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Density functional theory of inhomogeneous classical fluids: recent developments and new perspectives

H Löwen

Institut für Theoretische Physik II, Heinrich-Heine-Universität Düsseldorf, Universitätsstraße 1, D-40225 Düsseldorf, Germany

E-mail: hlowen@thphy.uni-duesseldorf.de

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Abstract

An introduction is given to this special issue which focuses on recent developments and future perspectives in density functional theory of inhomogeneous classical fluids. Different strategies and applications of classical density functional theory are discussed. The topics briefly treated are different approximation schemes for different interparticle interactions, binary mixtures and polydisperse systems, application to interfaces, wetting, confined geometries and porous media and also dynamical problems treated by density functional theory. Particular emphasis is placed on recent applications of Rosenfeld's fundamental measure approach. Finally a guide is presented to the subsequent articles in this Special Issue.

1. Introduction

Historically, the treatment of the inhomogeneous liquid–gas interface by van der Waals [23] in 1894 is probably the first density functional study. This can retrospectively be classified as a local density approximation [24]. The first quantum density functional study was performed by Thomas [25] and Fermi [26] in their seminal development of the theory of the electron gas. For classical fluids, the functional language was developed in the early 1960s (see e.g. [27, 28]). In 1964, Kohn and Hohenberg [29] derived the celebrated variational principle for the ground state energy of (quantum mechanical) electrons. One year later this was generalized to non-zero temperature by Mermin [30]. After a further decade it was realized that the density functional variational methods were readily applicable to classical fluids where they could also generate useful approximation schemes; see e.g. the work of Ebner and Saam [31, 32] and Yang *et al* [33]. A more detailed historical discussion can be found in [34].

In a nutshell, the foundation of classical density functional theory is based on the existence of a grand canonical free energy functional $\Omega(T, \mu, [\rho(\vec{r})])$ of the one-particle density $\rho(\vec{r})$ in the (one-component) system, which depends parametrically on the two thermodynamic

variables temperature T and chemical potential μ [34, 35]. The functional becomes *minimal* (at fixed T and μ) for the equilibrium one-particle density $\rho_0(\vec{r})$, i.e.

$$\left. \frac{\delta \Omega(T, \mu, [\rho])}{\delta \rho} \right|_{\rho=\rho_0(\vec{r})} = 0 \quad (1)$$

and the value of the functional at the equilibrium density $\Omega(T, \mu, [\rho = \rho_0])$ is the real equilibrium grand canonical free energy.

In general, the functional $\Omega(T, \mu, [\rho(\vec{r})])$ can be decomposed as follows:

$$\Omega(T, \mu, [\rho]) = \mathcal{F}_{id}(T, [\rho]) + \mathcal{F}_{excess}(T, [\rho]) + \int d^3r \rho(\vec{r}) V_{ext}(\vec{r}) - \mu \int d^3r \rho(\vec{r}) \quad (2)$$

where $V_{ext}(\vec{r})$ is the (given) external potential acting on the particles. Such a potential can describe system boundaries, gravitational fields or periodic laser-optical fields. The ideal Helmholtz free energy functional is known exactly:

$$\mathcal{F}_{id}(T, [\rho]) = k_B T \int d^3r \rho(\vec{r}) [\ln(\Lambda^3 \rho(\vec{r})) - 1] \quad (3)$$

where Λ is the thermal wavelength of the particles and k_B is Boltzmann's constant. If the system is an ideal gas, the excess part $\mathcal{F}_{excess}(T, [\rho])$ vanishes with the result that the density functional is known exactly. Note that this is different from the quantum case where it is much harder to represent the kinetic energy as a functional of the density. For a non-ideal system, characterized by a non-vanishing interaction (e.g. by a pair potential $V(r)$), the excess part $\mathcal{F}_{excess}(T, [\rho])$ is not known in general and one has to rely on approximations. The quality of different approximations can be checked via the relation between $\mathcal{F}_{excess}(T, [\rho])$ and the direct correlation function $c^{(2)}(\vec{r}, \vec{r}')$ in the homogeneous bulk fluid:

$$c^{(2)}(\vec{r}, \vec{r}') = - \frac{1}{k_B T} \left. \frac{\delta^2 \mathcal{F}_{excess}}{\delta \rho(\vec{r}) \delta \rho(\vec{r}')} \right|_{\rho_0(\vec{r})=\rho} \quad (4)$$

Approximations for $\mathcal{F}_{excess}(T, [\rho])$ have been performed on different levels. In the local density approach, one approximates

$$\mathcal{F}_{excess}(T, [\rho]) = \int d^3r f_{excess}(T, \rho(\vec{r})) \quad (5)$$

where $f_{excess}(T, \rho)$ is the excess free energy per volume of a homogeneous system with density ρ at temperature T . This yields a delta-like direct correlation function of zero range. A finite range of the direct correlation function is produced in the non-local mean-field approximation:

$$\mathcal{F}_{excess}(T, [\rho]) = \frac{1}{2} \int d^3r \int d^3r' V(|\vec{r} - \vec{r}'|) \rho(\vec{r}) \rho(\vec{r}') \quad (6)$$

which leads to $c^{(2)}(\vec{r}, \vec{r}') = -V(|\vec{r} - \vec{r}'|)/k_B T$. Traditionally the mean-field approximation is used only for the long-ranged attractive part of the interparticle pair potential while the short-ranged repulsive part is treated differently.

More sophisticated schemes take the direct correlation function as input and construct an approximation from a functional Taylor expansion around a homogeneous reference state. Possibly the first attempt in this direction was made by Ebner and co-workers [31, 32, 36, 37]. A similar approach was later applied to the freezing transition of hard spheres by Ramakrishnan and Yussouff [38]. As a next step, non-perturbative versions involving weighted densities in the argument of $f_{excess}(T, \rho(\vec{r}))$ in equation (5) were proposed and discussed by Tarazona [39, 40] and by Ashcroft *et al* [41, 42]; see also [43]. The next breakthrough was a hard-sphere functional relying on geometry and fundamental measure theory as proposed by Rosenfeld [44]; see also [45, 46]. This produces the analytically known Percus–Yevick approximation for

$c^{(2)}(\vec{r}, \vec{r}')$ as *output*. Rosenfeld's fundamental measure approach has given a major boost to recent density functional research as documented by many of the papers in this special issue.

With more and more reliable approximations available, density functional theory was applied to different problems of increasing complexity. The standard problem is an inhomogeneous fluid near a planar wall (modelled with a suitable interaction $V_{ext}(\vec{r})$ in equation (2)). The next step is to describe liquid–gas and fluid–fluid interfaces. Even solids can be viewed via density functional theory as strongly inhomogeneous fluids such that a unifying coherent theory of the freezing transition emerges.

The last few years have witnessed the emergence of several research directions in density functional theory. Extensive reviews of earlier work can be found in [34, 35]. First, density functional theory was generalized from the traditional system of hard spheres to soft interactions, to mixtures and to anisotropic particles. Second, density functional theory was applied to more and more complex situations. The papers contained in this issue [1–22] comprise an excellent collection of documents on different topics treated by density functional theory. An attempt is made to guide the reader to what is contained in the subsequent papers. Finally, some future perspectives and open problems in density functional theory of classical inhomogeneous fluids will be summarized.

2. Recent developments in density functional theory: increasing system complexity

2.1. Density functionals for soft interactions

As already stated, the hard-sphere system has been (and still is) the standard test bed of density functional theory. There are at least two reasons for this. First, for bulk hard spheres, the system density (or volume fraction) is the only thermodynamic parameter as temperature scales out trivially. Second, the direct correlation function of the hard-sphere fluid is well studied and the analytical Percus–Yevick approximation is available, which is reliable up to volume fractions of 30%. Though hard-sphere interactions are accurately realized for sterically stabilized colloidal suspensions, many other realistic interactions (e.g. for Coulomb systems, charged colloids and polymer coils) are soft. It is fair to say that density functional theory for soft interactions is much less developed than that for hard spheres. Let us mention and briefly discuss here some attempts at a generalization: the simplest way is to map a soft interaction onto an effective hard core. This yields realistic results for interactions which are still steep; see e.g. [47]. Some more studies are summarized in [48].

Among the more recent attempts is a generalization of Rosenfeld's fundamental measure theory to soft [49, 50] or bounded [51] interactions by Schmidt. One key problem here is the deconvolution of the Mayer function which can be done analytically only for certain classes of the interparticle interactions. This powerful concept is revisited and generalized in this issue by Sweatman [2].

Other important progress was made for bounded and very soft potentials which are realized for polymer coils [52, 53], star polymers [54] and polyelectrolyte stars [55], for instance. For bounded repulsive interactions $V(r)$, the mean-field approximation (6) becomes asymptotically exact for large densities and works amazingly well for finite densities [56]. Therefore, these systems are called mean-field fluids [57]. This has been exploited for mixtures of particles interacting via a bounded (Gaussian) potential, and the fluid–fluid interface [58] and wetting [59] were investigated within the mean-field approximation. Another application, namely the adsorption profiles of a binary mixture of star polymer solutions, is presented in this issue by Archer *et al* [10].

2.2. Density functionals in the canonical ensemble

Typically, density functional theory is formulated in the grand canonical ensemble, where the chemical potential μ of the particles is the prescribed thermodynamic variable. In the thermodynamic limit, all ensembles are equivalent, so a simple translation between different prescribed thermodynamic variables can be effected via a Legendre transform. The situation is different in finite systems, as e.g. for particles confined in a pore [60, 61], which has motivated the construction of density functional theory in the canonical ensemble [62–64]. As already briefly noted by Mermin in 1965 [30], the formalism itself can be applied in a similar way using a suitable Legendre transform. One discussion of a functional in the canonical ensemble is presented in this special issue by White and González [1].

2.3. Density functionals for binary mixtures

The density functional methods can be generalized to binary mixtures, hard-sphere mixtures being the case most frequently studied. In particular, the generalization of Rosenfeld's fundamental measure theory to a multicomponent hard-sphere mixture is straightforward. For the Asakura–Oosawa model which can be viewed as an extreme non-additive hard-sphere mixture, Rosenfeld's idea of a fundamental measure approach was recently generalized, leading to realistic correlations and fluid–fluid demixing [65, 66]. Other progress was made in the theory of effective interactions between two big particles embedded in a sea of small particles. This effective 'depletion' interaction can be obtained elegantly from a density functional description of the mixture as proposed by Roth and co-workers [67, 68]. This idea was further exploited to study effective interactions for non-additive mixtures [69], for polydisperse small particles [70], for non-spherical large particles [71] and for soft interactions [72]. In this issue, more applications to binary mixtures can be found as, e.g., in [3, 6, 10, 12, 14–16, 19].

2.4. Density functionals for polydisperse systems

Polydispersity is crucial in colloidal suspensions [73]. It is modelled by a system with infinitely many components, so the density functional is an appropriate tool for studying the effects of polydispersity. A large size polydispersity prevents crystallization in the hard-sphere system as shown in a pioneering density functional study by Barrat and Hansen [74]. In particular, a fractionation of the system into different phases can be obtained. Rosenfeld's hard-sphere functional was exploited for polydisperse systems e.g. by Cates and co-workers [75]. Another example, for colloids surrounded by a polydisperse polymer mixture, is presented by Denton and Schmidt [11]. Furthermore, the effect of polydispersity on the liquid–gas transition and the interfacial free energy was recently studied within density functional theory by Baus and co-workers [76]. Another example—Xu *et al* [17] examining fractionation and segregation in polydisperse fluids—can be found in this issue as well.

2.5. Anisotropic interactions and polymers

Particles interacting via an orientation-dependent pair potential such as dipoles or anisotropic bodies constitute a higher level of complexity than that governed by radially symmetric interactions. Progress has been made in several directions. First, the orientational dependence of a dipolar potential, as, e.g., for Stockmayer fluids, was treated perturbatively in a density functional theory by Groh and Dietrich [77]. A similar approach by Teixeira and Telo da Gama [18] can be found in this issue. Second, density functionals for anisotropic hard bodies

(such as spherocylinders and ellipsoids) were proposed (see e.g. [78]), generalizing the hard-sphere functional. In the Onsager limit of very high aspect ratios, a second-order virial theory yields the exact functional for describing the isotropic–nematic transition. Very recently, Rosenfeld’s fundamental measure theory for convex hard bodies of arbitrary shape has been generalized: one example presented by Cinacchi and Schmid [22] is contained in this issue. Another is the treatment of mixtures of rods and spheres [79]. A full explicit fundamental measure functional relying on a multipolar-type expansion is in progress [80].

Finally, let us mention applications of density functional theory to stiff and flexible particles which provide an alternative way to describe polymer solutions; see [19, 20] in this issue for examples.

3. Recent developments in density functional theory: applications to different problems

3.1. Interfaces and wetting

In order to describe an equilibrium interface between two coexisting phases, one needs a ‘unifying’ theory treating the two phases on the same level. Thus density functional theory is an appropriate tool for accessing the interfacial structure and thermodynamics. The hard-sphere solid–fluid interface is an ideal test set-up for density functional theories of freezing [81]. The orientation-dependent surface tensions have been calculated within different approximations (see [82] for a compilation of data) which can be tested against computer simulation results [83]. Unfortunately—due to technical problems in the minimization procedure—there has not yet been an investigation with Rosenfeld’s fundamental measure functional.

Furthermore, the fluid–fluid interface of a binary Gaussian core mixture was studied recently within the mean-field approximation [58]. Adsorption profiles of phase-separating binary fluid mixtures near a wall are another focus of research; see [10] in this issue for an example. Wetting transitions near a hard system wall were studied by density functional theory for the Asakura–Oosawa model [84]. A novel scenario of ‘entropic wetting’ was found and confirmed by computer simulations [85].

3.2. Confined geometries and porous media

As the external potential is one of the central variables in density functional language, confining geometries of different complexities can be described elegantly within density functional theory. One problem which is very important for biological applications is the transport of ions through channels. Effects of ion size selectivity were studied recently by Goulding *et al* [86] neglecting the ion charges using Rosenfeld’s density functional theory. The Coulomb nature of the interactions together with the dielectric discontinuities at the channel boundaries constitute a more complicated problem which is addressed in this issue by Allen and Hansen [7]. Moreover, a density functional approach for calculating the ion flux through an ion channel is discussed by Gillespie *et al* [16] in this issue.

Another active area of research concerns fluids in porous media. Again, density functional theory can be applied directly to fluids in a confined geometry of complicated topology; see the contribution of Frink and co-workers in this issue [19] for an example. Recently, it was shown by Schmidt [87] that the structure of a fluid mixture in a porous medium can be treated elegantly using the density functional approach. In this issue an extensive comparison of density functional results with integral equation theories was made by Schmidt *et al* [14], in particular for fluid–fluid phase separation, and good agreement was found.

3.3. Dynamics described within density functional theory

For dynamical phenomena, the language of density functional theory has to be generalized. The traditional approach is to use the density functional derivative to derive a chemical potential field. The gradient of the chemical potential causes a current and the continuity equation describes the time evolution of the density field. This so-called model B dynamics is often supplemented with noise terms mimicking fluctuations. The actual problem is that many kinds of dynamics are possible which lead to the same equilibrium distribution with the result that a dynamical extension of density functional theory has its ambiguities. Nevertheless, the model B dynamics has at least some intuitive justification and has been successfully applied to different situations. Clear insight into the dynamics was gained for a hard-rod system where the density functional is known exactly and different approximation levels for the dynamics can be obtained [88, 89].

One of the key applications is that to the kinetic glass transition which is understood as a structural arrest of dynamical correlations. An example of how density functional theory can be used to understand the glass transition is presented in this issue by Fuchizaki and Kawasaki [21]. A second application concerns lane formation in driven off-lattice binary systems where a dynamical extension of density functional theory has proven to reproduce the non-equilibrium computer simulation data [90]. Finally, the random sequential adsorption studied by Schmidt in this issue [15] represents another non-equilibrium situation which can be tackled by density functional theory.

4. A guide to the contents of this special issue

In any density functional study, first the *system* has to be specified via the microscopic interaction between the particles. This is schematically shown on the x -axis of figure 1 according to increasing complexity. The simplest non-trivial system is that of hard spheres. Soft spheres with a smooth interparticle interaction represent the next level and lattice fluids which require discrete variables are classified next. Then binary (two-component) and subsequently polydisperse systems follow. Anisotropic interactions require a proper treatment of the orientational degrees of freedom and finally flexible polymers have even more internal degrees of freedom.

On the other hand, the y -axis of figure 1 indicates different *problems* starting with bulk fluid thermodynamics and structural correlations in the fluid (the former being a special case of the latter). Density functional theory is the ideal tool if an external potential is present as e.g. realized for walls or confining geometries. Two coexisting fluid phases together with their interface constitute a more difficult problem. Bulk solids viewed as strongly inhomogeneous liquids require a good functional and these can be subjected to external fields as well. Even more difficult could be static questions of porous media and full dynamical situations.

The main focus of the different works contained in this special issue according to its 'system' and 'problem' is indicated as well. Although this might look a bit artificial, it may facilitate the search for a density functional study for a given system and problem. Obviously many possible combinations of different systems and problems are treated in this issue with a concentration on binary mixtures in inhomogeneous situations.

5. Future perspectives and open problems

The future will certainly see many more applications of classical density functional theory. In particular, it can be expected that the fundamental measure theory of Rosenfeld will be studied

problem	full dynamics	[21]						
	steady state situations	[15]	[16]		[16]			
	porous media	[19]			[14]			
	inhomogeneous solids	[9]						
	bulk solids			[13]	[12]		[17]	[20]
	fluid-fluid interfaces				[10]	[17]	[18]	
	fluids in external potential (e.g. walls, confined geometries)	[5]	[7]		[19] [6] [4] [12] [7] [5]	[17]		[19]
	bulk fluid: correlations	[1]	[2]	[8] [13]	[3] [6]	[11]	[17]	
	bulk fluid: thermodynamics	[1]	[2]	[8]	[12] [10]	[11] [17]	[18]	[20]
		hard spheres	soft spheres	lattice systems	binary mixtures	polydisperse systems	anisotropic interactions	polymers
		system						

Figure 1. A schematic guide to the papers contained in this issue. The system studied is shown on the x -axis and the problem addressed is listed on the y -axis. The numbers in brackets refer to the different papers in this special issue.

(This figure is in colour only in the electronic version)

further and applied to more complex questions. An application of the fundamental measure approach to *anisotropic hard bodies* [80] is promising and will most probably be elaborated for inhomogeneous situations of hard ellipsoids and spherocylinders. This could allow for a full calculation of the bulk phase diagram which involves many different liquid crystalline phases. It could also be used to study wetting transitions near walls far away from the Onsager limit.

Second, finding a flexible and reliable functional for *soft* interparticle interactions is very challenging. A generalization of the fundamental measure theory to charged hard-core particles would be highly desirable which e.g. reproduces the analytically known direct correlation function within the mean-spherical approximation. Such a functional for charged hard-core mixture would be very important for ionic solutions and many investigations of charged macromolecules.

Third, a direct functional for *attractive* interactions avoiding the standard perturbation theory is still not known. One intriguing strategy is to start from a mixture of repulsive particles and to construct a functional by integrating out one particle species leaving only a one-component system with an effective attraction. This strategy, however, has never been systematically applied to cover arbitrary attractions.

A very difficult problem concerns the role of fluctuations which are typically neglected in a mean-field-type approximation of the functional. Some important studies have been done in this direction but the problem is still far from being solved. For example, capillary wave fluctuations were systematically studied via density functional theory by Mecke and

Dietrich [91, 92] and a surface tension was found which depends in a non-monotonic way on the wavenumber of the capillary waves. It would be interesting to attack the general fluctuation problem for special cases where an exact density functional is known, as, for example, for a coexisting isotropic and nematic phase in the Onsager limit of very long rods.

The future will certainly see more applications of density functional theory to systems with more complicated interparticle interactions. It can for example, be anticipated that the mean-field approximation which becomes exact for bounded interaction potentials at high densities will provide a good starting point for studying dynamical questions within density functional theory.

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