. Wien
Klotsa	Daphne	d.klotsa@bath.ac.uk	University of Bath
Likhtman	Alexei	A.Likhtman@reading.ac.uk	University of Reading
Likos	Christos	christos.likos@univie.ac.at	Universität Wien
Lion	Thomas	T.Lion-2@sms.ed.ac.uk	University of Edinburgh
Löwen	Hartmut	hlowen@thphy.uni-duesseldorf.de	Universität Düsseldorf
Masters	Andrew	andrew.masters@manchester.ac.uk	University of Manchester
Mey	Antonia	ppxasjsm@nottingham.ac.uk	University of Nottingham
Parker	Steve	S.C.Parker@bath.ac.uk	University of Bath
Royall	Paddy	paddy.royall@bristol.ac.uk	University of Bristol
Salmon	Philip	p.s.salmon@bath.ac.uk	University of Bath
Sear	Richard	r.sear@surrey.ac.uk	University of Surrey
Siddorn	Mark	mjs215@bath.ac.uk	University of Exeter
Sollich	Peter	peter.sollich@kcl.ac.uk	King's College London
Taffs	Jade	jade_taffs@hotmail.com	University of Bristol
Tavacoli	Joseph	jtavacol@staffmail.ed.ac.uk	University of Edinburgh
Vorselaars	Bart	B.Vorselaars@reading.ac.uk	University of Reading
Wezka	Kamil	kw267@bath.ac.uk	University of Bath
Whittaker	Dean	d.whittaker@bath.ac.uk	University of Bath
Wilding	Nigel	n.b.wilding@bath.ac.uk	University of Bath
Williams	Ian	ian.Williams@bristol.ac.uk	University of Bristol
Williamson	John	pyjjw@leeds.ac.uk	University of Leeds
Wilson	Mark	mark.wilson@chem.ox.ac.uk	University of Oxford
Zaccone	Alessio	alessio.zaccone@chem.ethz.ch	ETH Zurich
Zeidler	Anita	az207@bath.ac.uk	University of Bath
Zhang	Isla	Isla.Zhang@bristol.ac.uk	University of Bristol

Notes

