

CHALLENGES IN STATISTICAL MECHANICS: FROM MATHEMATICS TO MOLECULAR DYNAMICS TO TECHNOLOGICAL APPLICATIONS

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Imperial College
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Organisers: Ben Goddard (Edinburgh), Serafim Kalliadasis (Imperial), Michela Ottobre (Heriot-Watt), Greg Pavliotis (Imperial), Johannes Zimmer (Bath).

ABSTRACTS

Matthew Borg (Edinburgh)

TBA

Peter Coeveny (UCL)

Combining Dynamical Models on Several Scales: Multiscale Modelling of Polymer-Clay Nanocomposites

We have developed an advanced multiscale modelling environment which predicts the properties of polymer-clay nanocomposites based on their molecular structures and composition. These methods have applications in modelling a wide range of materials and it is our aim to create a virtual lab to compute the properties of new soft materials based simply on knowledge of their chemical composition, molecular structure and processing conditions [1]. Here we will present our findings from modelling chemically specific combinations of clays and polymers, based on multiscale methods and tools which take us from a parameter free quantum description to atomistic and coarse-grained molecular dynamics simulations, ultimately leading to predictions of the materials properties of these nanocomposites. Our simulations approach realistic sizes of clay platelets at low clay volume fractions. These systems show property enhancements compared to the pristine polymer, but homogeneous dispersion of the clay sheets is required.

Our multiscale approach furnishes predictions of the melt intercalation and exfoliation behaviour, including final morphologies, of a range of chemically specific systems. Many hitherto unobserved phenomena also become accessible along the way, including the dynamical process of polymer intercalation into clay tactoids and the ensuing aggregation of such polymer-entangled tactoids into larger structures.

[1] J.L. Suter, D Groen, P.V. Coveney, Adv. Mater. 2015, 27, 966984

Joel De Coninck (de Mons)

Wetting dynamics: a case study

Wetting has a very long and fascinating history. The solid-liquid interactions are mainly physical, but they are a result of the specific chemistry at the interface. The flow of the liquids in contact with a solid is studied by fluid mechanics, and the solids are described in terms of material science. For about 200 years the basic equations derived from macroscopic arguments and describing the equilibrium configuration of partially wetting liquids have been known, due to Young and Laplace. And starting about 50 years ago, the dynamics of wetting became of central interest. Nowadays, still fundamental questions remain unresolved. Most of the open questions find their origin in the fact that wetting depends, to a large extent, on the microscopic characteristics of the considered materials. Young's equation, for example, has been validated at the microscopic scale only recently.

Apart from the fundamental problem of whether a given solid is wetted by a given liquid, many of the practical applications require the precise knowledge of the rates of wetting processes. Particularly, one is often interested to know how fast a liquid can wet a given area of a solid surface.

It is the goal of this presentation to review some recent results based on new experiments and new molecular dynamics simulations to study the details of drop spreading and to provide a review of the physical mechanisms controlling the dynamics of wetting.

We will use in particular these molecular considerations to show how to optimise significantly the ultimate limit to coating or wetting speeds, a very practical problem related to the important problem of air entrainment.

Arnaud Ducet (Oxford)

Gibbs flow for approximate transport with applications to Bayesian computation

Let π_0 and π_1 be two probability measures on \mathbb{R}^d . Any measurable function $T : \mathbb{R}^d \rightarrow \mathbb{R}^d$ such that $Y = T(X) \sim \pi_1$ if $X \sim \pi_0$ is called a transport map from π_0 to π_1 . If for any π_0 and π_1 , one could obtain an analytical expression for a transport map from π_0 to π_1 then this could be straightforwardly applied to sample from any distribution. One would map draws from an easy-to-sample distribution π_0 to the target distribution π_1 using this transport map. Although it is usually impossible to obtain an explicit transport map for complex target distributions, we show here how to build a tractable approximation of a novel transport map. This is achieved by moving samples from π_0 using an ordinary differential equation whose drift is a function of the full conditional distributions of the target. Even when this ordinary differential equation is time-discretized and the full conditional distributions are approximated numerically, the resulting distribution of the mapped samples can be evaluated and used as a proposal within Markov chain Monte Carlo and sequential Monte Carlo schemes. We show experimentally that it can improve significantly performance of state-of-the-art sequential Monte Carlo methods for a fixed computational complexity.

(This is joint work with Jeremy Heng (Oxford) and Yvo Pokern (UCL))

Andrew Duncan (Imperial)

Improving the performance of overdamped Langevin samplers by breaking detailed balance.

MCMC provides a powerful and general approach for generating samples from a high-dimensional target probability distribution, known up to a normalizing constant. There are infinitely many Markov processes whose invariant measure equals a given target distribution. The natural question is whether a Markov process can be chosen to generate samples of the target distribution as efficiently as possible. It has been previously observed that adding an appropriate nonreversible perturbation to a reversible Markov process will improve its performance. In this talk, I will describe some recent results which characterise the effect of adding a nonreversible drift to an overdamped Langevin sampler, in terms of rate of convergence to equilibrium and asymptotic variance. Finally, I will detail how such nonreversible Langevin samplers can be used in practice by describing a discretisation scheme which inherits the good performance of the underlying process.

Miguel Duran-Olivencia (Imperial)

Dynamical Density Functional Theory for Systems of Orientational Colloids Including Inertia and Hydrodynamic Interactions

Over the last few decades the classical density-functional theory (DFT) and its dynamic extensions (DDFTs) have become a remarkably powerful tool in the study of colloidal fluids. Recently there has been extensive research to generalise all previous DDFTs finally yielding a general DDFT equation (for spherical particles) which takes into account both inertia and hydrodynamic interactions (HI) which strongly influence non-equilibrium properties [1]. The present work will be devoted to a further generalisation of such a framework to systems of arbitrary-shape particles. To this end, the kinetic equation for the Brownian particle distribution function is derived starting from the Liouville equation and making use of the Zwanzig projection-operator techniques. By averaging over all but one particle, a DDFT equation is finally obtained with some similarities to that for spherical colloids. However, there is now an inevitable translational-rotational coupling which affects the diffusivity of asymmetric particles. Lastly, in the overdamped (high friction) limit the theory is notably simplified being in agreement with a recent derivation of DDFT for colloids with arbitrary shape [2].

[1] B. D. Goddard, A. Nold, N. Savva, P. Yatsyshin, and S. Kalliadasis. Unification of dynamic density functional theory for colloidal fluids to include inertia and hydrodynamic interactions: derivation and numerical experiments. *Journal of Physics: Condensed Matter*, 25(3):035101, 2013.

[2] R. Wittkowski and H. Lwen. Dynamical density functional theory for colloidal particles with arbitrary shape. *Molecular Physics*, 109(23-24):29352943, 2011

Gero Friesecke (TU Munich)

Pair densities in density functional theory: cross-over from strict correlations to mean field behaviour

(Electronic) density functional theory (DFT) provides the most widely used models for computing ground state electronic energies and densities in chemistry, materials science, biology, and nanosciences. The exact interaction energy of a many-electron system is determined by the electron pair density, and is not approximated very well in standard DFT models. In the talk, I

- (1) explain the observation by M. Levy that an exact density-to-pair-density map exists,
- (2) show how many common functionals including Dirac exchange arise from certain explicit approximations/models of this map, and
- (3) present numerical computations of the exact map for one-parameter families of (1D) homogeneous and inhomogeneous model densities varying from ‘concentrated’ to ‘dilute’.

The pair densities are seen to develop remarkable multi-scale patterns which cross over from mean-field to strongly correlated behaviour, show strong dependence on the particle number, and do NOT appear to agree with ANY of the common models. The simulation results are confirmed by rigorous asymptotic results in the concentrated respectively dilute limit. The former limit leads to the well-known concept of ‘exact exchange’, and the latter leads into optimal transport theory. Our numerical results lend theoretical support to the celebrated semi-empirical idea by A.Becke to mix in a fractional amount of exchange, albeit not to assuming the mixing to be additive and taking the fraction to be a system-independent constant. Joint work with Huajie Chen (Warwick).

Reference: H. Chen, G. F., Multiscale Model. Simul., 13(4), 12591289, 2015

Rosemary Harris (Queen Mary)

Random walkers with extreme value memory: modelling the peak-end rule

I will describe some recent interdisciplinary work using the tools of statistical mechanics to study the effect of the psychological “peak-end” memory heuristic in decision making. Specifically, this involves an analysis within a random walk framework of a discrete choice model where agents’ future choices depend on the peak of their past experiences. This approach facilitates an investigation of whether increased noise/disruption always leads to more switching between decisions. Here extreme value theory illuminates different classes of dynamics indicating that the long-time behaviour is dependent on the scale used for reflection; this could have implications, for example, in questionnaire design.

Carsten Hartmann (Berlin)

Probing the properties of soft matter: optimal design of single molecule experiments

Molecular dynamics simulation aims at predicting and quantifying material properties by driving the system out of equilibrium and probing rare events, such as the folding of a protein or a phase transition. Simulating such rare events is often prohibitive, especially if the equations of motion are high-dimensional. Various numerical methods have been proposed in the past that seek to enhance the sampling of the rare events by modifying the system’s energy landscape. In this talk I will describe recent advances in the field of enhanced sampling that combines ideas from optimal control and nonequilibrium statistical mechanics. The approach, that resembles nonequilibrium sampling based on Jarzynski’s equality for free energy calculations, employs cross-entropy minimization to devise optimized computational protocols that speeds up the sampling while (theoretically) giving variance-free estimators of the rare events statistics. I will discuss theory, numerics and implementation issues.

Rob Jack (Bath)

Protein (mis)folding and glass transitions

The dynamics of protein molecules is complex and co-operative, featuring multiple metastable states. While molecular dynamics (MD) simulations can describe the molecular motion, an accurate description of the slow molecular processes of interest requires scale-bridging methods. I will review some recent work on the construction of Markov State Models, which provide a simplified description of the protein dynamics, inferred from on extensive MD simulations. I will present a large deviation analysis of the resulting stochastic models, which revealed unexpected long-lived metastable states in these protein molecules [2,3]. Finally I will discuss potential consequences of these states.

[1] JH Prinz et al, J Chem Phys 134, 174105 (2011)

[2] JK Weber, RL Jack, and VS Pande, J Am Chem Soc 135, 5501 (2013)

[3] JK Weber, RL Jack, CR Schwandtes, and VS Pande, Biophys J 107, 974 (2014)

Yannis Kevrekidis (Princeton)

On the interplay of data mining with atomistic simulations: algorithms and issues from using Diffusion Map coordinates.

I will discuss several issues that arise when we try to assist/accelerate simulations of complex/multiscale systems (including atomistic/MD simulations) through data mining and, in particular, through diffusion maps.

The effective reduction of multiscale simulations, the extension beyond already sampled areas of phase space, the “intelligent” exploration of low-dimensional effective free energy surfaces, the translation of the dynamics from physical to transformed space, and the relation of data-based coordinates to physical ones are some of the subjects I will discuss.

Ben Leimkuhler (Edinburgh)

The state of the art of the timestep: enhanced sampling of molecular systems using extended dynamics

I will describe the development of methods for sampling complex molecular systems based on the introduction of auxiliary variables and the incorporation of stochastic perturbations. After a brief recap on the current state of the art of the timestep in molecular dynamics, my talk will focus on two illustrative examples: a method based on kinetic energy constraints for control of resonances in multiple timestep simulations [1], and a continuous tempering method to facilitate rare transitions by varying the temperature along trajectories [2].

[1] B. Leimkuhler, D. Margul and M. Tuckerman, Stochastic resonance-free multiple time-step algorithm for molecular dynamics with very large time steps, *Molecular Physics*, vol 111, no. 22-23, pp. 3579-3594, 2013.

[2] G. Gobbo and B. Leimkuhler, Extended Hamiltonian approach to continuous tempering, *Physical Review E* 91, 061301(R), 2015.

Youlong Lu (Warwick)

Understanding Transition Paths using Gamma Convergence

Determining the structure of transition paths at small temperature is a challenging computational and mathematical problem. This problem is studied here in the overdamped limit and in the regime where the transition time scales as the inverse temperature. Rescaling to a unit interval gives a diffusion with large potential and order one noise. Use of the idea of paths of maximal probability leads to transitions which exhibit physically unrealistic characteristics, and this is demonstrated numerically, and through the use of gamma convergence, in [1] and [2]. The difficulty is associated with ignoring entropic contributions to the pathspace probabilities. In [3] a method for finding the best Gaussian approximation to a pathspace measure was introduced, and this affords the possibility of including entropic effects; the method is based on minimizing the Kullback-Liebler divergence between the Gaussian approximation and the desired measure. Development of numerical methods based on this approach is described in [4].

In this work the methodology from [3] is applied and gamma limits of the resulting minimization problem, over a subclass of Gaussian measures, is studied. It is shown that this approach removes the unphysical effects described in [1], [2] and links with the large deviation approach to the problem are established. Furthermore the methodology provides Gaussian approximations, based on inhomogeneous Ornstein-Uhlenbeck processes, which characterize fluctuations about the mean transition path.

[1] F.J. Pinski and A.M. Stuart, Transition paths in molecules: gradient descent in pathspace. *Journal of Chemical Physics* 132 (2010), 184104.

[2] F.Pinski, A.M.Stuart and F. Theil, Gamma limit for transition paths of maximal probability. *Journal of Statistical Physics* 146/5 (2012) 955-974.

[3] F.J. Pinski, G. Simpson, A.M. Stuart and H. Weber, Kullback-Leibler approximation for probability measures on infinite dimensional spaces. arxiv.org/abs/1310.7845 (*SIAM J. Math. Analysis*, to appear)

[4] F.J. Pinski, G. Simpson, A.M. Stuart and H. Weber, Algorithms for Kullback-Leibler approximation for probability measures in infinite dimensions. arxiv.org/abs/1408.1920 (*SIAM J. Sci. Comp.* to appear)

Jens Marklof (Bristol)

Generalized linear Boltzmann equations for particle transport in polycrystals

The linear Boltzmann equation describes the macroscopic transport of a gas of non-interacting point particles in low-density matter. It has wide-ranging applications, including neutron transport, radiative transfer, semiconductors and ocean wave scattering. Recent research shows that the equation fails in highly-correlated media, where the distribution of free path lengths is non-exponential. We investigate this phenomenon in the case of polycrystals whose typical grain size is comparable to the mean free path length. Our principal result is a new generalized linear Boltzmann equation that captures the long-range memory effects in this setting. A key feature is that the distribution of free path lengths has an exponential decay rate, as opposed to a power-law distribution observed in a single crystal. Based on joint work with Andreas Strombergsson (Uppsala University).

Angelos Michaelidis (UCL)

Structure and dynamics of water at interfaces: “Surfing” water droplets and ice formation

Water/solid interfaces are relevant to a broad range of physicochemical phenomena and technological processes such as corrosion, lubrication, heterogeneous catalysis and electrochemistry (Nature Mater 11, 667 (2012)). In this talk some of our recent computer simulation work in this area will be covered. Specifically results on water droplet diffusion on the surfaces of layered materials will be presented and a novel “surfing” mechanism for droplet diffusion discussed (Nature Mater, in press; doi:10.1038/nmat4449). In addition, simulations of ice nucleation on various nanoparticles with different physicochemical characteristics will be presented and the fundamental insight obtained from these into heterogeneous ice nucleation discussed (J. Am. Chem. Soc. 137, 1365 (2015)). Time permitting some recent ab initio molecular dynamics results at wet interfaces in which rapid proton transfer is observed will also be discussed.

Andreas Nold (Imperial)

From the nano- to the macroscale – Bridging the scales for the moving contact line problem

Understanding the physics of the moving contact line is — alongside turbulence — one of the last unsolved fundamental problems in fluid mechanics. There are two significant challenges: First, this is a nanoscopic region that is extremely difficult to scrutinise experimentally. Second, the relevant physical phenomena span multiple scales, from molecular to macroscopic. Here, we link classical macroscale approaches with meso- and nanoscale models, offering a systematic theoretical framework to include nanoscale details in a continuum description of the moving contact line.

At the macroscale, it is shown that classical asymptotic analysis is applicable to the moving contact line, therefore allowing a direct matching procedure between the inner (nanoscale) region and the outer (macroscale) region. This corrects classical papers and misunderstandings in the literature for several decades [J. Fluid Mech. 764, 445 (2015)].

The macroscopic asymptotics are then shown numerically to also hold in the sharp-interface limit of isothermal diffuse interface models (Navier-Stokes/Cahn-Hilliard), including dissipation effects. We then account for thermal effects in a unified manner, consolidating two contradictory models present in the literature.

Finally, the nanoscale structure of the density profile is incorporated in a continuum description. This is achieved by combining classical density functional theory (DFT) for simple fluids with dynamic DFT approaches for colloidal systems. Numerical computations for spontaneously advancing and receding contact lines are presented for a wide range of contact angles [Phys. Fluids 26, 072001 (2014) (selected for Research Highlights from Physics of Fluids), Math. Model. Nat. Phenom. 10, 111 (2015)].

Computations are performed using novel numerical tools by discretizing unbounded two-dimensional domains using mapped Chebyshev polynomials. For DFT computations, this allows for an efficient real-space computation of convolution matrices. For diffuse-interface computations, it allows to cover a wide range of time- and length scales whilst keeping the computational cost to a minimum.

Mark Peletier (Eindhoven)

Open problems in the upscaling of dislocations

In this talk I will dwell on the question ‘can one derive macroscopic plasticity equations by scaling up the behaviour of many dislocations?’ If the answer were Yes, then much could be gained: metals could be designed at the workstation with tailor-made properties, design of hybrid materials would become much easier, and generally the holy grail of ‘materials by design’ would come a little closer.

I will describe some recent results in this field, outline some of the challenges, and mention some open questions and one or two mysteries.

Marc Pradas (Open)

Noise-induced critical transitions in multiscale systems

External or internal random fluctuations are ubiquitous in many physical systems and can play a key role in their dynamics often inducing a wide variety of complex spatio-temporal phenomena, including noise-induced spatial patterns and noise-induced phase transitions. Examples can be found in several fields: from biology, climate modelling and technological applications to fluid dynamics and granular media. Many of these phenomena and applications can be modelled by noisy multiscale systems which are characterized by the presence of a wide range of different time- and lengthscales interacting nontrivially with each other.

Here we analyse the effects of additive noise on different multiscale systems, including Brownian motion in rugged energy landscapes which are characterized by a clear lengthscale separation, and spatially extended systems that are close to the instability onset (and hence there is a clear time scale separation). We will demonstrate that noise may induce several nontrivial and largely unexpected dynamic-state transitions, including stabilisation and intermittency, which can be characterized in terms of critical exponents.

Celia Reina (Imperial)

Geometry of dissipative evolution equations

The modeling of continuum dissipative evolution equations remains a challenge and is primarily based on phenomenological constitutive relations. In this talk we present some connections between the geometry of dissipative gradient flows, the principle of maximum entropy production, large deviation principles for stochastically augmented evolution equations and fluctuation-dissipation relations. Applications to microstructure evolution in materials will also be discussed.

Gabriel Stoltz (Cermics)

Error estimates for transport coefficients in molecular dynamics

In this talk, I will present error estimates for transport coefficients, which can be obtained either by the linear response of appropriately perturbed stochastic dynamics, or, equivalently, through the time integration of correlation functions. I will consider Langevin dynamics, numerically integrated with splitting schemes; and overdamped Langevin dynamics, possibly corrected by a Metropolis/Hastings procedure in order to remove the bias on the invariant measure.

Doros Theodorou (Athens)

Multiscale Molecular Simulations of Polymer Matrix Nanocomposites

The dispersion of nanoparticles within polymer matrices can serve as a basis for developing materials with novel properties. How these properties depend on the molecular characteristics of the constituent chains and nanoparticles is still not fully understood, however. Molecular modelling and simulation hold great promise as means for elucidating and predicting structure-property relations, but face serious challenges associated with the very broad spectra of time and length scales governing the behaviour of polymer matrix nanocomposites.

In this presentation we will outline a hierarchical strategy for predicting the structure, thermomechanical, and rheological properties of materials consisting of spherical nanoparticles of roughly spherical shape dispersed in amorphous polymers. This strategy encompasses (a) detailed molecular dynamics (MD) simulations [1]; (b) coarse-grained Monte Carlo (MC) simulations, in which every repeat unit of the polymer is represented as a single interaction site [1]; (c) Field Theory-inspired Monte Carlo (FTiMC) simulations, in which chains are treated as sequences of Kuhn statistical segments [2,3]; (d) Brownian Dynamics/kinetic Monte Carlo (BD/kMC) simulations, where chains are reduced to strings of beads connected by springs, each bead encompassing 5-10 Kuhn segments, and entanglement points are reduced to slip-springs connecting beads on different chains. Each level of model representation invokes parameters that can be derived from more detailed levels, so that, ultimately, all predictions are based on an atomistic force field.

Invoking these computational tools, we will explore (i) how the conformations, segmental motions, and glass transition of atactic polystyrene are affected by dispersion of fullerenes; (ii) how the structure and dimensions of the corona of grafted polystyrene chains on the surface of a silica nanoparticle, used to promote dispersion in molten polystyrene, depend on molar mass and surface grafting density; (iii) how the stress relaxation modulus, which quantifies the linear viscoelasticity of cis-1,4 polyisoprene melts, is affected by their molecular characteristics.

[1] Vogiatzis, G.G.; Theodorou, D.N. "Local segmental dynamics and stresses in polystyrene-C₆₀ mixtures" *Macromolecules* 2014, 47, 387-404.

[2] Vogiatzis, G.G.; Theodorou, D.N. "Structure of polymer layers grafted to nanoparticles in silica-

polystyrene nanocomposites” *Macromolecules* 2013, 46, 4670-4683.

[3] Theodorou, D.N.; Vogiatzis, G.G.; Kritikos, G. “Self-consistent field study of adsorption and desorption kinetics of polyethylene melts on graphite and comparison with atomistic simulations” *Macromolecules* 2014, 47, 6964-6981.

Joint work with Georgios G. Vogiatzis.

Urbain Vaes (Imperial)

Hermite spectral method for multiscale SDEs

In this talk, we present a new approach for the simulation of multiscale SDEs at the diffusive time scale. The best known method for these problems is the heterogeneous multiscale method (HMM), which relies on appropriate time and ensemble averages to calculate the effective drift and diffusion, using the solution of a system of SDEs built from the fast processes while freezing the slow variables. In contrast, our approach is based on space averages of the solution of a Poisson equation obtained from the generator of the fast processes, which we calculate using a Hermite spectral method. While less general than the HMM, this approach has very good convergence properties, and is the ideal choice in many cases. In the talk, we present the method, summarize the main convergence results, and show some numerical experiments.

Julia Yeomans (Oxford)

Droplets bouncing on superhydrophobic surfaces

Drops bounce easily on superhydrophobic surfaces because of low friction. We discuss how the design of the surface can affect the bouncing, leading to a droplet leaving the surface shaped as a flattened disc or an extended cylinder. Lattice Boltzmann simulations and simple theories are used to help understand the reasons behind the unusual bouncing pathways.