New directions in classical density functional theory online workshop

3rd-6th May 2021 (all times BST/UTC+1)

Organisers: Andrew Archer (Loughborough University), Ben Goddard (University of Edinburgh), Roland Roth (University of Tübingen)

https://www.icms.org.uk/events/workshops/cdft

Contributed talk abstracts are available at the end of the document

Monday 3rd May

09:15-09:30   Welcome

09:30-11:00   Plenary: Bob Evans (H.H.Wills Physics Laboratory, University of Bristol)
Equilibrium Classical Density Functional Theory: A physicist's introduction

This introductory lecture will present the basics of classical DFT and the role it plays in the statistical physics of liquids. I will give some historical background and describe the links with electronic DFT. Both approaches are based on a rigorous variational principle for the grand potential of the inhomogeneous liquid as a functional of the average one-body density. In the classical case the density corresponds to particles (atoms or ions, tackled at the Angstrom scale, or to colloidal particles, tackled at the micron length scale) as opposed to the electron density. As with its electronic counterpart, the usefulness of classical DFT depends on finding reliable approximate functionals. I shall discuss this strategy. In the final part of the lecture, I shall describe a recent application of DFT to the solvation of a 'hydrophobic' solute.

11:00-11:30   Discussion

11:30-14:00   Break and informal discussions

14:00-14:30   Alina Ciach (Instytut Chemii Fizycznej PAN, Warszawa)
Correlation functions in concentrated electrolytes from combined density functional and statistical field theories

14:30-15:00   Martin Oettel (University of Tübingen)
The direct correlation function of a solid

15:00-15:30   Peter Cats (Utrecht University)
The Puzzling Decay Length in Concentrated Electrolytes

15:30-16:00   Discussion

Tuesday 4th May

09:30-11:00 **Plenary: Greg Pavliotis** (Department of Mathematics, Imperial College London)
Mean field limits for interacting particles and dynamical density functional theory

In this introductory lecture we will explain how one can derive dynamical density functional theory (DDFT)-type equations as the mean field limit of a system of weakly interacting particles driven by white noise. After obtaining the mean field PDE (DDFT), we will show that it is a gradient flow with respect to the mean field free energy. We will then discuss about convergence to equilibrium and characterise the stationary states as critical points of the free energy functional. Furthermore, we will discuss about the connection between non uniqueness of stationary states and phase transitions and we will provide a rigorous characterisation of phase transitions for a particular class of interaction potentials. Finally, we will discuss about fluctuations around the mean field/DDFT limit and we will formally derive stochastic DDFT models that are described by stochastic partial differential equations.

11:00-11:30 **Discussion**

11:30-14:00 Break and informal discussions

14:00-14:30 **Sabine Jansen** (LMU Munich)
A new inversion theorem with applications to density functionals

14:30-15:00 **Peter Yatsyshin** (The Alan Turing Institute, London)
Data-Driven Classical Density Functional Theory: A Case for Physics Informed Learning

15:00-15:30 **Matthias Schmidt** (Universität Bayreuth)
Fluctuation profiles for fluids and Noether's Therorem in Statistical Mechanics

15:30-16:00 **Discussion**

17:00-18:00 **Public Lecture: Priya Subramanian** (University of Oxford)
Wielding the knowledge of what is not possible

Abstract: John Werner Cahn was a leading figure in material science and had a distinguished career spanning four decades. He thought that, `Thermodynamics strictly is the science which tells one what is not possible', and wielded it extensively to understand and predict diverse physical phenomena. Starting with his ideas on how to control the properties of alloys, we look at his work which helped understand how materials solidify. In the latter part of the talk we focus on the role that he played in the discovery of quasicrystals. Such quasicrystals found in metallic alloys were discovered in 1984 and garnered a Nobel prize for their discoverer Dr. Dan Schectman in 2011, which is a remarkably short time scale in science. We finish with a look at how Prof. Cahn helped shape the reception by the scientific community on the news of the existence of such unexpected quasicrystals.

Wednesday 5th May

09:30-11:00 Plenary: Joachim Groß (Institute of Technical Thermodynamics and Thermal Process Engineering, University of Stuttgart)

This contribution first presents some recent developments in perturbation theory for attractive fluids. The uf-theory is based on a combination of a first-order u-expansion and a first order f-expansion and leads to an accurate description of simple pure fluids and mixtures. As opposed to other engineering models, where a one-fluid approximation needs to be applied for the attractive parts of the interaction potential, the uf-theory can be applied to mixtures beyond the one-fluid approximation.

The lecture will then highlight applications of DFT, with focus on mixtures of real substances. Helmholtz energy functionals are suitable for non-spherical, dipolar and hydrogen-bonding fluids and the models are based on the (PC-)SAFT model (Statistical Associating Fluid Theory) using simple weighted density approximations. Applications for fluid-fluid and solid-fluid interfaces will be presented in one, two and three dimensional problems. Finally, time-dependent applications of these models within a hydrodynamic DFT will be discussed.

11:00-11:30 Discussion

11:30-14:00 Break and informal discussions

14:00-14:30 Antoine Barthes (Laboratory for the Thermodynamics of Complex Fluids and their Reservoirs - LFCR / UMR 5150)
Confinement of a water fluid film during crystallization in nanopores : a DFT study

14:30-15:00 Thomas Bernet (Imperial College London)
Beyond the mean-field approximation for pair correlations in classical density functional theory: SAFT-VR Mie DFT

15:00-15:30 Alberto Scacchi (Department of Chemistry and Materials, Aalto University)
Sensitive dependence on molecular interactions of length scales in sheared soft matter

15:30-16:00 Discussion

Thursday 6th May

09:30-10:00   **Daniel de las Heras** (University of Bayreuth)
Out-of-equilibrium internal forces in Brownian systems

10:00-10:30   **Jonna Roden** (University of Edinburgh)
PDE-Constrained Optimization for Multiscale Particle Dynamics

10:30-11:00   **Discussion**

11:00-11:30   **Michael te Vrugt** (Institute of Theoretical Physics, Center for Soft Nanoscience, University of Münster)
Effects of social distancing and isolation on epidemic spreading modeled via dynamical density functional theory

11:30-12:00   **Alastair Rucklidge** (University of Leeds)
Soft matter quasicrystals with six-fold symmetry: pattern formation, mode interactions and tilings

12:00-12:30   **Discussion, Lightning Talks + Closing**

12:30 –   Informal Discussion

Contributed Talk Abstracts

Alina Ciach (Instytut Chemii Fizycznej PAN, Warszawa)
Correlation functions in concentrated electrolytes from combined density functional and statistical field theories

Experiments show anomalous increase of correlations with increasing concentration of ions in concentrated electrolytes, whereas classical theories predict decreasing screening length. In the talk, a self-consistent theory for concentrated electrolytes will be presented. In our theory, oscillatory decay of the charge-charge correlation function with the decay length that shows perfect agreement with the experimentally discovered and so far unexplained scaling is obtained. For the density-density correlations, monotonic asymptotic decay with the decay length comparable with the decay length of the charge correlations is found. From the theory it follows that the correlation lengths in concentrated electrolytes depend crucially on the local variance of the charge density.

Martin Oettel (University of Tübingen)
The direct correlation function of a solid

Direct correlation functions (DCFs), linked to the second functional derivative of the free energy with respect to the one-particle density, play a fundamental role in a statistical mechanics description of matter. This holds in particular for the ordered phases: DCFs contain information about the local structure including defects and encode the thermodynamic properties of crystalline solids; they open a route to the elastic constants beyond low temperature expansions. Via a numerical tour de force we have explicitly calculated for the first time the DCF of a solid: based on the fundamental measure concept we provide results for the DCF of a hard sphere crystal. We demonstrate that this function differs at coexistence significantly from its liquid counterpart – both in shape as well as in its order of magnitude – because it is dominated by vacancies. We provide evidence that the traditional use of liquid DCFs in functional Taylor expansions of the free energy is conceptually wrong and show that the emergent elastic constants are in good agreement with simulation-based results.

Peter Cats (Utrecht University)
The Puzzling Decay Length in Concentrated Electrolytes

Recent experiments show that the distance-dependence of the force between two external surfaces immersed in a variety of concentrated electrolytes and ionic liquids is of much longer range than theoretically predicted. These experimental findings are puzzling and inspired a lot of theoretical and computational efforts recently. We investigate this anomaly using a classical Density Functional Theory (DFT) approach in which electrostatics and packing effects of the Restrictive Primitive Model (RPM) are taken into account at the level of the Mean Spherical Approximation (MSA) and the Fundamental Measure Theory, supported by molecular dynamics simulations. We study electrolytes in a similar setting/geometry as in the experiments, which opens a playground to investigate the

structure and the thermodynamics of these systems for a variety of system parameters. In particular, we calculate the decay length of charge-charge and number-number correlations and compare those to the decay length of the force between two planar surfaces.

We indeed find that the force-decay length from DFT follows the expected charge-charge correlation length at low concentrations and is taken over by the number-number decay length at high concentrations, in agreement with old theoretical predictions from integral equation theory. However, although the various theoretical predictions for the RPM are all consistent, and seem to be supported by sophisticated simulations, there is still a large discrepancy between theory and experiments.

Sabine Jansen (LMU Munich)
A new inversion theorem with applications to density functionals

The talk presents a novel inversion theorem for functionals in infinite-dimensional Banach spaces in situations where Banach inversion theorems may fail. The spaces may represent, for example, spaces of density profiles in a gas or probability distributions on rod orientations in a liquid crystal. The functional maps an activity profile $z(x)$, possibly given by $z(x) = z_0 \exp(- V_{ext}(x)/k_BT)$ with V_{ext} some external potential, to a density profile $\rho(x)$. The inversion theorem is used to give a rigorous proof of convergence of an Onsager-type functional for the free energy of a liquid crystal or polydisperse mixtures with unbounded object size in a regime of overall low density. Based on joint work with Tobias Kuna and Dimitrios Tsagkarogiannis (arXiv:1906.02322 [math-ph]).

Peter Yatsyshin (The Alan Turing Institute, London)
Data-Driven Classical Density Functional Theory: A Case for Physics Informed Learning

In traditional sense, physical modeling is often associated with analytic derivations, followed by computation and validation against data. On the other hand, modern statistical inference offers principled means to accomplish similar goals numerically, whilst staying in touch with the data at all stages of modelling. In the present talk we explore the synthesis of both these paradigms, applied to modelling classical many-body systems. We propose a data-driven physics-informed inference framework for Helmholtz free energy functionals of such systems. Our approach is fully Bayesian and yields uncertainty quantification of the inferred model about its own predictions. The proposed algorithm trains humanly interpretable analytic free energy functionals using particle data, obtained from small-scale simulations. We focus on classical statistical-mechanical systems with excluded volume repulsive interactions and use a prototypical case of a one-dimensional fluid for algorithm validation. We are able to train canonical and grand-canonical representations of the underlying system. Extensions to higher-dimensional systems are conceptually straightforward. Using standard coarse-graining techniques, our results can also be made applicable to fluids with attractive-repulsive interactions.

Matthias Schmidt (Universität Bayreuth)
Fluctuation profiles for fluids and Noether's Therorem in Statistical Mechanics

I give an overview of new tools for practical applications of classical density functional theory along with fresh insights into fundamental sum rules. First, a set of three one-body fluctuation profiles [1] is introduced. These fields measure locally the covariance of the density distribution with either particle number, entropy, or energy. The first of these profiles is the local compressibility, as much advocated in recent work by Evans and his coworkers for the analysis of drying and hydrophobicity. Secondly, I show that Noether's mathematical calculus of invariant variations can be fruitfully applied to density functional theory, enabling one to both derive classical sum rules with ease and also to extend these results systematically, both in and out of equilibrium [2]. As a specific example, active interface polarization is shown to be a state function [3], as was recently confirmed in experiments [4] and numerically [5].

[1] Fluctuation profiles in inhomogeneous fluids, Tobias Eckert, Nico C. X. Stuhlmüller, Florian Sammüller, and Matthias Schmidt, Phys. Rev. Lett. 125, 268004 (2020).
[2] Noether's Theorem in Statistical Mechanics, Sophie Hermann and Matthias Schmidt (submitted).
[3] Active interface polarization as a state function, Sophie Hermann and Matthias Schmidt, Phys. Rev. Res. 2, 022003(R) (2020).
[4] Active-particle polarization without alignment forces, Nicola Andreas Söker, Sven Auschra, Viktor Holubec, Klaus Kroy, Frank Cichos, arXiv:2010.15106
[5] Polarization-density patterns of active particles in motility gradients, Sven Auschra, Viktor Holubec, Nicola Andreas Söker, Frank Cichos, Klaus Kroy, arXiv:2010.16234

Antoine Barthes (Laboratory for the Thermodynamics of Complex Fluids and their Reservoirs - LFCR / UMR 5150)
Confinement of a water fluid film during crystallization in nanopores : a DFT study

Water confined in porous materials has attracted great attention due to its large number of applications such as the conservation of porous building materials in civil engineering. Crystallization of water in porous media involves extremely high pressures able to produce the deformation of the porous matrix. When crystallization occurs in a pore, the interactions between the crystal and the skeleton have led to the concept of "crystallization pressure". It has been supposed that the interaction should be mediated by the presence of a thin water fluid film (a few nanometer thick) located in between them.

This study aims to describe the thin water film occurring between the ice crystal and the solid surface of a porous material during crystallization and to compute the pressure of this inhomogeneous film. A molecular non-local Density Functional Theory (NLDFT)   coupled with the Statistical Associative Fluid Theory for potential of variable range (SAFT-VR)   has been developed and employed to obtain the equilibrium distribution of water molecules confined into this slit-like nanopore consisting of the wall of ice on one side and a graphitic surface on the other side. Several configurations are explored by changing both the thermodynamic conditions and the water film width.

Thomas Bernet (Imperial College London)
Beyond the mean-field approximation for pair correlations in classical density functional theory: SAFT-VR Mie DFT

We present a free energy functional that explicitly takes into account pair correlations between molecules in inhomogeneous fluids. The framework of classical density functional theory (DFT) is used to describe variations in the density of molecules interacting with a Mie potential (a generalized Lennard-Jones potential). The statistical associating fluid theory developed for this intermolecular potential (SAFT-VR Mie) is selected as a reference for the homogeneous bulk limit of the DFT model. We make note of the importance of having an accurate description of the pair correlation for the estimation of the free energy thus formulate the theory following the Barker-Henderson high temperature expansion to find an inhomogeneous equivalent of the SAFT-VR Mie free energy as a functional of the local density. In order to use this new functional in adsorption studies, a non-local DFT version is considered, with specific weighted densities describing the neighbourhood effects of molecules. The computation of these quantities is possible in three-dimensional space, for any pore geometry, with repulsive or attractive walls. We showcase examples to validate the new functional, revealing a very good agreement with molecular simulations. The new SAFT-DFT model is well-adapted to describe realistic complex confined systems, extending the SAFT EoS to model the adsorption in confined media.

The example of a fluid confined in a cylindrical pore with continuous wall is considered to point out the effects of a wall curvature on the fluid density distribution and adsorbed quantities. The approach also can deal with explicit surfaces and roughness. The density profile of a fluid around a single fixed molecule is a specific example of this formulation, which reproduces the radial distribution function of a Mie fluid. This case is a reference test to show the validity of the approach with non-ideal walls.

Alberto Scacchi (Department of Chemistry and Materials, Aalto University)
Sensitive dependence on molecular interactions of length scales in sheared soft matter

The structure and degree of order in soft matter and other materials is intimately connected to the nature of the interactions between the particles. One important research goal is to find suitable control mechanisms, to enhance or suppress different structures. Using dynamical density functional theory, we investigate the interplay between external shear and the characteristic length scales in the interparticle correlations of a model system.

We show that shear can controllably change the characteristic length scale from one to another quite distinct value. Moreover, with specific small changes in the form of the particle interactions, the applied shear can either selectively enhance or suppress the different characteristic wavelengths of the system, thus showing how to tune these. Our results suggest that the nonlinear response to flow can be harnessed to design different actively responsive materials.

Daniel de las Heras (University of Bayreuth)
Out-of-equilibrium internal forces in Brownian systems

Understanding and predicting nonequilibrium phenomena is a challenge in Statistical Physics, relevant in several research fields from quantum-mechanical to biophysical systems. We provide fundamental steps forward in that direction for systems undergoing Brownian dynamics, such as e.g. colloidal and active systems. Four different types of force fields determine the time evolution of a Brownian system: (i) the diffusive term due to the random Brownian motion, (ii) the external force, (iii) the friction force due to the solvent-particle interaction, and (iv) the internal force field due to the interparticle interactions. The internal force field is the only nontrivial contribution that needs to be approximated in any theoretical treatment. Here we rationalize and classify the internal force field and identify four fundamentally different types of internal forces that naturally split into forces that act on the flow and forces that act on the structure of the system. We provide a method to obtain all forces in computer simulations and also construct a power functional theory that reproduces the observed behaviour [1].

[1] Flow and structure in nonequilibrium Brownian many-body systems, D. de las Heras and M. Schmidt, Phys. Rev. Lett. 125, 018001 (2020)

Jonna Roden (University of Edinburgh)
PDE-Constrained Optimization for Multiscale Particle Dynamics

There are many industrial and biological processes, such as beer brewing, nano-separation and bird flocking, which can be described by integro-PDEs. These PDEs describe the dynamics of a particle density within a fluid bath, under the influence of diffusion, external forces and particle interactions, and can be regarded as DDFTs. They often include nonlinear, nonlocal boundary conditions.

A key challenge is to optimize these types of processes. For example, in nano-separation, it is of interest to determine the optimal inflow rate of particles (the control), which leads to high separation of the particles (the target), at a minimal financial cost. Mathematically, this requires tools from PDE-constrained optimization. A standard technique is to derive a system of optimality conditions and solve it numerically, but the nonlocal nature of the PDE and boundary conditions presents additional theoretical and numerical challenges.

I will present the integro-PDEs that describe the optimality conditions for such a DDFT optimization problem. Furthermore, I will introduce a numerical method, which combines pseudospectral methods with a sweeping algorithm. This provides a tool for the fast and accurate solution of these optimality systems. Finally, some examples of current work and future industrial applications will be given. This is joint work with Ben Goddard and John Pearson.

Michael te Vrugt (Institute of Theoretical Physics, Center for Soft Nanoscience, University of Münster)
Effects of social distancing and isolation on epidemic spreading modeled via dynamical density functional theory

For preventing the spread of epidemics such as the coronavirus disease COVID-19, social distancing and the isolation of infected persons are crucial. However, existing reaction-diffusion equations for epidemic spreading are incapable of describing these effects. In this talk, we present an extended model [1] for disease spread based on combining a susceptible-infected-recovered model with a dynamical density functional theory [2] where social distancing and isolation of infected persons are explicitly taken into account. We show that the model exhibits interesting transient phase separation associated with a reduction of the number of infections, and provides new insights into the control of pandemics. An extension of the model [3] allows for an investigation of adaptive containment strategies. Here, a variety of phases with different numbers of shutdowns and deaths are found, an effect that is of crucial importance for public health policy.

[1] M. te Vrugt, J. Bickmann, R. Wittkowski, Nature Communications 11, 5576 (2020)
[2] M. te Vrugt, H. Löwen, R. Wittkowski, Advances in Physics 69, 121-247 (2020)
[3] M. te Vrugt, J. Bickmann, R. Wittkowski, arXiv:2010.00962 (2020)

Alastair Rucklidge (University of Leeds)
Soft matter quasicrystals with six-fold symmetry: pattern formation, mode interactions and tilings

Since their discovery, there has been a strong connection between quasicrystalline material structures and aperiodic tilings. The inflation rule for constructing the aperiodic Penrose tiling guarantees ten-fold rotation symmetry in the power spectrum and tilings based on squares and equilateral triangles can have twelve-fold symmetry, matching the ten-fold or twelve-fold symmetry in the diffraction spectrum of metallic and soft-matter quasicrystals. What is less clear is: given an aperiodic tiling, are there systems of particles that will assemble to match the tiling? Here we examine two tilings based on combinations of small and large equilateral triangles along with a rectangular tile whose edges match the two triangles. We use the diffraction spectrum of the two tilings and mode interaction ideas from pattern formation to design soft particle interaction potentials that encourage quasicrystal formation with these structures.