

PREFACE

New developments in classical density functional theory

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Preface

New developments in classical density functional theory

Guest editors

Robert Evans

*H H Wills Physics Laboratory,
University of Bristol, Bristol
BS8 1TL, UK*

E-mail: Bob.Evans@bristol.ac.uk

Martin Oettel

*Institut für Angewandte Physik,
Universität Tübingen,
72076 Tübingen, Germany*

E-mail: Martin.Oettel@uni-tuebingen.de

Roland Roth

*Institut für Theoretische Physik,
Universität Tübingen,
72076 Tübingen, Germany*

E-mail: Roland.Roth@uni-tuebingen.de

Gerhard Kahl

*Institute for Theoretical
Physics, Technische Universität
Wien, Wiedner Hauptstraße
8–10, A-1040 Wien, Austria*

E-mail: Gerhard.Kahl@tuwien.ac.at

1. Classical density functional theory: background

The majority of Journal of Physics: Condensed Matter readers will be familiar with the basics of electronic density functional theory (DFT), developed by Hohenberg and Kohn (HK) [1] and Kohn and Sham [2] in 1964–5, and will be aware of the importance of its applications in solid state physics, quantum chemistry and in computational materials science; for recent overviews with historical perspective see [3, 4]. Fewer readers will be familiar with classical DFT, a formalism designed to tackle the statistical mechanics of inhomogeneous fluids. Whereas in electronic DFT the fundamental variable is the electron density in classical DFT this is the average one-body ‘particle’ density where the particles refer to atoms or ions, tackled at the Angstrom scale, or to colloidal particles, tackled at the micron length scale. Classical DFT has also been developed for polymeric systems and for liquid crystals. The *equilibrium* phenomena investigated using classical DFT range from the properties of fluid interfaces, including interfacial structure, surface tension, physics of adsorption and interfacial phase transitions such as wetting, to fluids subject to confining geometries as occur in porous materials and at structured substrates, and to the chemical physics of solvation. The theory of freezing, where the crystal is regarded as a particularly relevant case of a very inhomogeneous fluid, is also addressed within DFT. In recent years dynamical DFT (DDFT) has become increasingly important as a theory to treat the *non-equilibrium* physics in overdamped systems and this approach has found many applications in the study of properties away from equilibrium in colloidal science.

The development of classical DFT has similarities with that of electronic DFT. If one chooses to argue that Thomas–Fermi–Dirac theory is a precursor of HK theory, then one might also argue that van der Waals’ 1893 treatment of the liquid–gas interface [5], which used the particle density as a basic variable, and Onsager’s treatment of the isotropic to nematic transition in hard-rod model fluids, using particle position and orientation as fundamental variables [6], were early examples of classical DFT. However, without the fundamental variational principle of HK the basis of both electronic and classical DFT would be questionable. Thus the Guest Editors associate the origins of what is now termed classical DFT with papers from the late seventies where various authors built upon ideas from HK. More specifically these papers built upon the less-well recognized work of Mermin [7] whose beautiful three page paper in 1965 extended HK to non-zero temperature and developed a variational principle for the grand potential as a functional of the electron density. The Mermin treatment translates straightforwardly to classical (Boltzmann) statistics appropriate for most liquids; one has a rigorous variational principle for the grand potential as a functional of the average particle density. The first application, using an approximate functional based on a partial summation of the gradient expansion due to HK, was reported in 1976 by Ebner *et al* [8] (see also [9]) who studied the surface tension of the liquid–gas interface and the density profile of a repulsive wall–liquid interface for a simple Lennard–Jones fluid. It is interesting that in the same year Yang *et al* [10], not knowing about the HK–Mermin formalism for electrons, published a formal derivation of square gradient theory for a fluid interface. In Appendix A of their paper a Legendre transformation from external potential as variable to particle density as variable is introduced¹—which we now recognize as a key ingredient of DFT. The article by Evans published in 1979 [12] showed that earlier formal developments in the classical statistical mechanics of

¹ In this context, Yang *et al* refer to the paper [11], a far-reaching contribution which describes a stationary entropy principle involving functionals of distribution functions.

inhomogeneous fluids, employing functional methods, could be derived in a straightforward way using the variational approach of DFT. Reference [12] also pointed to the possibility of developing new approximate treatments based on DFT ideas and to applications of these.

Significant developments of classical DFT occurred throughout the 1980s. In particular, the introduction of weighted DFT's, designed to tackle the structure and thermodynamics of inhomogeneous hard-sphere (HS) liquids, was influential. The HS model constitutes a basic reference system for treating the strongly repulsive interactions between atoms and between colloidal particles. Incorporating the effects of HS packing occurring at high local density constitutes a major challenge for a DFT description. It was soon recognized that a non-local HS functional is required in which a weighted, or smoothed, density enters a 'local' functional. The weighted density is an integral over the actual, highly oscillatory, particle density multiplied by a suitable weight function. Early attempts are reviewed in [13]. A key contribution was that of Tarazona [14] but the major breakthrough came in the ingenious work by Rosenfeld in 1989 [15] who introduced fundamental measure theory (FMT) to characterize geometrically what the set of weight functions should be. There have been several sophisticated improvements on and applications of Rosenfeld's theory. Some of these are described in this Issue.

The roots of DDFT are equally diverse. There were many attempts to formulate *microscopic* descriptions of dynamics within a DFT framework. Reference [12] provides an early empirical one. The field was placed on a firm footing by the papers of Marconi and Tarazona [16, 17] showing that for Brownian dynamics, appropriate to colloidal particles, one can establish a proper theoretical framework. The essence is a drift-diffusion equation where the gradient of a local chemical potential drives the one-body particle density. A later paper by Archer and Evans [18] provided an alternative derivation of the basic equation of DDFT starting from the Smoluchowski equation. The recent treatments of Brader and Schmidt [19, 20] are important. They go much further in that the authors derive a variational treatment, based upon what they term a power functional, that provides (i) a rigorous framework for formulating dynamical treatments within the DFT formalism and (ii) a systematic means of deriving new approximations.

There are several review and introductory articles on classical DFT that we recommend. Work on equilibrium DFT up to 1990 is reviewed by Evans [13]. More recent developments in HS and hard particle DFT are treated by Roth [21] and by Tarazona *et al* [22]. Some readers might find the two sets of lecture notes from a Summer School in 2009 [23, 24] useful introductions. Perhaps the most recent review is that of Lutsko [25]. One should note that classical DFT has made it into the text books; the most recent edition of Hansen and McDonald contains an admirable treatment [26]. The foundations of DDFT are less well documented. These are introduced briefly in [24, 25]; for up to date accounts see [19, 20].

The articles in this Special Issue cover the full gamut of the subject area.

2. Articles in the special issue

This preface is a humble attempt by the Guest Editors to provide a first impression and a reading map to the readers of this Special Issue. It should not be taken as an exhaustive and authoritative summary of all the outstanding contributions that follow. As a rough guide, we distinguish between contributions that develop a new approach or a new functional and contributions that apply existing theories to a certain problem. Both areas are very active. Moreover these complement each other and demonstrate that there are many productive new developments emerging in the classical DFT community. In several manuscripts we find both aspects, i.e. construction of new functionals often goes hand in hand with applications.

2.1. Fundamentals and new functionals

There is much activity in the development of new functionals and methods. These efforts allow the practitioners of DFT to employ steadily improving theories for a growing number of different classes of soft matter systems. As mentioned in section 1, one of the central model systems in liquid state physics is the hard-sphere (HS) fluid. While there are

several functionals for HS systems within the framework of FMT [15, 21, 22], which perform accurately when results are compared to computer simulations, there is scope for improvement. Since the range of the FMT weight functions is given by the HS radius it follows that the ranges of the direct correlation functions are similarly restricted; this is only valid approximately. A generalized FMT approach that extends the range of the HS weight functions is described by Hansen–Goos [27].

FMT for HS and mixtures of HS has often proved a good starting point for tackling other hard particle systems. However, it is well-known that phase transitions are particularly sensitive to details of the actual particle shape. González-Pinto *et al* [28] investigate the phase behavior and correlation functions of a 2D system of parallel hard squares in bulk and confined in narrow channels, comparing results from a FMT approach with those from transfer matrix methods and simulation. Wittmann *et al* [29] describe results for the liquid crystal phase diagram and the Frank elastic constants of hard spherocylinders, obtained using Fundamental Mixed Measure Theory and a new variant of this.

The close link between coarse-graining and DFT methods is described by Ciach and Gozdz [30]. Their objective is to construct a DFT for mesoscopic inhomogeneities, e.g. those generated in systems with competing interactions.

Molecular systems, most notably water, provide a long-standing challenge for the DFT community. The idea of formulating a molecular DFT in terms of density and polarization variables is pursued by Jeanmairet *et al* [31]. Their aim is to develop a DFT, using as input the structural properties of bulk water (the solvent), that is suitable for general investigations of solvation. The solute acts as an external potential for the ordering of the inhomogeneous solvent.

Electrostatic (Coulomb) interactions are important in both simple and complex fluids. However, such interactions are difficult to treat within DFT due to the long-ranged character of the pair interaction and the necessity of having an accurate treatment of screening in ionic systems. In this Special Issue there are two contributions focusing on functionals for charged fluids. Roth and Gillespie [32] provide a new interpretation of the thermodynamics of the Mean Spherical Approximation for charged HS in terms of the interaction of shells of charge. This leads to a new functional for this important model system. The second contribution, by Härtel *et al* [33], focuses on dense ionic solutions confined in planar capacitors. Here HS packing is treated within FMT while electrostatics are incorporated using a mean-field treatment. The framework of DFT allows the authors to investigate two-body correlations, measured parallel to the walls, as well as one-body density profiles in the electrical double layer.

2.2. Directional interactions, Wertheim perturbation theory and functionals for polymer systems

An important step on the path from a simple to a complex fluid can be made by utilizing the Wertheim theory for associating fluids [34] for patchy particles and for polymers. An appealing aspect of the Wertheim approach is that it can be extended to inhomogeneous systems; for a formulation within the framework of FMT see [35]. Several contributors to this issue present new extensions of the Wertheim approach.

The potential richness of the bulk phase behavior in such systems is demonstrated for models with temperature activated patches—see de las Heras and Telo da Gama [36]. An extension of Wertheim’s theory, which was designed originally for only one bond per patch, is presented by Haghmoradi *et al* [37]. Their DFT treatment of an inhomogeneous polymeric fluid accounts for multiple bonds per patch and therefore includes chain and ring configurations.

Wertheim’s approach [34, 35] is developed for 2D polymers by Słyk *et al* [38]. The resulting DFT is used to investigate the adsorption of polymeric monolayers, making connections with self-consistent field theoretical treatments. An alternative approach to polymer DFT originates with Woodward and co-workers in the 1990s. In this issue Wang *et al* [39] extend the theory to living random copolymers and employ this to investigate a model of amyloid peptide adsorption on surfaces with varying attraction.

The contributions in this subsection illustrate the applicability and usefulness of DFT for complex soft matter systems.

2.3. Phase transitions and interfaces between phases

Some of the earliest applications of classical DFT [12] were centered on problems of phase transitions and how to describe the inhomogeneous density distributions that arise in the regions where different phases meet. Such problems continue to attract much attention as can be seen from several contributions in the present issue.

Nanobubbles, which are generically difficult to treat in the grand canonical ensemble and hence within DFT, are investigated by Okamoto and Onuki [40] using a binary mixture model for a solvent with traces of solute. The authors study the stability of a solute-rich gas bubble immersed in a liquid solvent, mimicking water, using equilibrium DFT and also present a treatment of the bubble dynamics that evolve on decompressing the liquid.

Although the liquid–vapor interface is well-investigated, there remain fundamental questions about the nature of interfacial fluctuations and two-body correlations even for a simple (Lennard–Jones type) fluid. A controversial topic concerns the validity and usefulness of the concept of a wavelength-dependent surface tension. Using different approaches, Parry *et al* [41] and Chacón and Tarazona [42] address this topic, targeting the connection between DFT and capillary wave models.

Ibagon *et al* [43] investigate the three-phase contact line formed by the liquid–gas interface of an electrolyte at a charged substrate. Using DFT for a lattice model, the authors determine the structure of the contact line and describe how the line tension depends on surface charge density and temperature.

Koga and Widom [44] use square-gradient DFT to determine interfacial properties for two simple models of a three-component fluid mixture that exhibit critical endpoints and a tricritical point. At the latter, where three previously distinct phases lose their separate identities and become a single phase, there are profound implications for the interfacial tensions.

As stated earlier, a crystal can be considered as an extremely inhomogeneous fluid and is therefore accessible to treatment by DFT. Archer and Malijevský [45] investigate surface freezing and melting at a planar wall and in a wedge for a 2D system of soft, purely repulsive particles. Using a mean-field DFT, equivalent to the random phase approximation, they find a rich phenomenology emerging. A new DFT treatment of the crystalline phase of the Asakura–Oosawa (AO) model of a colloid–polymer mixture is described by Mortazavifar and Oettel [46]. Results for the full phase diagram (gas, liquid and solid) of the AO mixture, obtained within the context of a single FMT based theory, are in good agreement with available simulation data.

2.4. Dynamics

In section 1 we mentioned that overdamped Brownian dynamics in classical systems can be treated within the original DDFT approach [16–18] or the generalized framework of the power functional [19, 20]. DDFT in its original form builds directly on the equilibrium free energy functional and, as such, is well-suited for immediate applications to colloidal flow in solvents and to other dynamical phenomena in colloid physics.

Zimmermann *et al* [47] employ DDFT to investigate the flow of 2D colloidal crystals and fluids driven through a linear channel with a constriction. The functional that is employed accounts for the bulk freezing transition in the model, i.e. particles with dipole–dipole interactions. DDFT captures the flow scenarios found in particle resolved Brownian dynamics simulations.

An extension of DDFT to cluster formation arising from chemical reactions is described by Lutsko [48]. The impetus for the study is an attempt to understand the occurrence of dense, disordered clusters which appear to play a role in a nucleation pathway for protein crystallization.

The derivation of generalized diffusion equations, that incorporate long-ranged hydrodynamic interactions, is discussed by Bleibel *et al* [49]. The authors use DDFT to develop a theory for the diffusion behavior of a colloidal monolayer at a fluid interface focusing on long wavelength anomalies.

Binary mixtures of rod-like colloids undergoing shear are investigated by Lugo-Frías and Klapp [50]. Starting with a microscopic DFT, the authors develop a mesoscopic free energy

functional in terms of orientational order parameter tensors. Doi–Hess order parameter dynamics is then employed to reveal a rich variety of dynamical states.

DDFT is an approximate theory. Inspired by results for exactly solvable limits, Scacchi *et al* [51] describe how to make systematic corrections to DDFT for the important case of driven systems and show that results for Poiseuille flow are in good agreement with those from Brownian dynamics simulations.

An important conceptual question about DDFT is addressed by de las Heras *et al* [52]. Given its foundations, equilibrium DFT lives naturally in the grand canonical ensemble. However, the dynamics treated by DDFT conserves the (average) number of particles in the system. The contributors argue that the particle conserving dynamical theory presented is ‘applicable to any system for which a grand canonical DFT is available’.

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