

# Sketchy View on Classical Density Functional Theory (cDFT)

## Introductory Points

Classical Density Functional Theory (cDFT) is based on the idea that the free energy of an inhomogeneous fluid is a functional of the average one-body density. Minimizing the functional determines the equilibrium density profile and free energy while further derivatives provide correlation functions. The prime motivation behind classical density functional theory development is that methods of functional differentiation yield formally exact results more readily and elegantly than methods focusing on the partition function.

Molecular Dynamics simulations and Monte Carlo calculations with simplified Hamiltonians, often composed of additive pair potentials, are the most popular techniques used to compute properties of inhomogeneous liquids. However these can be quite expensive due to the long equilibration times and extensive phase-space sampling necessary to compute thermodynamic averages.

In contrary theories in terms of the equilibrium densities rather than individual configurations of molecules avoid this phase-space sampling and hence are much more efficient for the computation of equilibrium properties. Classical DFT focuses on the direct connection between free energy and molecular structure (density profiles) rather than on the overwhelming data generated by the trajectories of all constituent particles in molecular simulation. A microscopic state of a many-body system entails  $6N$  degrees of freedom (where  $N$  is the number of defined particles in the system), whereas the density of a spherical object is a simple function that depends solely on the three-dimensional vector  $\mathbf{r}$ . Therefore use of classical density functional

theory provides deeper insights into the underlying physics of natural phenomena and which is more important, reduces the computational demands.

Therefore density functional theory emerges as a powerful computational tool for study of the structure and thermodynamic properties of both bulk and inhomogeneous fluids. On the one hand, DFT is able to describe the microscopic structure and meso / macroscopic properties on the basis of intermolecular forces; and on the other hand, it connects seamlessly with conventional phenomenological equations for modeling macroscopic phenomena. The cDFT-based methods are generic yet versatile they are naturally applicable to systems with multiple length scales that may fail alternative computational methods. A full presentation requires review of the basic concepts of DFT for classical systems, the mathematical relations linking the microstructure and correlation functions to measurable thermodynamic quantities, and connections of DFT to conventional liquid-state theories. The term density functional theory has two interrelated versions in circulation:

1. The quantum approach developed by Hohenberg and Kohn / Kohn and Sham.
2. The classical approach first applied by Ebner, Saam, and Stroud on the basis of Mermin's pivot paper and advocated vigorously by Evans.

A brief account of the history elicits their causal relationship:

### **Density Functional Theory Chronology.**

**1964: Hohenberg and Kohn (HK) variational principle for the inhomogeneous electron gas at  $T = 0$**

*(P. Hohenberg and W. Kohn, Inhomogeneous Electron Gas, Phys. Rev. 136, B 864 (1964))*

The mathematical foundation of DFT (in quantum mechanical context), was first established by Hohenberg and Kohn in a seminal article published in 1964 concerning the ground-state properties of an electron gas. There Kohn and Hohenberg derived the celebrated variational principle for the ground state energy.

In summary:

1. Electron density  $\mathbf{n}(\mathbf{r})$  in the ground state as basic variable.
2. Electron density  $\mathbf{n}(\mathbf{r})$  determines uniquely the external potential  $\mathbf{V}_{\text{ext}}$ .
3. Existence of an unique energy / density functional  $\mathbf{E}_v[\mathbf{n}]$  with the following properties  
 $\mathbf{E}_v[\mathbf{n}_0] = \mathbf{E}_0$  and  $\mathbf{E}_v[\mathbf{n}] > \mathbf{E}_0$ .

**1965: Mermin formulates Hohenberg and Kohn (HK) variational principle for  $T > 0$**

*(N. D. Mermin, Thermal Properties of the Inhomogeneous Electron Gas, Phys. Rev. 137, A 1441 (1965))*

Hohenberg–Kohn theorem was established originally in the quantum mechanics of the ground-state energy of electrons at **0 K**. Its generalization to electrons at a finite temperature was given by Mermin. Indeed, from a mathematical perspective, classical DFT closely resembles electronic DFT (unfortunately both have the same acronym) except that in the former case, the density functional applies to the structure of atoms or e.g coarse-grained elements of a polymeric molecule, whereas the latter applies to electrons.

### **1965: Kohn and Sham equations**

*(Kohn and Sham, Self-Consistent Equations Including Exchange and Correlation Effects, Phys. Rev. 140, A 1133 (1965)).*

In the second paper, Kohn and Sham *postulated* that a system of many electrons can be equivalently represented by a noninteracting reference system where each electron moves independently in an effective potential that consists of the attractive energy due to the nuclei, the direct Coulomb repulsion among electrons, and a self-consistent local potential arising from the exchange and correlation effects. The effective one-electron *ansatz* provides a starting point for modern applications of DFT to quantum many-body problems. Today there are numerous versions of DFT, ranging from simplistic local density approximations (LDA) to more sophisticated versions. Different versions of DFT differ mostly in the exchange-correlation potential. Fueled with a pragmatic computational scheme proposed by Kohn and Sham electronic DFT has evolved into a powerful approach in computational chemistry.

### **Around 1976: application of DFT to classical systems**

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. The connection of the variational method in statistical mechanics with DFT in quantum chemistry was first recognized by Ebner, Saam and Stroud. Bob Evans summarized early developments of DFT for classical systems and applications to inhomogeneous fluids. While early developments of DFT for classical systems were primarily focused on simple fluids, much progress has been made in recent years towards more accurate formulation of the Helmholtz energy functionals

applicable to complex fluids, including those containing block copolymers, polyelectrolytes, and biomacromolecules.

## **1998: Nobel Prize in Chemistry for W. Kohn for his development of the Density**

### **Functional Theory**

So, finally, we have the powerful tool of classical density functional theory with a strong statistical mechanics foundation, with the underlying motive to express the free energy of an inhomogeneous system in terms of its density field functional. Once this functional is obtained, it can be used to calculate the structure and thermodynamic functions. We embark on our cDFT journey with description of the basic structure of the theory, followed by approximations for the free energy functional and recent developments important for our future work for both atomic and polyatomic systems.

### **Theoretical Basis**

The main task in DFT is to construct the Grand potential / Helmholtz free energy functional of density. For a (model) fluid with given effective potential one can devise approximations for the Helmholtz functional  $F[\rho]$  that should be applicable to all inhomogeneities. Thus the key idea boils down to the fact that the Helmholtz functional is a unique functional of density and its form does not depend on the external potential  $V(r)$ . Density functional theory is naturally formulated in the grand canonical ensemble. Being in the grand canonical ensemble we think in the following order so as to connect thermodynamic properties to the one-body density.

## **1. Statistical mechanics in the grand canonical ensemble**

Define Hamiltonian. Use Hamiltonian to calculate grand canonical partition sum. The grand canonical partition sum contains all the information of the system in equilibrium. From the grand canonical partition sum we can (in principle) calculate everything. If it would be possible to calculate exactly, we would not require the formalism of classical DFT. However, in general it is not possible to calculate it easily, especially for arbitrary external fields. It turns out that it is simpler to make useful approximations within the framework of density functional theory than in the evaluation of the partition sum. With the help of the partition sum we can define the equilibrium probability density. Then - average equilibrium density distribution.

## **2. Functional definition for the “grand potential”**

The grand potential is a functional of the molecular density - straightforward to prove but first consider that it is a functional of the equilibrium probability distribution:

1. Definition of an additional so called Mermin Functional.
2. For the the equilibrium probability density the functional reduces to the grand potential of the system.

## **3. Hohenberg-Kohn-Mermin variational principle**

Consider different probability distributions and compare thus defined Mermin functional with the equilibrium one by using the Gibbs inequality. The realization for the bound of the grand potential functional is a crucial first step to the variational principle of density functional theory. All above align together as the final statement of the variational principle relative to density distribution.

#### **4. Classical analog to Kohn-Sham equations**

Formally, the functional can be minimized through the variational principle. The result is technically reached via the corresponding Euler-Lagrange equation with the notable presence of the so-called direct correlation function. Given the chemical potential, the external potential and an expression for the variational Helmholtz energy functional  $F$  (contains all the information about the interparticle interaction) we can solve for the equilibrium density  $\rho$  from the Euler-Lagrange equation. The equilibrium density can then be used to determine the grand potential and all thermodynamic properties of interest.

#### **5. The total Helmholtz free energy functional can be decomposed into an ideal and excess contribution**

Whereas the mathematical framework of DFT is formally exact, a precise expression of the Helmholtz energy as a functional of the molecular density profiles is unknown for most systems of practical interest. Formulation of the Helmholtz energy functional is a task essentially equivalent to enumeration of the statistical partition function for the particular system under investigation. A viable approach, practiced in classical thermodynamics for more than 100 years, is to divide the Helmholtz energy into an ideal part and an excess part. The ideal part represents the contribution of an ideal gas where all nonbonded interactions are turned off; the excess part accounts for interactions leading to the thermodynamic nonideality.

The Helmholtz energy functional can be calculated either from the density distribution functions or from the direct correlation functions. These relations are formally exact and provide a useful starting point for developing statistical-mechanical theories of inhomogeneous fluids in terms of classical DFT.

## 5.1 Ideal Functional

For the ideal part, that is free of interactions, the Helmholtz energy functional is known exactly.

## 5.2 Excess Functional:

The functional derivatives of the excess functional are essential in solving the Euler-Lagrange equation. The functional derivatives are given as direct correlation functions. Direct correlation functions specify the response of the Helmholtz energy functional with respect to the density changes. Because there is no intermolecular correlations in an ideal-gas system, the direct correlation functions applies only to the nonideal part of the Helmholtz energy functional, i.e., the excess intrinsic Helmholtz energy.

The first-order direct correlation function can also be interpreted as the distribution of the effective one-body potential due to the intermolecular interactions. The direct one-particle correlation function vanishes for the homogeneous ideal gas; for interacting fluids it defines the chemical excess potential, both for homogeneous and inhomogeneous systems.

The second- and higher-order direct correlation functions are defined by consecutive functional derivatives of the first order direct correlation function. Because the first order direct correlation function is the functional derivative of the excess intrinsic Helmholtz energy with respect to the density distribution, the  $m_{\text{th}}$ -order direct correlation function, corresponds to the  $m_{\text{th}}$ -order functional derivative of the Helmholtz energy with respect to the density distribution. The density distribution and correlation functions provide a quantitative representation of the fluid structure and statistics. They also facilitate effective application of liquid-state theories including DFT to realistic systems.

## **6. Construction of Free Energy Functionals – the Atomistic / Molecular View**

Classical Density functional theory provides an exact mathematical framework for predicting fluid structure and thermodynamic properties. However, it does not prescribe a generic procedure for formulation of the intrinsic Helmholtz energy as a functional of the molecular density profiles. Development of a density functional is a task essentially equivalent to solving the statistical mechanical problem for the particular system under consideration. The value of classical DFT is reflected in its efficiency for analyzing thermodynamic properties directly in terms of the molecular density profile, i.e. in the context of the microscopic structure. The straightforward way to derive exact expression for the excess free energy is based on density expansions of the functional.

From an atomistic viewpoint, a generic Helmholtz energy functional must account for the contributions to the thermodynamic nonideality from each element of the intermolecular forces. In addition, it must reflect faithfully the microscopic architectures of the constituent molecules (i.e. molecular shape, chain connectivity, and conformation). The excess intrinsic Helmholtz energy is typically formulated on the basis of mathematical expansions in combination with insightful analysis of the physical phenomena under consideration. Each component of the intermolecular potential makes a distinct contribution to the excess intrinsic Helmholtz energy. The approximations introduced in developing these excess intrinsic Helmholtz energy functionals underlie different versions of classical DFT. Because excess intrinsic Helmholtz energy functionals arise from the nonbonded interactions between centers defined at atomic level (molecular structure), we make use of a variational ansatz that the excess Helmholtz energy can be expressed as a functional depending only on the atomic / molecular density details. Because the nonbonded interatomic forces are conventionally expressed in several terms e.g. short-range

repulsion, attraction, long range electrostatic and so on, each component of the intermolecular potential makes a distinct contribution to the excess free energy.

### **6.1. Short-range Repulsion.**

In statistical mechanics, the short range repulsion between two atomic particles (atoms or coarse grained elements of a polymer) is often represented by the hard-sphere model, which assumes that each particle has a physical volume prohibiting an overlap with other particles. This excluded-volume effect plays a central role in determining the structure and thermodynamic properties of condensed materials. It has been long recognized that, with an analytical theory for hard spheres, the thermodynamic nonideality arising from other components of the intermolecular forces can be included relative to this reference system. The structure and thermodynamic properties of a bulk hard sphere fluid can be accurately described by various analytical theories. Over the past two decades, numerous versions of classical DFT have been published for representing the structure and thermodynamic properties of inhomogeneous hard spheres (Evans). Among them - the fundamental measure theory (FMT), first proposed by Rosenfeld. Much work has been done to develop density functionals for the hard-sphere the standard in the field being the fundamental measure theory. Kierlik and Rosinberg (KR) formulated an alternative version of Rosenfeld's FMT. The hard-sphere functional can be used as a reference for representing the hard core interactions in a molecular system, and other interactions such as Lennard-Jones and Coulombic interactions can be added in the functional as a perturbation in order to model realistic molecular fluids, including water solutions and complex molecular environments.

## **6.2 Attractive interactions**

In addition to short-range repulsion, the attractive component is another essential component of nonbonded interatomic interactions to be considered. Most versions of DFT take a mean-field approach to account for the contribution of van der Waals forces to the excess Helmholtz energy functional. A step towards an improvement is by a quadratic density expansion of the excess Helmholtz energy functional relative to that for a uniform fluid.

This approach requires the excess chemical potential and the direct correlation function of a uniform atomic fluid as input. For that purpose, the analytical correlation functions derived from the first-order mean-spherical approximation (FMSA) are particularly useful. It has been demonstrated that, at least for relatively simple models such as Lennard–Jones systems and coarse-grained models of polymers, excellent agreement between theory and simulation results can be attained. Because the analytical expressions of both the excess chemical potentials and direct correlation functions are readily available from FMSA, the numerical implementation and computational cost of the quadratic approximation are very comparable to those for a mean-field approach.

## **10.3 Weak Association – Hydrogen bonds**

Another important component in a conventional force field is the formation of hydrogen bonds as in associating fluids. For fluid-phase equilibrium calculations, the thermodynamic perturbation theory has been successfully used to develop the statistical associating fluid theory (SAFT). By incorporation of basic concepts from classical DFT, various extensions of SAFT have been applied.

## 10.4 Correlations Attributed to Chain Connectivity

In this approach, the Helmholtz energy functional includes an exact formalism for the ideal chains that retains the details of bond connectivity and an excess part accounting for the contributions from all nonbonded inter- and intramolecular interactions. The excess Helmholtz energy functional is expressed in terms of a weighted-density approximation for short range forces and a first-order perturbation theory for chain correlations. In the weighted-density method, we assume a priori the excess Helmholtz energy functional of an inhomogeneous system is identical to that of a uniform system, except the bulk density is replaced by a locally averaged or weighted density. As extensively used for simple fluids, the weighted-density approximation provides a simple yet effective way.

In conclusion - any application of the density functional theory to a realistic physical problem requires an approximation to the free energy functional. The crux of the solution is the formulation of an effective free energy functional which in turn is guided by the specific intermolecular interactions in the considered system. Once the free energy functional is obtained, the equilibrium density field and the grand potential of the system can be determined.

## **Sketch of current density functional theories implementations.**

### **1. Preliminary Notes about Atomic vs Polyatomic fluids.**

Below is a summary of the approaches followed for atomic and polyatomic fluids.

#### **1.1 Atomic type fluids**

Evans addresses several approaches for approximating the above excess free energy functional for atomic type fluids. One of the more popular methods chosen is based on weighted density approximations (WDA) because of its highly accurate scheme and ability to adapt to most systems. Actually WDA is the first successful nonperturbative approximation for the excess Helmholtz free energy and first-order direct correlation functions. Because of its versatility and accuracy, the weighted-density approximation is the main approximation method and has many variations. The development of weighted-density approximations originates as a modification of the local density approximation (LDA). Weighted-density-functional (WDF) methods are modifications of the usual Local Density Approximation for inhomogeneous systems. The local density approximation (LDA) is the simplest scheme to build a density functional approximation. For slowly varying densities it is reasonable to assume that the macroscopic thermodynamical relations remain valid on a local scale. In the LDA, the free energy density at a point in a system with inhomogeneous single-particle density is given by the free energy per particle of a homogeneous system, evaluated at the value of the single-particle density at point. There is a systematic, although limited, way to improve the LDA in terms of density gradient expansions assuming that the generic functional is not just a locally dependent on density but also on its local gradient. LDA failures can be overcome by smearing out the density over a small spatial region, using a suitable weighting function. In the weighted-density method, we assume *a priori*

the excess Helmholtz energy functional of an inhomogeneous system is identical to that of a uniform system, except the bulk density is replaced by a locally averaged or weighted density.

## **1.2 Polyatomic fluids**

Unlike an atomic fluid, for a molecular system, intramolecular energetics (bonding constraints between the polymer segments constituting a chain) govern behavior. In classical DFT the most common molecular model for a polyatomic molecule is a chain of spherical segments which are tangentially bonded to each other. The preliminary step in developing the free energy for such a fluid is to split the free energy into an ideal and an excess part. The existing density functional methods for polyatomic systems differ in whether the intramolecular interactions are accounted for in the ideal functional contribution, the excess contribution or a combination of both. Further, a polyatomic DFT can be formulated in terms of molecular density or segment density, and can require additional input from other theories or simulations. Each therefore has its own advantages and disadvantages in regard to accuracy and computational expense. Some of the more popular and well established density functional theories, and how they differ in regard to their formulations and approximations As in the case for atomic fluids, weighted-density approximations are popular methods for estimating the free energy functionals in polyatomic fluids. The application of these approximations follows much the same procedure as in the case for atomic fluids.

## **2. Classification according to the treatment of the free energy density functional**

The wide diversity of different versions of classical DFT reflects not only the variety and complexity of natural phenomena induced by rich molecular architecture and nonbonded interactions, but also the generality of the basic idea of DFT and its applicability to a broad range of problems. For practical applications, the selection of a particular version of DFT is influenced by several factors, including not only by its numerical performance in terms of both accuracy and computing efficiency, but also by the underlying physical models, by the problems of interest and, very often, by personal taste. The approximate expressions for the excess Helmholtz energy functional discussed here allow us to address quantitatively most nonbonded interactions in a complex fluid. However, significant efforts are still required for the development of more accurate density functionals accounting for more realistic intermolecular forces. Although the mathematical framework of DFT is exact, its successful application critically depends on judicious choice of an appropriate Helmholtz energy functional suitable for the system under investigation.

Popular applications of DFT follow one of the following routes:

### ***2.1 Chandler, McCoy and Singer for macromolecules***

Classical density functional theory was first applied to polymeric systems by Chandler, McCoy, and Singer (CMS-DFT) within the framework of interaction site model. Molecules are modeled as chains of freely jointed spheres which interact with spherically symmetric site-site potentials. These interacting sites coincide with the centers of their respective segments. The free energy for such a system can be expressed as a functional of the site densities. A variational principle still exists which states that the free energy has a global minimum for the equilibrium site densities. This free energy functional has two contributions, an ideal part and a non-ideal / excess part. It is based on a functional expansion truncated at second order. This implementation is based on the

direct correlation function (DCF) for a bulk fluid at the bulk density of interest. The roots of the method are nourished by segment density functionals. In the CMS-DFT, all intramolecular interactions are accounted for in the ideal functional, while all intermolecular interactions are included in the excess contributions (site-site correlation function of the corresponding uniform fluid). As a result, their ideal functional is very accurate and is exact for an ideal chain system. The intramolecular correlation functions come at the expense of a single-chain simulation.

## **2.2 Density functionals based on thermodynamic perturbation theories TPT**

Wertheim's thermodynamic perturbation theory holds a great value and has been utilized for a wide range of applications and systems. Kierlik and Rosinberg became the first to introduce a density functional theory based on Wertheim's theory.

These theories include molecular level details to make predictions on how molecular structure affects self – assembly of associating species. For this, one needs a theory whose starting point is the interaction potential between two associating species which includes this molecular level detail. Development of accurate molecular theories for associating fluids is hampered by the strength and directionality of the association interaction. This problem was largely solved by Wertheim in the 1980's. Wertheim's cluster theory incorporates the geometry of the association interaction at an early point in the derivation. This allowed Wertheim to develop the theory in such a way that accurate and simple approximation methods could be applied such as thermodynamic perturbation theory. The TPT is based on the calculation of the excess Helmholtz free energy over a reference, the properties of which are assumed to be known (or obtainable) with reasonable accuracy. It means that the TPT assumes first the separation of the total intermolecular potential into a reference part and a perturbation. There are thus two possible sources of errors in calculations of the thermodynamic properties from the TPT: 1. An inaccurate

description of the reference system and 2. Neglect of the higher order contributions in the expansion.

In comparison with alternative methods, TPT has a great virtue in the decoupling of the nonbonded intermolecular interactions and polymer-chain connectivity. The former defines all short-range correlations that can be effectively treated by various density-functional methods developed for monatomic systems. With a reliable model for the excess Helmholtz energy, TPT provides a satisfactory description of the structure and thermodynamic properties for a wide variety of polymeric systems.

Wertheim's TPT1 is used to calculate excess free energy by forcing a mixture of spherical segments to bond in a specified order to form the polymer or solvent molecules of interest. The change in free energy due to association is obtained as a perturbation to a hard sphere reference fluid. By letting the association energy become infinitely large, complex polyatomic molecules can be constructed allowing the development of polymer density functional theories, in the framework of thermodynamic perturbation theory. Thus, the chain contribution to the free energy functional is obtained by finding appropriate association free energy functional. The equilibrium density distribution of segments can be determined by minimizing the grand free energy, yielding a corresponding set of Euler-Lagrange (EL) equations.

In 1997, Segura, Chapman, and Shukla introduced a density functional theory for describing atomic associating fluids. The work of Segura et al. is based on Wertheim's perturbation theory. From TPT1, the free energy functional for such a system of associating hard spheres can be written as a perturbation to the reference hard sphere fluid. The weighted density approximation for hard-spheres is employed, and intermolecular association effects can be included through a Wertheim's associating fluid functional.

## **Molecular Self-Assembly via classical DFT**

Amphiphilic molecules (such as surfactants) may self-organize into a variety of intriguing ordered structures in a solution. The self-assembly processes have been of prime scientific interest for decades. Applications include formation of vesicles or liposomes as carriers of therapeutic agents and as simplified models for biological membranes. The basic idea is that the organized microscopic structures satisfy a local minimum of the grand potential energy, which can be described in terms of the density-functional formalism. Based on coarse-grained models of amphiphilic molecules, DFT is able to represent not only the conditions required for vesicle formation but also the microscopic structures of vesicles, and bilayer membranes made of either one-component or multicomponent amphiphiles.

## **Future**

Future applications of DFT depend on continuing progress toward more faithful representation of density functionals reflecting molecular-level interactions and, corresponding numerical implementation methods.