

# TOWARDS STUDYING NON-EQUILIBRIUM STATISTICAL MECHANICS THROUGH DYNAMICAL DENSITY FUNCTIONAL THEORY

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## Abstract

In this brief article, the extension of density functional theory for non-equilibrium systems is presented. Density functional theory is a powerful framework in order to study the static properties of electronic systems via a variational principle whereby the density (varies in 3 dimension space) holds a key role instead of the many-body wave function. Evans (*Adv. Phys.*, 1979) fully realized the importance of this and extended the theory for inhomogeneous fluid systems. Then in an urgent need to extend the theory for dynamical equilibrium or non-equilibrium systems, comes dynamical density functional theory. Here, the idea behind dynamical density functional theory is given based on the Smoluchowski equation.

**Keywords:** density functional theory, non-equilibrium systems, variational principle, Smoluchowski equation

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## Introduction

In everyday life many physical phenomena are non-equilibrium in nature. These phenomena includes, transport processes in biological systems[1-3], (out-of-equilibrium) pattern formation[4-5], weather forecast[6-8], the behavior of a group of insects[1,9], birth and death rate[10], the evolution of the stock market[11], and so forth.

In physics, a wide variety of non-equilibrium behavior can be observed ranging from high energy physics[12-14], nano-scale phenomena[15], quantum optics (laser and maser)[12,16], radioactive decay[17], chemical reactions[18], soft materials, e.g. sedimentation of colloids[19,20], and liquid crystals[21,22], up to astrophysics and cosmology[23].

There is an interesting underlying principle of such diverse physical phenomena which is worthwhile to be studied. This is their stochastic behavior driven by external forces such that non-vanishing current occurs in the systems.

Hence, it is clear that these phenomena should be studied through statistical physics. However, we cannot directly apply the usual equilibrium statistical physics to non-equilibrium systems. This is of course a consequence of the systems being driven by some external potential which need not be thermally activated. In equilibrium regime, such currents are absence. That is why the so called non-equilibrium statistical mechanics is needed.

## Equilibrium and Non-Equilibrium Statistical Mechanics

Equilibrium statistical mechanics deals with static microscopic properties of a system, which is the basis for thermodynamics. The foundation of equilibrium statistical mechanics itself is well-established, especially with the concept of Gibbs ensemble. Using the latter, we may

construct the partition function of a system, and then the thermodynamic properties of the system may be derived.

This is in contrast with non-equilibrium statistical mechanics. Although, abundant phenomena are non-equilibrium, there is no consensus on the foundation of non-equilibrium statistical mechanics. One reason is that there is no widely accepted definition of an ensemble. This drives physicists to study non-equilibrium systems using various kinetic theories. Furthermore, the connections between these theories are still lacking. In other words, non-equilibrium statistical mechanics is still under construction.

There are, however, two main approaches in order to study stochastic processes, i.e. i) studying the trajectory a single Brownian particle, which is governed by a stochastic differential equation, and ii) studying the time evolution of the probability density,  $f(\mathbf{r}, t)$ , that satisfies the Fokker-Planck equation. Especially in this article, we use the second approach.

### Density Functional Theory

As mentioned above, the standard method in exploring a physical system using equilibrium statistical mechanics is to construct the partition function of the system. Now, the partition function is still dependent upon the microscopic details of the system, i.e. all of the degrees of freedom that make up the system. Thus, if more particles are involved in the system (many-body problem) then the form of the partition function may become more complicated.

An alternative way to study static equilibrium systems without invoking directly the partition function is through the so-called classical density functional theory (DFT). This is a powerful framework to study static equilibrium systems based on a variational principle. This theory is utilized in classical statistical physics for describing phenomena in inhomogeneous fluids including adsorption [24,25], freezing [26], surface and interface behavior [27], and colloid-polymer mixtures [28].

In general, the main objective of DFT is to construct an approximate functional for the intrinsic free energy  $\mathcal{F}$  of a classical system. In order to achieve this, the theory uses the concept that  $\mathcal{F}$  can be written as a functional of the one-body density  $\rho(\mathbf{r})$ , viz.  $\mathcal{F}[\rho(\mathbf{r})]$ , where  $\mathbf{r}$  is the position coordinate. Moreover,  $\mathcal{F}[\rho(\mathbf{r})]$  may be obtained via a Legendre transform of the grand potential functional  $\Omega[\rho(\mathbf{r})]$ , which is also a functional of the density. A functional derivative of the free energy with respect to density gives the one-body direct correlation function, i.e.:  $c^{(1)}[\rho; \mathbf{r}]$ . An important step in any DFT is the variational principle, in which  $\Omega[\rho]$  is minimized, i.e. the functional derivative of  $\Omega[\rho]$  with respect to  $\rho(\mathbf{r})$  vanishes at the correct equilibrium density  $\rho_0(\mathbf{r})$ . Once  $\rho_0(\mathbf{r})$  is attained, one may then derive other thermodynamic quantities of the system.

This is why classical DFT in some respect ‘simplifies’ the standard method of statistical mechanics, i.e.: rather than determining the many-body probability density of the system, we directly use the one-body density which only depends upon three space variables. However, one problem concerning any DFT is that  $\mathcal{F}[\rho]$ , is unknown, except for a special case of the hard rods model. That is why, most often, the (excess) free energy is largely obtained by various approximation. If we are not careful in constructing an approximation for the free energy, we may drift away from the true physical aspect of the system. The functional might not reflect the true behavior of the system. This resulted in the so-called uncontrolled approximations.

### Towards Dynamical DFT

DFT was first formulated for quantum mechanical systems by P. Hohenberg and W. Kohn in 1964, which is contained in [29]. DFT was fully operational via a method introduced by Kohn and L. J. Sham in 1965 [30]. For his part in the development of DFT, W. Kohn together with J. Pople received the noble prize in chemistry in 1998. Because of the simplicity in its application, DFT is now considered as

the standard method in studying the structure of matter in chemistry.

The use of DFT is not just limited to quantum systems. Extension of DFT for finite systems was formulated by Mermin [31]. This is the basis for classical DFT, which is fully realized by Evans [32].

The success of classical DFT in describing various properties of equilibrium systems leads to a natural desire to use it in attempts to treat non-equilibrium systems [32-34]. There is an appealing advantage of using DFT for dynamical systems, i.e. it provides insights into the dynamics of the systems on the microscopic level via statistical mechanics.

Recently, there have been a vast number of results coming out of DFT that are devoted to dealing with off-equilibrium, near-equilibrium or relaxation to equilibrium systems. The extension of classical DFT to dynamical systems is known as dynamical DFT (DDFT) [34-36] or time-dependent DFT (TDDFT) [37-38].

### Applying Dynamical DFT

To our knowledge the idea of using DFT to study dynamical systems and non-equilibrium systems following the success of (equilibrium) classical DFT was initially introduced around 1979 in [32], to analyze the kinetics of spinodal decomposition at the level of a varying time-dependent one-body density. In this early development of the DDFT, it is postulated [32, 33], without rigorous derivation, that the current density of a system is thermodynamically driven by the gradient of the (equilibrium) chemical potential, the latter being obtained as the functional derivative of the (equilibrium) free energy functional  $\mathcal{F}[\rho]$ . In [33], a time-dependent one-body density, which has a structure of a generalized Smoluchowski equation, is derived using the aforementioned assumption combined with the continuity equation and the functional  $\mathcal{F}[\rho]$ . Formal derivations of the DDFT or TDDFT then follows from numerous articles [34, 35, 37, 39] using various assumptions and kinetic equations as starting points, e.g. Brownian motion [35], the Langevin equation [34], hydrodynamic equation [39], and

Newton's equation of motion [40]. Interestingly, the equation for the time evolution of the one-body density that is gained from these derivations has a rather similar form [41]. DDFT has been employed to study the dynamics of soft matters, including the glass transition of dense colloidal suspension [42], salvation of simple mixtures [43], ultrasoft particle under time-varying potentials [44], relaxation of model fluids of plate like colloidal particles [45], and sedimentation of hard-sphere-like colloidal particles confined in horizontal capillaries [46].

The concept of DDFT relies, as an input, on  $\mathcal{F}[\rho]$ , which is a functional of the one-body density. The current density, i.e. the average number of particles going through a given volume per unit time, is obtained as an output of the theory. Based on the Smoluchowski equation, one obtains the equation [35],

$$\zeta \frac{\partial \rho(\mathbf{r}, t)}{\partial t} = \nabla \rho(\mathbf{r}, t) \nabla \frac{\delta \Omega[\rho]}{\delta \rho(\mathbf{r}, t)}, \quad (1)$$

where  $\rho(\mathbf{r}, t)$  is the time-dependent one-body density. The above equation gives the time evolution of the one-body density at position  $\mathbf{r}$ . Equation (1) also relies on the postulate that the non-equilibrium fluctuation comes from the thermal fluctuation of the equilibrium system. Here, one strictly uses the equilibrium grand potential functional.

### Conclusion

We have explained in general equilibrium and non-equilibrium statistical mechanics. We then explain qualitatively about DFT. Finally, we describe the extension of DFT to dynamical systems, called dynamical DFT.

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