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VIEWPOINT

Density functional theory: from statics to dynamics

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The cornerstone of density functional theory of inhomogeneous classical fluids [1] is based on a variational principle as first derived in 1964 by Kohn and Hohenberg [2] for zero temperature and later generalized by Mermin [3] to finite temperatures T . This principle guarantees the existence of a grand canonical free-energy functional $\Omega(T, \mu, [\rho(\vec{r})])$ of the one-body density $\rho(\vec{r})$ depending parametrically on the temperature and the chemical potential μ . If the functional is minimized, the minimum is the actual grand canonical free energy of the system and—even more importantly—one can generate any static many-body correlations by taking functional derivatives with respect to the one-body density $\rho(\vec{r})$. Hence the full thermodynamics and structure of the system can in principle be calculated.

To date, there have, however, been two serious limitations on and obstacles to making practical use of the density functional approach:

- For a given interparticle interaction, the density functional is not known exactly. It is only in special cases (such as one-dimensional hard rods) that the functional is explicitly known. In general, one has to rely on approximations.
- The density functional language itself is limited to time-independent structural correlations. For dynamical quantities, both in equilibrium and non-equilibrium, there is an urgent need to generalize density functional theory.

As regards the first limitation, tractable approximations have been developed during the last few decades. Recent progress is comprehensively summarized in a Special Issue of the Liquids and Soft Matter section of the Journal of Physics: Condensed Matter (issue 46 of volume 14, 2002). This issue is dedicated to the memory of the late Y Rosenfeld, one of the leading pioneers in classical density functional theory. For steep repulsive pair interactions between the particles (e.g. for hard spheres), Rosenfeld's fundamental measure approach [4] provides a very accurate approximation scheme which can be generalized to multi-component systems and non-convex bodies. For very soft repulsions, on the other hand, it has been shown by Likos and co-workers [5] that the simple mean-field approximation becomes asymptotically exact for large densities and works amazingly well for finite densities. This approximation—also known as RPA (random-phase approximation) in the liquid integral equation context—approximates the direct correlation function $c(r) \approx -V(r)/k_B T$ where $V(r)$ is the interparticle interaction potential and $k_B T$ is the thermal energy. Numerous realizations of such soft interactions

are found in solutions of polymers coils, star polymers and polyelectrolyte stars. Mean-field density functionals for soft interactions are very popular now and have been used to study various static equilibrium problems including those of interfaces [6] and wetting [7].

Apart from those using the traditional local Cahn–Hilliard equation, attempts to generalize non-local density functional theory to dynamical properties are rare. Generalizing Fick’s law in the density functional context, Dieterich *et al* [8] proposed and discussed the following equation for the time-dependent density field $\rho(\vec{r}, t)$:

$$\frac{k_B T}{D} \frac{\partial \rho(\vec{r}, t)}{\partial t} = \vec{\nabla} \left[\rho(\vec{r}, t) \cdot \vec{\nabla} \frac{\delta \Omega}{\delta \rho(\vec{r}, t)} \right] \quad (1)$$

where D is the short-time self-diffusion coefficient of the underlying ‘microscopic’ Brownian dynamics. The continuity-like equation (1) immediately implies conservation of the total particle number. Unfortunately, the paper of Dieterich *et al* went almost unnoticed, although the dynamical equation (1) plays a basic role in density functional theory. In fact, more recently, Marconi and Tarazona [9, 10] have justified equation (1) on a more fundamental level; the only approximation left is the assumption that the equal-time two-point correlation function out of equilibrium has the same properties as its equilibrium version. Equation (1) was used in various different contexts with a noise term added to its right-hand side; valuable former approaches of model-B-like dynamics which use such additional fluctuations were developed in the groups of Kirkpatrick [11] and Kawasaki [12]. One main point of the analysis of Marconi and Tarazona is that such additional noise terms artificially double the thermal noise if the exact density functional is taken in equation (1). For the system of one-dimensional rods where the density functional is known exactly, Marconi and Tarazona [9, 10] found that the non-equilibrium relaxational dynamics as predicted by equation (1) agrees well with ‘exact’ data from Brownian dynamics computer simulations. This is a remarkable result, building a basis for tackling dynamical problems with density functional theory in a very simple way for systems governed by a Brownian ‘microscopic’ dynamics. Still, as far as a systematic comparison with simulations is concerned, only the one-dimensional hard-rod model was tested and one can ask whether it is the peculiar one-dimensional dynamics with non-crossing of hard rods which leads to a fortunate coincidence with the ‘exact’ simulation dynamics.

In a letter in this issue of *Journal of Physics: Condensed Matter*, Dzubiella and Likos [13] go one step further and apply equation (1) to three-dimensional systems with soft interparticle interactions approximating the density functional within the accurate mean-field approach. For various time-dependent external potentials corresponding to the physical case of squeezing and relaxing Brownian soft particles in a time-dependent external (e.g. optical) trap, the dynamical density fields agree almost perfectly with non-equilibrium Brownian dynamics computer simulations. What is amazing is that not only are the qualitative features of the different dynamical processes reproduced by the dynamical density functional theory, but also even the full quantitative time resolution is contained in equation (1). The importance of the letter of Dzubiella and Likos is that it opens the way to applying dynamical density functional theory to various important problems of soft matter driven to non-equilibrium. A generalization of equation (1) to two-component mean-field fluids that exhibit an equilibrium fluid–fluid phase separation is immediate. Therefore an accurate microscopic description of homogeneous and heterogeneous gas–liquid nucleation [14] and wetting dynamics [7] lies ahead. In particular, it is interesting to investigate how these phenomena are controllable by external potentials [15] (e.g. an optical tweezer for the soft particles), since density functional theory is perfectly suited to treat different external potentials. Another area where a considerable stimulus from the work of Dzubiella and Likos [13] can be expected is the microscopic dynamical understanding of spreading and dewetting phenomena in thin polymer films. What is still open, however, is

the problem of finding a tractable framework for including hydrodynamic interactions in the dynamical description.

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