Dynamical density functional theory for interacting Brownian particles: stochastic or deterministic?

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Abstract
We aim to clarify confusions in the literature as to whether or not dynamical density functional theories for the one-body density of a classical Brownian fluid should contain a stochastic noise term. We point out that a stochastic as well as a deterministic equation of motion for the density distribution can be justified, depending on how the fluid one-body density is defined—i.e. whether it is an ensemble averaged density distribution or a spatially and/or temporally coarse grained density distribution.

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1. Introduction

In equilibrium statistical mechanics, one can prove that the grand canonical free energy of the system can be written as a functional of the one-body density only [1]. The density distribution, which minimizes the grand potential functional, is the equilibrium density distribution. This statement is the basis of the equilibrium density functional theory for classical fluids which has been used with great success to describe a variety of inhomogeneous fluid phenomena [2]. Out of equilibrium there is no such rigorous principle. However, macroscopically one can find phenomenological equations for the time evolution which are based on macroscopic quantities only, e.g. the diffusion equation, the heat transport equation and the Navier–Stokes equations for hydrodynamics.

In perhaps one of the most simple microscopic cases, a system of interacting Brownian particles, a number of equations for the time evolution of the particle density have been proposed which aim to incorporate results from equilibrium density functional theory. These equations are usually referred to as dynamical density functional theory (DDFT) or time-dependent density functional theory. Most of the equations take a rather similar form but
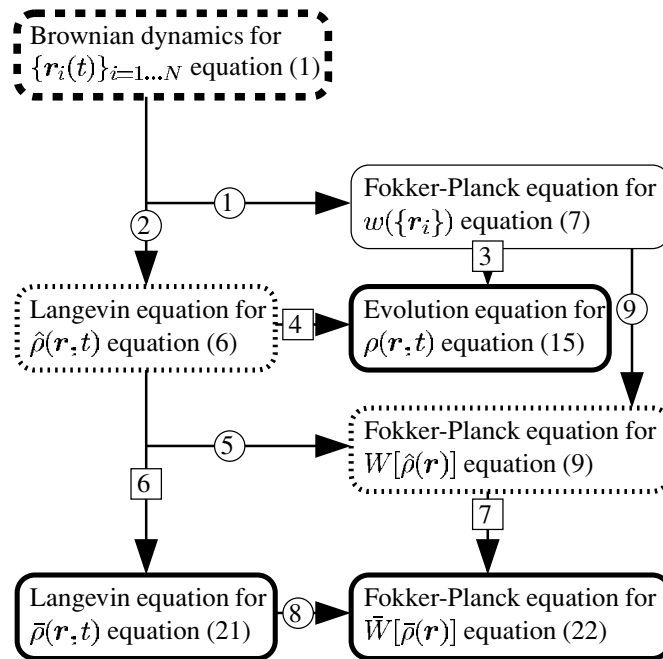
Figure 1. Flow chart outlining the various possible routes for deriving a DDFT for pairwise interacting Brownian particles. The starting point for all attempts to derive a DDFT is equation (1) (thick dashed line box at the top). The end point is either a theory for the coarse grained density $\bar{\rho}(r, t)$ (Langevin or Fokker–Planck equation, thick solid outlined boxes at the bottom) or, for the ensemble averaged density $\rho(r, t)$, a deterministic equation, (thick solid outlined box on right). The Langevin and Fokker–Planck equation for the microscopic density $\hat{\rho}(r, t)$ are only intermediate results (dotted boxes). Steps 1, 2, 5, 8 and 9 are exact (in circles) whereas steps 3, 4, 6 and 7 involve approximations (in square boxes).

there has been some controversy as to whether the time evolution ought to be stochastic [3–7] or deterministic [8–10] in nature. In [7] the authors attempt to address these issues. However, we believe further clarifications are necessary. The reason for the controversy is that one has to state precisely what type of density distribution one is talking about, namely whether one speaks of the instantaneous density $\hat{\rho}(r, t)$ at time t, an ensemble averaged density $\rho(r, t)$, or a spatially and/or temporally coarse grained density $\bar{\rho}(r, t)$. We will give proper definitions for these densities later. The time evolution equation for $\hat{\rho}(r, t)$ is discussed in [5–8], and for Brownian particles this is, of course, a stochastic equation. $\rho(r, t)$ results from taking an ensemble average over the stochastic noise and is therefore uniquely valued at time t; the equation governing its dynamics must therefore be deterministic—this is the approach in [8–10]. The equation governing the dynamics of $\bar{\rho}(r, t)$, the coarse grained density, will, of course, still contain a noise term with the amplitude of this term dependent on the degree of coarse graining. The main objective of this paper is to clarify the relationships between these three approaches and to discuss the similarities and differences. In order to visualize better the connections between the DDFTs for $\hat{\rho}(r, t)$, $\rho(r, t)$ and $\bar{\rho}(r, t)$, we employ the flow chart in figure 1.

This paper proceeds as follows: in section 2, we formulate the dynamics of a system of interacting Brownian particles. We derive a deterministic DDFT for the ensemble (or noise) averaged density in section 3. In section 4, we formulate the stochastic DDFT for the coarse grained density and finally, in section 5, we discuss the results.

2. Brownian dynamics of interacting particles

The starting point for our considerations is the Langevin equation for a system of N identical Brownian particles with positions $\{r_i(t)\}_{i=1,\ldots,N}$ (see the dashed box in figure 1) in the (overdamped) high friction limit. The particles interact pairwise via the (pair) potential $V(r)$. In addition, there is a one-body external potential $\Phi(r_i, t)$. This equation reads

$$\frac{\mathrm{d}r_i}{\mathrm{d}t} = \sum_{j=1,\ldots,N} F(r_i - r_j) + G(r_i, t) + \eta_i(t), \tag{1}$$

where $F(r_i - r_j) = -\nabla_i V(|r_i - r_j|)$ is the interaction force between a pair of particles, and $G(r_i, t) = -\nabla_i \Phi(r_i, t)$ is the external force on particle i. The uncorrelated Gaussian random force on each particle $\{\eta_i(t)\}_{i=1,\ldots,N}$ is fully characterized by

$$\langle \eta_i(t) \rangle = 0 \qquad \text{and} \qquad \langle \eta_i^\ell(t) \eta_j^m(t') \rangle = 2T \delta_{ij} \delta^{\ell m} \delta(t - t'). \tag{2}$$

The particles are labelled with lower roman indices, and the spatial directions (i.e., x, y and z in three dimensions) are labelled with upper indices. A possible prefactor (mobility constant) in front of the deterministic part of (1) can be eliminated via the Einstein relation and a corresponding rescaling of time. T is the temperature. Note that the noise term in (1) is additive, i.e. it does not have a prefactor which depends on the particle position. In this case, the Ito and the Stratonovich stochastic calculus are equivalent [11].

In the next step, we define the instantaneous microscopic density $\hat\rho(r, t; \{r_i(t)\}) = \sum_{i=1}^N \delta(r_i(t) - r)$. This density depends implicitly on the actual positions of all particles $\{r_i(t)\}$ and it should be considered a density 'operator' rather than a measurable particle density. Using Ito stochastic calculus, one can show that the time evolution of this sum of delta functions is given by (see [8, equation (8)] or [5, equation (17)]):

$$\frac{\partial \hat\rho(r, t)}{\partial t} = \nabla \cdot \left[-\hat\rho(r, t) G(r, t) - \hat\rho(r, t) \int \hat\rho(r', t) F(r - r') \, \mathrm{d}^3 r' \right.$$
$$\left. + T \nabla \hat\rho(r, t) + \sqrt{\hat\rho(r, t)} \xi(r, t) \right], \tag{3}$$

i.e., an equation which, at a first glance, does not depend upon the individual particle positions. This step corresponds to path 2, which leads to the left dotted box in figure 1. The random forces on the particles $\eta_i(t)$ have been replaced by a Gaussian random field $\xi(r, t)$ with

$$\langle \xi(r, t) \rangle = 0 \qquad \text{and} \qquad \langle \xi^\ell(r, t) \xi^m(r', t') \rangle = 2T \delta^{\ell m} \delta(r - r') \delta(t - t'). \tag{4}$$

Introducing the 'energy' functional $\mathcal{H}[\hat\rho]$ [7]

$$\mathcal{H}[\hat\rho] = \int \left\{ T \hat\rho(r, t) [\ln \Lambda^3 \hat\rho(r, t) - 1] + \hat\rho(r, t) \Phi(r, t) \right.$$
$$\left. + \frac{1}{2} \int \hat\rho(r, t) V(|r - r'|) \hat\rho(r', t) \, \mathrm{d}^3 r' \right\} \mathrm{d}^3 r, \tag{5}$$

where Λ is the de Broglie wavelength, (3) can be written as

$$\frac{\partial \hat\rho(r, t)}{\partial t} = \nabla \cdot \left[\hat\rho(r, t) \nabla \frac{\delta \mathcal{H}[\hat\rho]}{\delta \hat\rho(r, t)} + \sqrt{\hat\rho(r, t)} \xi(r, t) \right]. \tag{6}$$

In contrast to the noise in equation (1), the noise in (6) is multiplicative. However, as shown in [12], for a conserved multiplicative noise, Ito and Stratonovich calculus are equivalent and

therefore (6), the Langevin equation for $\hat{\rho}(\boldsymbol{r}, t)$, should have the same form when obtained by Stratonovich calculus.

We denote the probability density for finding the particles in the system at time t with the positions $\{\boldsymbol{r}_\ell\}_{\ell=1,\dots,N}$ by $w(\boldsymbol{r}_1, \dots, \boldsymbol{r}_N, t)$. The time evolution of this probability is given by the Fokker–Planck equation for (1), namely

$$\frac{\partial w(\{\boldsymbol{r}_\ell\}, t)}{\partial t} = -\sum_{i=1,\dots,N} \nabla_i \cdot \left[\sum_{j=1,\dots,N} \boldsymbol{F}(\boldsymbol{r}_i - \boldsymbol{r}_j) + \boldsymbol{G}(\boldsymbol{r}_i, t) - T\nabla_i \right] w(\{\boldsymbol{r}_\ell\}, t). \tag{7}$$

In figure 1 the derivation of (7) is denoted by path 1. Equation (7) is also referred to as the Smoluchowski equation, namely the drift–diffusion equation for a many-particle system [11, 10].

However, we are more interested in the particle density distribution, rather than in the positions of the individual particles. The probability of finding the system in a configuration with the density $\rho(\boldsymbol{r}, t)$ is given by

$$W[\rho] = \int w(\{\boldsymbol{r}_\ell\}, t) \delta\left[\rho(\boldsymbol{r}, t) - \hat{\rho}(\boldsymbol{r}, t; \{\boldsymbol{r}_i\})\right] \mathrm{d}^3 r_1 \cdots \mathrm{d}^3 r_N. \tag{8}$$

$\hat{\rho}(\boldsymbol{r}, t; \{\boldsymbol{r}_i\})$ is a sum of N δ-functions and therefore, from the above definition, $W[\rho]$ can only be nonzero when $\rho(\boldsymbol{r}, t)$ is also a sum of exactly N δ-functions. In order to make a clear distinction between smooth densities and spiky sums of delta functions, we will keep a hat on the argument of W. The time evolution for $W[\hat{\rho}]$, which in fact is the Fokker–Planck equation corresponding to (6), is given by [7] (see also [13] or appendix 8 in [14]):

$$\frac{\partial W[\hat{\rho}]}{\partial t} = -\int \frac{\delta}{\delta\hat{\rho}(\boldsymbol{r}, t)} \left\{ \nabla \cdot \hat{\rho}(\boldsymbol{r}, t) \nabla \left[T \frac{\delta}{\delta\hat{\rho}(\boldsymbol{r}, t)} + \frac{\delta\mathcal{H}[\hat{\rho}]}{\delta\hat{\rho}(\boldsymbol{r}, t)} \right] W[\hat{\rho}] \right\} \mathrm{d}^3 r \tag{9}$$

with the functional $\mathcal{H}[\hat{\rho}]$ as given in (5). The derivation of (9) from the Langevin equation (6) is path 5 connecting the two dotted boxes in figure 1. Equivalently, one could also obtain (9) via a change of variables from $\{\boldsymbol{r}_i\}_{i=1,\dots,N}$ in (7) to $\hat{\rho}(\boldsymbol{r}, t)$; this is path 9 in figure 1. The equilibrium distribution corresponding to (9) is given by $W^{(\mathrm{eq})}[\hat{\rho}] \propto \exp\left[-\frac{1}{T}(\mathcal{H}[\hat{\rho}] + \mu\hat{\rho})\right]$ with an arbitrary chemical potential μ. The freedom of choice for μ comes from the fact that (3) has the form of a conservation law.

Equation (6) together with equation (5) is a DDFT for $\hat{\rho}(\boldsymbol{r}, t)$, i.e. an equation of motion for the instantaneous microscopic density. However, although equation (6) is written in terms of $\hat{\rho}(\boldsymbol{r}, t)$, this sum of delta functions contains the exact positions of all particles (modulo permutations), and the solution of (6) is formally equivalent to integrating (1)—see also the appendix in [15]. Generally, one is not interested in the individual trajectories of the particles, rather in the time evolution of quantities (in particular the fluid density) averaged over many realizations of the noise or, alternatively, in the evolution of coarse grained quantities.

3. Ensemble averaged density

We define the ensemble averaged density as the density $\hat{\rho}(\boldsymbol{r}, t)$ averaged over many solutions of (3) with equal initial conditions but different realizations of the noise term $\boldsymbol{\xi}(\boldsymbol{r}, t)$, i.e.

$$\rho(\boldsymbol{r}, t) = \int \hat{\rho}(\boldsymbol{r}, t; \{\boldsymbol{r}_i\}) w(\{\boldsymbol{r}_i\}, t) \, \mathrm{d}^3 r_1 \cdots \mathrm{d}^3 r_N = \langle \hat{\rho}(\boldsymbol{r}, t) \rangle. \tag{10}$$

In other words, in order to measure $\rho(\boldsymbol{r}, t)$ one solves (3) many times for different realizations of the noise $\boldsymbol{\xi}(\boldsymbol{r}, t)$ and averages the result at each time t. Since the particles

are indistinguishable, $w(\{r_i\}, t)$ is symmetric with respect to permutations of particles and therefore $\rho(r, t) = N \int w(r, r_2, \ldots, r_N, t) \, d^3r_2 \cdots d^3r_N$. We can obtain the time evolution of $\rho(r, t)$ by integrating out $N - 1$ degrees of freedom in (7) to obtain [10, 16]:

$$\frac{\partial \rho(r, t)}{\partial t} = -\nabla \cdot \left\{ [G(r, t) - T\nabla]\rho(r, t) + \int \rho^{(2)}(r, r', t) F(r - r') \, d^3r' \right\}, \tag{11}$$

where

$$\rho^{(2)}(r, r', t) = N(N - 1) \int w(r, r', r_3, \ldots, r_N, t) \, d^3r_3 \cdots d^3r_N, \tag{12}$$

is the two-body density distribution function. We have assumed that surface terms which appear in the partial integrations vanish. Here we see that for interacting particles, the time evolution of the one-body density distribution $\rho(r, t)$ depends upon the two-body density distribution function, i.e. on the particle correlations in the system. In fact, (11) is the first equation of a hierarchy of equations for the n-body density distribution functions (similar to the BBGKY hierarchy) which one obtains by integrating out $(N - n)$ degrees of freedom in (7)—see [10].

So far, everything is exact, but in order to make use of this hierarchy one needs a closure. One way, which is employed in [10], makes use of a result from equilibrium density functional theory, in which there is an exact sum rule connecting the equilibrium two-body density distribution function $\rho_{\text{eq}}^{(2)}(r, r')$ to the gradient of the one-body direct correlation function $c^{(1)}(r)$

$$k_B T \rho(r) \nabla c^{(1)}(r) = \int \rho_{\text{eq}}^{(2)}(r, r') F(r - r') \, d^3r'. \tag{13}$$

In equilibrium, $c^{(1)}(r)$ is the effective one-body potential due to interactions in the fluid and is given by the functional derivative of $\mathcal{F}_{\text{ex}}[\rho]$, the excess (over ideal) part of the Helmholtz free energy functional, $-k_B T c^{(1)}(r) = \frac{\delta \mathcal{F}_{\text{ex}}[\rho]}{\delta \rho}$ [1, 10], and we obtain the following exact result:

$$\rho(r) \nabla \frac{\delta \mathcal{F}_{\text{ex}}[\rho]}{\delta \rho(r)} = -\int \rho_{\text{eq}}^{(2)}(r, r') F(r - r') \, d^3r'. \tag{14}$$

Assuming this relation remains valid for the non-equilibrium fluid is equivalent to assuming that the two-body correlations in the non-equilibrium fluid are the same as those in an equilibrium fluid with the *same* one-body density profile [8, 10]. Within this *approximation* we can write the time evolution equation (11) as [8, 10]:

$$\frac{\partial \rho(r, t)}{\partial t} = \nabla \cdot \left[\rho(r, t) \nabla \frac{\delta \mathcal{F}[\rho(r, t)]}{\delta \rho(r, t)} \right], \tag{15}$$

with the Helmholtz free energy functional[4]

$$\mathcal{F}[\rho(r, t)] = \int \rho(r, t)[T(\ln \Lambda^3 \rho(r, t) - 1) + \Phi(r, t)] \, d^3r + \mathcal{F}_{\text{ex}}[\rho(r, t)]. \tag{16}$$

Since $\rho(r, t)$ is a quantity averaged over the realizations of the noise, the time evolution equation (15) is necessarily deterministic. Equation (15) was originally written down (without derivation) by Evans [1]. The derivation of (15) presented in this section corresponds to path 3 in figure 1. In [8] Marconi and Tarazona follow path 4 in figure 1, and (15) is derived from (3) by performing an ensemble average. Note that (15) also remains valid when the particles interact via multi-body potentials [10].

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[4] Note that the equilibrium excess Helmholtz free energy functional $\mathcal{F}_{\text{ex}}[\rho]$ is only known exactly for the case of hard-rods in one dimension [17] (see also [8]). In practice one can only obtain an approximation to the exact functional. Some of the more recently derived functionals are rather sophisticated and very accurate [2].

4. Coarse grained density

The ensemble averaged density $\rho(\boldsymbol{r}, t)$ discussed in section 3 is the quantity often considered by theorists, but it is not the quantity one would measure by performing one individual experiment (numerical or real). In order to measure the density as a function of time in an experiment one must define a probe volume in space and a time window and count the number of particles in that probe volume averaged over the time window. Since we intend to resolve the atomistic structure of the fluid, the spatial resolution has to be very good. In other words, we assume an experimental resolution function of the form $K_1(\boldsymbol{r}, t) = K(t)\delta(\boldsymbol{r})$ and then the measured density is

$$\bar{\rho}(\boldsymbol{r}, t) = \int K(t - t')\hat{\rho}(\boldsymbol{r}, t') \, dt'. \tag{17}$$

For simplicity we assume further that $K(t)$ has a compact support of size τ. Similarly, we can define a two-particle probe, with a resolution function of the form $K_2(\boldsymbol{r}, \boldsymbol{r}', t) = K(t)\delta(\boldsymbol{r})\delta(\boldsymbol{r}')$. The two-particle distribution function that we measure is (cf equation (A6) in [1])

$$\int K(t - t')\hat{\rho}(\boldsymbol{r}, t')\hat{\rho}(\boldsymbol{r}', t') \, dt' = \int K(t - t') \sum_{i \neq j} \delta(\boldsymbol{r}_i(t') - \boldsymbol{r})\delta(\boldsymbol{r}_j(t') - \boldsymbol{r}') \, dt'$$

$$+ \int K(t - t') \sum_i \delta(\boldsymbol{r}_i(t') - \boldsymbol{r})\delta(\boldsymbol{r}_i(t') - \boldsymbol{r}') \, dt'$$

$$= \bar{\rho}^{(2)}(\boldsymbol{r}, \boldsymbol{r}', t) + \bar{\rho}(\boldsymbol{r}, t)\delta(\boldsymbol{r}' - \boldsymbol{r}). \tag{18}$$

This equation defines the coarse grained two-particle density distribution function, $\bar{\rho}^{(2)}(\boldsymbol{r}, \boldsymbol{r}', t)$. When the fluid is in equilibrium, assuming ergodicity, and if the time window of $K(t)$ is large, as compared to the time the system needs to explore phase space locally, then $\bar{\rho}^{(2)}(\boldsymbol{r}, \boldsymbol{r}') \approx \rho^{(2)}(\boldsymbol{r}, \boldsymbol{r}')$; we therefore assume $\bar{\rho}^{(2)}(\boldsymbol{r}, \boldsymbol{r}', t) \approx \rho^{(2)}(\boldsymbol{r}, \boldsymbol{r}', t)$. Here, locally means on the scale of the correlation length and therefore this may not be true for long-ranged correlations.

Using (3) together with (17) and (18), the time evolution of $\bar{\rho}(\boldsymbol{r}, t)$ is given by

$$\frac{\partial \bar{\rho}(\boldsymbol{r}, t)}{\partial t} = T\nabla^2 \bar{\rho}(\boldsymbol{r}, t) - \nabla \cdot \bar{\rho}(\boldsymbol{r}, t)\boldsymbol{G}(\boldsymbol{r}, t) - \nabla \cdot \int \bar{\rho}^{(2)}(\boldsymbol{r}, \boldsymbol{r}', t)\boldsymbol{F}(\boldsymbol{r} - \boldsymbol{r}') \, d^3r'$$

$$+ \nabla \cdot \int K(t - t')\sqrt{\hat{\rho}(\boldsymbol{r}, t')}\boldsymbol{\xi}(\boldsymbol{r}, t') \, dt'. \tag{19}$$

The delta function term in (18) leads to a term containing $\boldsymbol{F}(0) = -\nabla V(r)|_{r=0}$, namely the force between particles when the centres are at zero separation. We assume that this is zero [5]. Equation (19) is exact when $\boldsymbol{G}$ does not change over time or when it only changes on time scales much longer than τ, the support of $K(t)$. However, in this form equation (19) is of little use, since the right-hand side involves $\hat{\rho}(\boldsymbol{r}, t)$ explicitly. In the following, we give a number of 'hand-waving' arguments in which we approximate the right-hand side in terms of $\bar{\rho}(\boldsymbol{r}, t)$ only. These arguments are far from being rigorous and are by no means a proper derivation of a DDFT for $\bar{\rho}(\boldsymbol{r}, t)$. The reason for giving these arguments is that they lead to a stochastic time evolution equation for $\bar{\rho}(\boldsymbol{r}, t)$ which has the same form as the time evolution equation of $\rho(\boldsymbol{r}, t)$, i.e. (15), but with an additional conserved noise term. In [6] Kawasaki uses a more formal spatial coarse graining procedure and in [18] Pérez-Madrid et al use a mesoscopic approach to obtain a similar result.

The time integration in the last term of equation (19) in principle leads to a non-Markovian time evolution for $\bar{\rho}(r, t)$, with the amplitude of the noise term dependent on the characteristic time, τ, of the resolution function $K(t)$. If τ is sufficiently long, then the amplitude of the noise term in (19) will be negligible and (19) reduces to an equation of the same form as (11) and the theory becomes equivalent to that for the ensemble averaged density of the previous section. For smaller values of τ, the noise term in (19) will still be significant. In this situation, on time scales large as compared to τ, the dynamics of $\bar{\rho}(r, t)$ should be approximately Markovian and, without strict justification we write the last term of equation (19) in the same form as in (3), but with $\hat{\rho}(r, t)$ replaced by $\bar{\rho}(r, t)$ and an amplitude proportional to $\sqrt{\tau_0/\tau}$, where τ_0 is a microscopic time scale. For large but finite τ we have a time evolution equation identical to (11) but with an additional multiplicative noise term

$$\frac{\partial \bar{\rho}(r, t)}{\partial t} = -\nabla \cdot \left\{ [G(r, t) - T\nabla]\bar{\rho}(r, t) + \int \bar{\rho}^{(2)}(r, r', t) F(r - r') \, \mathrm{d}^3 r' \right.$$
$$\left. - \nabla \cdot \sqrt{\bar{\rho}(r, t)} \sqrt{\frac{\tau_0}{\tau}} \xi(r, t) \right\}. \tag{20}$$

Using the local equilibrium assumption applied in section 3, we assume equation (14) with ρ replaced by $\bar{\rho}$ and $\rho^{(2)}$ replaced by $\bar{\rho}^{(2)}$ applies for the non-equilibrium coarse grained density distributions, and we substitute the term involving $\bar{\rho}^{(2)}(r, r', t)$ in (20) by a term involving the functional derivative of the excess part of the Helmholtz free energy functional, to obtain a stochastic version of (15):

$$\frac{\partial \bar{\rho}(r, t)}{\partial t} = \nabla \cdot \left[\bar{\rho}(r, t) \nabla \frac{\delta \mathcal{F}[\bar{\rho}(r, t)]}{\delta \bar{\rho}(r, t)} + \sqrt{\bar{\rho}(r, t)} \sqrt{\frac{\tau_0}{\tau}} \xi(r, t) \right]. \tag{21}$$

Note the similarity with the time evolution equation (6) for the instantaneous microscopic density $\hat{\rho}(r, t)$. However, a significant difference is that it is the Helmholtz free energy functional, $\mathcal{F}[\bar{\rho}]$, given by equation (16) with ρ replaced by $\bar{\rho}$, that enters into equation (21)[5], whereas $\mathcal{H}[\hat{\rho}]$ entering equation (6) is simply the functional as defined in (5). Unfortunately, in [7], this distinction is not made clear. In developing (21) we followed path 6 in figure 1. We can obtain the Fokker–Planck equation corresponding to equation (21) by discretizing it in space. Taking the continuum limit of the Fokker–Planck equation for the discretized Langevin equation [3, 12], we obtain an equation very similar to (9):

$$\frac{\partial \bar{W}[\bar{\rho}]}{\partial t} = -\int \frac{\delta}{\delta \bar{\rho}(r, t)} \left\{ \nabla \cdot \bar{\rho}(r, t) \nabla \left[T \sqrt{\frac{\tau_0}{\tau}} \frac{\delta}{\delta \bar{\rho}(r, t)} + \frac{\delta \mathcal{F}[\bar{\rho}]}{\delta \bar{\rho}(r, t)} \right] \bar{W}[\bar{\rho}] \right\} \mathrm{d}^3 r. \tag{22}$$

This calculation corresponds to path 8 in figure 1. The equilibrium distribution corresponding to (22) is given by $\bar{W}^{(\mathrm{eq})}[\bar{\rho}] \propto \exp\left[-\frac{1}{T} \sqrt{\frac{\tau}{\tau_0}} (\mathcal{F}[\bar{\rho}] + \mu \bar{\rho}) \right]$ with an arbitrary chemical potential μ. This result justifies *a posteriori* our, initially unjustified, approximation for the noise term in (19), which we used to obtain (21). Note that the time coarse graining reduces the fluctuations by an amount corresponding to a smaller temperature $T\sqrt{\frac{\tau_0}{\tau}}$. However, the free energy functional $\mathcal{F}[\bar{\rho}]$ is that for the given temperature T (see footnote 5).

In this section, we considered the temporally coarse grained density $\bar{\rho}(r, t)$ because we wished to make a comparison with the DDFT obtained for the ensemble averaged density $\rho(r, t)$ in the previous section, which is used to describe the time evolution of the structure of the system at microscopic length scales. We wish to emphasize that the derivation was by no means rigorous. However, a spatial coarse graining of (9) can also lead to an equation of

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[5] More strictly, we expect the free energy functional in (21) to be a coarse grained free energy functional, $\bar{\mathcal{F}}[\bar{\rho}]$. We are making the approximation $\bar{\mathcal{F}}[\bar{\rho}] \simeq \mathcal{F}[\bar{\rho}]$. See [19] for a recent discussion of the difference between these free energy functionals.

the same form as (22) but with a particular (approximate) form for the Helmholtz free energy functional—see [6]. This last route follows path 7 in figure 1.

5. Discussion

In sections 2 and 4, we derived stochastic DDFTs (Langevin equations) for the instantaneous microscopic density $\hat{\rho}(r, t)$, equation (6), and the coarse grained density $\bar{\rho}(r, t)$, equation (21), respectively, as well as the corresponding Fokker–Planck equations. In section 3, we also derived a deterministic DDFT, equation (15), for the ensemble (or noise) averaged density $\rho(r, t)$. The equations for the instantaneous microscopic density $\hat{\rho}(r, t)$ are of little use because $\hat{\rho}(r, t)$ directly encodes the positions of all particles (modulo permutations); it is simpler in this case to follow the particle trajectories directly by integrating equation (1). But, depending on the situation one is trying to describe, it can be reasonable to consider either the coarse grained density $\bar{\rho}(r, t)$ or the ensemble averaged density $\rho(r, t)$. In fact, their time evolution equations, (21) and (15) respectively, are identical except for the additional noise term in (21). Both (approximate) equations are consistent with equilibrium thermodynamics. The equilibrium value of $\rho(r, t)$ (i.e. in the limit $t \to \infty$ for a time-independent external potential), which we denote by $\rho(r)$, is correctly given by the stationary point of the Helmholtz free energy functional $\frac{\delta \mathcal{F}[\rho]}{\delta \rho(r)} = \mu$ [8, 10, 1]. This stationary density $\rho(r)$ is also the density with the highest probability in the stationary distribution of the coarse grained density $\bar{W}^{(eq)}[\bar{\rho}]$, independent of the choice of coarse graining time scale τ. Note that for $\tau \to \infty$, $\bar{W}^{(eq)}[\bar{\rho}]$ becomes sharply peaked at $\rho(r)$. For finite τ coarse graining $\bar{W}^{(eq)}[\bar{\rho}]$ has a finite width due to thermal fluctuations. For non-interacting particles, as pointed out in [8], the deterministic DDFT in equation (15) reduces to the (exact) drift–diffusion equation for Brownian particles in an external potential. These observations suggest that the DDFT provides a good approximation to the exact time evolution of the particle density, particularly when the system is either close to equilibrium or when the particles interact weakly.

We ought to re-iterate that our approach in section 4 is not intended to provide a rigorous derivation of a stochastic DDFT, rather we aim to point out that one can use a *temporal* coarse graining to arrive at a stochastic density functional theory, equation (22), similar to that obtained in [6] via a different *spatial* coarse graining. The main difficulty in rigorously deriving a coarse grained DDFT is to express the coarse grained two-body density distribution function $\bar{\rho}^{(2)}(r, r')$ as a functional of the one-body density. By varying the coarse graining parameter τ between zero and infinity, in principle one should be able to go smoothly from the microscopic dynamics in equation (6) to a deterministic DDFT for the ensemble averaged density. We expect that the intermediate equations of motion should have a form similar to (21), but with a τ-dependent, partially coarse grained free energy functional. However, since we do not know of any formal procedure for obtaining such a functional, as an *approximation* for large τ, we propose using the free energy functionals from equilibrium density functional theory [2].

We believe that the origin of the debate as to whether the DDFT should be a stochastic or deterministic equation is a matter of confusion between the three types of densities defined in this paper. In particular, the distinction between the instantaneous microscopic density $\hat{\rho}(r, t)$ and the coarse grained density $\bar{\rho}(r, t)$ is of great importance, as noted also in [15]. The confusion is most apparent in a recent contribution to the field [7]. In this paper, the Langevin and Fokker–Planck equation for $\hat{\rho}(r, t)$, namely (3) and (9), respectively, are derived correctly, but then the microscopic instantaneous density $\hat{\rho}(r, t)$, which is a sum of delta functions, is confused with the coarse grained density $\bar{\rho}(r, t)$. In addition to this confusion there is, in [7],

a lack of a clear distinction between the functional $\mathcal{H}[\hat{\rho}]$ and the free energy functional $\mathcal{F}[\bar{\rho}]$. Bearing in mind the results from equilibrium density functional theory [1, 2] this distinction should be evident immediately.

The authors of [7] argue that a DDFT must be stochastic in nature. This misconception has its roots in [5] where the difference between $\hat{\rho}(r, t)$ and $\bar{\rho}(r, t)$ is not, in our view, expounded sufficiently clearly. This difference is further obscured by the fact that the time evolution equation for the *spatially* coarse grained density derived in [6] involves a free energy functional whose form is strikingly similar to $\mathcal{H}[\hat{\rho}]$ in (5). However, the crucial difference is that (5) contains the bare pair interaction potential while the functional derived in [6] contains the direct pair correlation function, instead of $V(r)$, and therefore leads to the proper thermodynamic equilibrium state. We wish to emphasize that a DDFT for $\rho(r, t)$, the density distribution averaged over all realizations of the stochastic noise, must be deterministic.

In summary, one can justify both a stochastic as well as a deterministic DDFT, depending on the quantities of interest. In this sense, there is a confusion rather than a controversy about the nature of DDFT.

Acknowledgments

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