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PAPER

General framework for fluctuating dynamic density functional theory

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Abstract

We introduce a versatile bottom-up derivation of a formal theoretical framework to describe (passive) soft-matter systems out of equilibrium subject to fluctuations. We provide a unique connection between the constituent-particle dynamics of real systems and the time evolution equation of their measurable (coarse-grained) quantities, such as local density and velocity. The starting point is the full Hamiltonian description of a system of colloidal particles immersed in a fluid of identical bath particles. Then, we average out the bath via Zwanzig's projection-operator techniques and obtain the stochastic Langevin equations governing the colloidal-particle dynamics. Introducing the appropriate definition of the local number and momentum density fields yields a generalisation of the Dean–Kawasaki (DK) model, which resembles the stochastic Navier–Stokes description of a fluid. Nevertheless, the DK equation still contains all the microscopic information and, for that reason, does not represent the dynamical law of observable quantities. We address this controversial feature of the DK description by carrying out a nonequilibrium ensemble average. Adopting a natural decomposition into local-equilibrium and nonequilibrium contribution, where the former is related to a generalised version of the canonical distribution, we finally obtain the fluctuating-hydrodynamic equation governing the time-evolution of the mesoscopic density and momentum fields. Along the way, we outline the connection between the ad hoc energy functional introduced in previous DK derivations and the free-energy functional from classical density-functional theory. The resultant equation has the structure of a dynamical density-functional theory (DDFT) with an additional fluctuating force coming from the random interactions with the bath. We show that our fluctuating DDFT formalism corresponds to a particular version of the fluctuating Navier–Stokes equations, originally derived by Landau and Lifshitz. Our framework thus provides the formal apparatus for *ab initio* derivations of fluctuating DDFT equations capable of describing the dynamics of soft-matter systems in and out of equilibrium.

1. Introduction

Classical fluids can be categorised into two generic classes: simple (atomic-molecular) fluids where the particles are the atoms-molecules themselves, hence of nanometer size, and colloidal fluids with particles of μm size suspended in a simple fluid bath made of much smaller and lighter particles, namely atoms or small molecules [1]. Colloidal fluids are of theoretical interest, but they are also ubiquitous in many everyday materials, e.g. tea, milk, detergents, lubricants and paints, to name just a few [2]. Due to the mass separation between the bath and colloidal particles, such fluids exhibit intricate dynamics with a wide range of interrelated timescales. This leads to significant challenges in both theoretical and computational modelling [3–5]. Over the last few decades, significant theoretical work has been devoted to approximating the dynamics of colloidal fluids by coarse graining the full Newtonian description of both bath and colloidal particles to obtain appropriate reduced models [6–16]. The ultimate goal underlying these models is to judiciously eliminate the enormous number of degrees of freedom (DoF) related to the bath particles, traditionally via projection-operator techniques, which

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essentially average over the bath dynamics to obtain the effective dynamics of the colloidal particles. As a consequence of this coarse graining, the resultant time-evolution equations for the colloidal-particle DoF are no longer deterministic but random. These stochastic time-evolution equations describing the dynamics of the colloidal particles are widely known as the Langevin equations (LEs) [17]. Whilst the LEs were initially proposed heuristically to describe Brownian motion observed in nature, and restricted to non-interacting and spherically-symmetric particles immersed in a fluid bath [18], they have been formally justified and generalised to describe a wide spectrum of colloidal fluids [7, 11, 19, 20].

The theoretical description of such fluids involves at least one LE per particle, with the total number of particles, N, being approximately of the order of Avogadro's number. This makes the LE formalism intractable from a computational point of view as also discussed in [4, 5]. A typical approach to circumvent such a difficulty consists in transforming the system of LEs to an equivalent time-evolution equation for the probability density function (PDF), which is commonly known as the Fokker–Planck equation (FPE). For the N-particle system under consideration, a standard procedure in statistical mechanics is to average the FPE over $(N-1)$ particles which gives rise to the evolution equation of the one-body density [21, 22]. In general, the mean-field dynamics obtained for the one-body distribution consists of a continuity equation for the local density and a conservation law for the momentum density, which is now a functional of the density [22]. The exact expression for the functional relating the momentum density and the local density is generally unknown, although it can be approximated via physical arguments. In particular, for systems with strong dissipation due to the bath, it can be argued that the functional can be written in terms of the free-energy functional of a system with the same density at equilibrium. This is convenient not only because such a functional has been extensively studied in the statistical mechanics of classical fluids [21, 22], but also because it ensures that the resultant equation reduces to the corresponding equilibrium density functional theory (DFT) [4, 5]. That is why this mean-field equation is called dynamical DFT (DDFT), as it extends the original equilibrium DFT to describe the dynamics of simple and more general colloidal fluids out of equilibrium [4, 5, 11, 23–25, 26, 27, 28–30].

The DDFT framework has been shown to successfully model a wide variety of phenomena, from hard rod and hard sphere systems [5], mixtures [31], to the calculation of the van Hove distribution function for Brownian hard spheres [32] and even crystallisation [33]. Nevertheless, DDFT itself has no inherent capability of describing processes governed by fluctuations since they are averaged out during the derivation from the LE. And simply adding an additional noise term (as for instance in the study by Elder *et al* [34]) to e.g. cross energy barriers and study homogeneous nucleation, raises questions in relation to the physical interpretation of this noise because fluctuations have already been included in the theory which is 'mean field' by the one-body density (which can also be seen as the probability to find a particle at a certain position). It is for this reason that it is generally thought that DDFT and noise effects are incompatible, a debate that remains vivid as was also pointed out by Archer and Rauscher [35]. Yet, fluctuations are crucial in wide-ranging and important phenomena such as nucleation in phase transitions and other barrier-crossing processes, e.g. diffusion in solids, chemical reactions or transport in biological systems. In addition, systems are rather susceptible to noise in the vicinity of phase boundaries. For these reasons, a fluctuating counterpart of DDFT to describe nonequilibrium dynamics of spherically-symmetric colloidal fluids has been derived. This is precisely what is now referred to in general as fluctuating hydrodynamics (FH).

The first derivations of FH go back to the early works of Landau *et al* [36]. This derivation, however, was mostly phenomenological. Landau *et al* [36] simply added the fluctuating fluxes to the usual hydrodynamic equations and, also, the fluctuation-dissipation theorem (which relates time-correlation functions to transport coefficients) was assumed to hold even out of equilibrium. Follow-up studies have focused on deriving rigorously the Landau–Lifshitz fluctuation formalism, initiated by the works of Bixon and Zwanzig [37], Fox and Uhlenbeck [38] and Mashiyama and Mori [39]. But, it was not until the appearance of the works of Munakata [40], Kawasaki [41] and Dean [42] that FH was interpreted as a fluctuating DDFT (so-called 'Dean–Kawasaki model'), with a heuristic energy functional. Nevertheless the Dean–Kawasaki (DK) model describes the evolution of the instantaneous *microscopic density* field, and thus contains the same physical information as the set of LEs [28]. Therefore, the DK model cannot be understood as a model equation for the evolution of the observable fields. One could argue that either averaging over a mesoscopic temporal window or by averaging over spatially-finite domains, the DK equation can be transformed into the fluctuating time-evolution equation of a coarse-grained density, and hence can be seen as a DDFT with fluctuations [24]. Nevertheless, these averaging methods require the use of typical time scales or experimental resolution kernels, which depend on the properties of the particular system under consideration, to define the coarse-grained density. Hence, there is still a need of formalising the connection between DK and FH from first principles to describe the evolution of observable fields and remove the dependence on the microscopic LEs. Also, the effects of local angular velocity have not been taken into account in such methodologies. Yet, the orientational DoF play a crucial role in the behaviour of systems of nonspherical particles [11, 29, 30], which often exhibit complex phase diagrams and

associated phase transions [43, 44]. To describe the dynamics of these fluids and their phase transitions we require a mean-field nonequilibrium formalism analogous to that previously developed for point-like particles.

While the authors already generalised DDFT to include the effects of asymmetric particles [11], the incorporation of fluctuations in a self-consistent way requires a different ab-initio approach. Specifically, in this work we start with the Hamiltonian description of the system and connect with the DK model by introducing the definition of the microscopic fields. By making this connection, we will highlight again why the original DK equation still depends on all microscopic DoF. Then, we show that carrying out an ensemble average over a general nonequilibrium distribution, the dynamics for the microscopic density and momentum fields governed by the DK equation can be transformed into a fluctuating DDFT for the *mesoscopic quantities* that are experimentally observed. This ensemble average allows us to avoid the phenomenological temporal or spatial coarse-graining techniques mentioned above. The nonequilibrium distribution needed for that purpose is decomposed into a local-equilibrium and a purely nonequilibrium contribution, the latter only contributing to high-order moments such as the stress tensor or the heat flux [5, 11]. Along the way, we show that the free-energy functional appearing in the resulting mesoscopic fluctuating DDFT exhibits the properties of the thermodynamic free-energy functional from classical DFT [21, 22]. This, in some sense, supports the current state-of-the-art modus operandi, namely interpreting the energy functional of DK descriptions as the Helmholtz free-energy functional. More crucially, our work provides a formal and alternative answer to the question on whether DDFT is stochastic or deterministic [24].

In section 2, we rederive the LEs for a system of general colloidal particles [11]. We also define the microscopic local number and momentum density fields which allows us to rewrite the LEs in a much more compact way. Section 3 is devoted to deriving a closed microscopic FH equation (FHE) which only depends on the fields previously defined. To get an equation for the coarse-grained density, the microscopic FHE is integrated over a finite-time interval under the assumption of strong dissipation due to the thermal bath. The integration produces a *generalised* DK equation which now exhibits an unavoidable coupling between the translational and rotational DoF. Finally, section 4 introduces an alternative coarse graining method by averaging over a nonequilibrium distribution function consisting of a local-equilibrium and a purely nonequilibrium contribution. With this nonequilibrium ensemble average we obtain an underdamped FHE which shows exactly the same structure as the DDFT [11] but with an additional noise term. After taking the limit of strong damping, the mesoscopic FHE obtained before reduces in structure to the generalised DK model, with a subtle difference in the definition of the free-energy functional involved. Finally, we introduce a flow diagram to summarise our derivation and the relationship with previous approaches in figure 1. Concluding remarks, implications of our results and a discussion of open problems are offered in section 5.

2. Microscopic description

2.1. Hamilton's and Liouville's equations

In the most general scenario, the dynamical state of a system of particles is determined by the generalised coordinates and momenta of the constituent particles. A colloidal suspension can be considered as a system of N identical, arbitrarily shaped colloidal particles with mass m immersed in a fluid of $n \gg N$ bath particles with mass m_b. In the absence of mechanical constraints [45], the configuration of the particles is defined by the position vectors locating the centre of mass of each particle and the rotational DoF to describe the particle orientation with respect to a space-fixed coordinate system. Assuming a canonical bath of point-like (non-orientable) particles, the dynamics of a bath particle is uniquely determined by its translational DoF and their conjugate (linear) momenta, $\mathbf{x}_i = (\mathbf{r}_i^b, \mathbf{p}_i^b)$. The configuration state of a colloidal particle is, however, determined not only by the translational DoF and its linear momentum, $\mathbf{X}_i = (\mathbf{r}_i, \mathbf{p}_i)$, but also by the rotational DoF, e.g. the Eulerian angles $\boldsymbol{\alpha}_i = (\theta_i, \phi_i, \chi_i)$ defined using the $ZY'Z''$ convention [7, 45, 46], which determine the orientation of the principal-axes frame of the particles, $\mathfrak{B}$, relative to the space-fixed frame, $\mathfrak{S}$. Thus, the dynamics of the colloidal particles will be determined by the evolution of $\boldsymbol{\Omega}_i = (\boldsymbol{\alpha}_i, \boldsymbol{\pi}_i)$, with $\boldsymbol{\pi}_i$ being the rotational conjugate momenta [8], whose relationship with the angular momenta $\mathbf{L}_i$ will be specified below. We know that $\mathbf{L}_i = \mathbb{I}_i \boldsymbol{\omega}_i$ with $\boldsymbol{\omega}_i$ the angular velocity and $\mathbb{I}_i$ the inertial tensor. This tensor is diagonal with respect to $\mathfrak{B}$, such that $\mathbb{I}_i = \mathbb{I} = \mathrm{diag}(I_1, I_2, I_3)$. The transformation between the frames $\mathfrak{B}$ and $\mathfrak{S}$ is given by the rotation operator $\mathcal{R}_i$, such that $\mathbf{x} = \mathcal{R}_i \mathbf{x}'$ where $\mathbf{x} \in \mathfrak{B}$ and $\mathbf{x}' \in \mathfrak{S}$ [46]. In the principal-axes frame, $\boldsymbol{\omega}_i(\boldsymbol{\alpha}_i) = \dot{\boldsymbol{\Phi}}_i(\boldsymbol{\alpha}_i) = \boldsymbol{\Lambda}_i^\top \dot{\boldsymbol{\alpha}}_i$, where the dot denotes time derivative, $\boldsymbol{\Phi}_i$ highlights the fact that $\boldsymbol{\omega}_i$ is the vector accounting for the rate of change of angular displacement over the Cartesian frame $\mathfrak{B}$ [7, 46], and $\boldsymbol{\Lambda}_i$ can be found elsewhere [11, 46]. Accordingly, $\boldsymbol{\omega}_i' = \mathcal{R}_i^\top \boldsymbol{\omega}_i = \boldsymbol{\Xi}_i \dot{\boldsymbol{\alpha}}_i$ under the space-fixed frame, with $\boldsymbol{\Xi}_i = \mathcal{R}_i^\top \boldsymbol{\Lambda}_i^\top$. Hence $\boldsymbol{\omega}_i = \mathcal{R}_i \boldsymbol{\omega}_i'$, with $\boldsymbol{\omega}_i'$ the angular velocity in $\mathfrak{S}$, and $\mathbb{I}_i' = \mathcal{R}_i^\top \, \mathbb{I} \, \mathcal{R}_i$, which is neither diagonal nor constant.

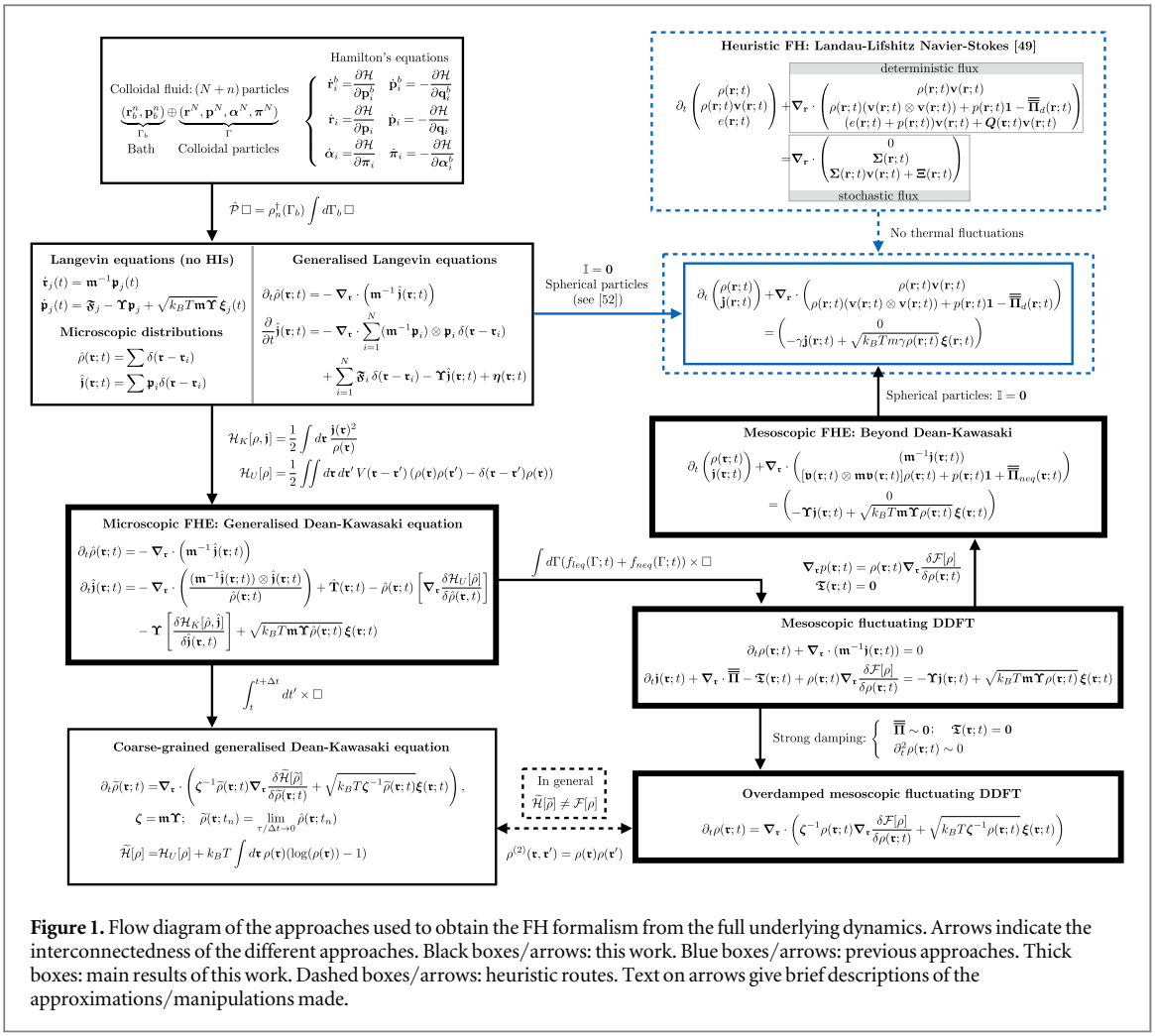


Figure 1. Flow diagram of the approaches used to obtain the FH formalism from the full underlying dynamics. Arrows indicate the interconnectedness of the different approaches. Black boxes/arrows: this work. Blue boxes/arrows: previous approaches. Thick boxes: main results of this work. Dashed boxes/arrows: heuristic routes. Text on arrows give brief descriptions of the approximations/manipulations made.

The Lagrangian of the system, $\mathcal{L}$, can now be expressed as the sum of two terms:

$$\mathcal{L}_b = \sum_{i=1}^{n} \frac{1}{2} m_b\, \dot{\mathbf{r}}_i^b \cdot \dot{\mathbf{r}}_i^b - \mathcal{U}(\mathbf{r}_b^n,\, \mathbf{r}^N,\, \boldsymbol{\alpha}^N),$$
$$\mathcal{L}_B = \sum_{i=1}^{N} \frac{1}{2} (m\dot{\mathbf{r}}_i \cdot \dot{\mathbf{r}}_i + \dot{\boldsymbol{\alpha}}_i \cdot (\boldsymbol{\Xi}_i^\top \mathbb{I}_i' \boldsymbol{\Xi}_i)\dot{\boldsymbol{\alpha}}_i) - V(\mathbf{r}^N,\, \boldsymbol{\alpha}^N), \tag{1}$$

with $\mathcal{L}_b$ and $\mathcal{L}_B$ referring to the *bath* and *Brownian* (colloidal) contribution, respectively, $V(\mathbf{r}^N,\, \boldsymbol{\alpha}^N)$ being the potential energy due to short-range interactions exclusively between colloidal particles, and

$$\mathcal{U}(\mathbf{r}_b^n,\, \mathbf{r}^N,\, \boldsymbol{\alpha}^N) = U(\mathbf{r}_b^n) + \sum_{\mu=1}^{N} \mathbf{u}_\mu(\mathbf{r}_b^n,\, \mathbf{r}_\mu,\, \boldsymbol{\alpha}_\mu), \tag{2}$$

the short-range intermolecular potential energy coming from the interaction between bath particles, $U(\mathbf{r}_b^n)$, and the interaction of each colloidal particle with the whole bath, $\mathbf{u}_\mu(\mathbf{r}_b^n,\, \mathbf{r}_\mu)$, for all $\mu = 1, \ldots, N$. Note that we have used the compact notation $\mathbf{r}_b^n = (\mathbf{r}_1^b \ldots \mathbf{r}_n^b)$, $\mathbf{r}^N = (\mathbf{r}_1 \ldots \mathbf{r}_N)$ and $\boldsymbol{\alpha}^N = (\boldsymbol{\alpha}_1 \ldots \boldsymbol{\alpha}_N)$ for the sake of convenience. From classical mechanics, we obtain the conjugate momenta:

$$\mathbf{p}_i^b = \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_i^b} = m_b \dot{\mathbf{r}}_j^b, \quad \mathbf{p}_i = \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_i} = m\dot{\mathbf{r}}_i, \quad \boldsymbol{\pi}_i = \frac{\partial \mathcal{L}}{\partial \dot{\boldsymbol{\alpha}}_i} = (\boldsymbol{\Xi}_i^\top \mathbb{I}_i' \boldsymbol{\Xi}_i)\dot{\boldsymbol{\alpha}}_i. \tag{3}$$

Thus, $\boldsymbol{\pi}_i = (\boldsymbol{\Xi}_i^\top \mathbb{I}_i' \boldsymbol{\Xi}_i)\dot{\boldsymbol{\alpha}}_i = \boldsymbol{\Lambda}_i \mathbf{L}_i$ [7, 47], which allows us to construct the Hamiltonian function of the system,

$$\mathcal{H} = \sum_{i=1}^{n} \frac{\mathbf{p}_j^b \cdot \mathbf{p}_j^b}{2m_b} + \mathcal{U}(\mathbf{r}_b^n,\, \mathbf{r}^N,\, \boldsymbol{\alpha}^N) + \sum_{i=1}^{N} \left(\frac{\mathbf{p}_j \cdot \mathbf{p}_j}{2m} + \frac{1}{2} \boldsymbol{\pi}_j \cdot (\boldsymbol{\Xi}_j^\top \mathbb{I}_j' \boldsymbol{\Xi}_j)^{-1} \boldsymbol{\pi}_j \right) + V(\mathbf{r}^N,\, \boldsymbol{\alpha}^n), \tag{4}$$

so that the dynamics of the particles is uniquely defined by Hamilton's equations:

$$\begin{aligned}\dot{\mathbf{r}}_i^b &= \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i^b}, \quad \dot{\mathbf{p}}_i^b = -\frac{\partial \mathcal{H}}{\partial \mathbf{q}_i^b},\\ \dot{\mathbf{r}}_i &= \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i}, \quad \dot{\mathbf{p}}_i = -\frac{\partial \mathcal{H}}{\partial \mathbf{q}_i},\\ \dot{\boldsymbol{\alpha}}_i &= \frac{\partial \mathcal{H}}{\partial \boldsymbol{\pi}_i}, \quad \dot{\boldsymbol{\pi}}_i = -\frac{\partial \mathcal{H}}{\partial \boldsymbol{\alpha}_i^b},\end{aligned} \tag{5}$$

and the initial conditions for positions and momenta of the bath and colloidal particles. However, the lack of information about the initial conditions turns this classical (deterministic) problem into a stochastic one, where whatever initial configuration compatible with the total energy of the system is assumed equally probable. Thus, at a given time t, the probability of finding the system with phase-space coordinates $\Gamma(t) = (\mathbf{x}^n(t), \mathbf{X}^N(t), \boldsymbol{\Omega}^N(t))$ is determined by the $n + N$ particle distribution $\varrho^{(n+N)}(\Gamma; t)$. According to Liouville's theorem, such a distribution will evolve according to [48]

$$\partial_t \varrho^{(n+N)}(\Gamma; t) + \mathrm{i}\mathfrak{L}\, \varrho^{(n+N)}(\Gamma; t) = 0 \tag{6}$$

with the Liouvillian, $\mathfrak{L}$, being the sum of the following operators:

$$\begin{aligned}\mathrm{i}\mathfrak{L}_T &= \sum_{j=1}^{n}\left(\frac{\mathbf{p}_i^b}{m_b}\cdot\frac{\partial}{\partial \mathbf{r}_j^b} + \mathbf{f}_j\cdot\frac{\partial}{\partial \mathbf{p}_j^b}\right) + \sum_{j=1}^{N}\left(\frac{\mathbf{p}_j}{m}\cdot\frac{\partial}{\partial \mathbf{r}_j} + \mathbf{F}_j\cdot\frac{\partial}{\partial \mathbf{p}_j}\right),\\ \mathrm{i}\mathfrak{L}_R &= \sum_{j=1}^{N}\left(\dot{\boldsymbol{\alpha}}_j\cdot\frac{\partial}{\partial \boldsymbol{\alpha}_j} + \dot{\boldsymbol{\pi}}_j\cdot\frac{\partial}{\partial \boldsymbol{\pi}_j}\right),\end{aligned} \tag{7}$$

where $\mathbf{f}_i = -\frac{\partial}{\partial \mathbf{r}_i^b}(U + \sum_{\mu=1}^{N}\mathbf{u}_\mu)$ and $\mathbf{F}_i = -\frac{\partial}{\partial \mathbf{r}_i}(V + \mathbf{u}_i)$ are the instantaneous forces acting on bath and colloidal particles, respectively. As we are only interested in the dynamics of the colloidal particles, we need to average out the bath-particle DoF to obtain the dynamics of the reduced N particle distribution. But, before applying such a 'projection' on the Liouville equation (6), we want to perform a change of variables to express the dynamics of the arbitrarily shaped colloidal particles in terms of more convenient quantities, namely the angular velocities and momenta $\boldsymbol{\omega}_i$ and $\mathbf{L}_i$, respectively. The probability distribution in terms of the new phase-space coordinates $\widetilde{\Gamma}(t) = (\mathbf{x}^n(t), \mathbf{X}^N(t), \widetilde{\boldsymbol{\Omega}}^N(t))$, with $\widetilde{\boldsymbol{\Omega}}(t) = (\boldsymbol{\alpha}^N, \mathbf{L}^N)$, is given by the transformation law:

$$F^{(n+N)}(\widetilde{\Gamma}; t) = \left|\frac{\partial \Gamma}{\partial \widetilde{\Gamma}}\right| \varrho^{(n+N)}(\widetilde{\Gamma}; t) = \prod_{j=1}^{N} \sin\theta_j\, \varrho^{(n+N)}(\widetilde{\Gamma}; t). \tag{8}$$

With this, equation (6) can be transformed into an equivalent equation for $F^{(n+N)}(\widetilde{\Gamma}; t)$,

$$\partial_t F^{(n+N)}(\widetilde{\Gamma}; t) + (\mathrm{i}\mathfrak{L}_T + \mathrm{i}\widetilde{\mathfrak{L}}_R) F^{(n+N)}(\widetilde{\Gamma}; t) = 0, \tag{9}$$

with [7, 8, 11, 47]

$$\mathrm{i}\widetilde{\mathfrak{L}}_R = \sum_{i=1}^{N}\frac{\partial}{\partial \boldsymbol{\Phi}_i}\cdot\boldsymbol{\omega}_i + (\mathbf{N}_i + \mathbf{L}_i\times\boldsymbol{\omega}_i)\cdot\frac{\partial}{\partial \mathbf{L}_i}, \tag{10}$$

where $\frac{\partial}{\partial \boldsymbol{\Phi}} = \mathbf{e}_x\frac{\partial}{\partial \Phi_x} + \mathbf{e}_y\frac{\partial}{\partial \Phi_y} + \mathbf{e}_z\frac{\partial}{\partial \Phi_z}$ is the angular-gradient operator (also known as orientational gradient [49]), with $\mathbf{e}_i$ the unitary vector along axis $i \in \{x, y, z\}$ of the Cartesian frame $\mathfrak{B}$, with components:

$$\begin{aligned}\frac{\partial}{\partial \Phi_x^j} &= \cos\chi_j\frac{\partial}{\partial\theta_j} + \csc\theta_j\cos\chi_j\frac{\partial}{\partial\phi_j} - \cot\theta_j\sin\chi_j\frac{\partial}{\partial\chi_j}\\ \frac{\partial}{\partial \Phi_y^j} &= -\sin\chi_j\frac{\partial}{\partial\theta_j} + \csc\theta_j\sin\chi_j\frac{\partial}{\partial\phi_j} - \cot\theta_j\cos\chi_j\frac{\partial}{\partial\chi_j}\\ \frac{\partial}{\partial \Phi_z^j} &= \frac{\partial}{\partial\chi_j}.\end{aligned} \tag{11}$$

Also, $\mathbf{T}_i = \mathbf{N}_i - \boldsymbol{\omega}_i\times\mathbf{L}_i$ represents the net torque acting on a given colloidal particle, with

$$\mathbf{N}_i = -\frac{\partial}{\partial \boldsymbol{\Phi}_i}[V(\mathbf{r}^N, \boldsymbol{\alpha}^N) + \mathbf{u}_i(\mathbf{r}_b^n, \mathbf{r}_i, \boldsymbol{\alpha}_i)] \tag{12}$$

the torque due to intermolecular interactions along the principal axes of inertia of the ith particle. Inserting the definitions $\mathfrak{m} = \mathrm{diag}(m\mathbf{1}, \mathbb{I})$, $\mathfrak{r}_i = (\mathbf{r}_i, \boldsymbol{\Phi}_i)$, $\mathfrak{p}_i = (\mathbf{p}_i, \mathbf{L}_i)$, $\widetilde{\mathfrak{p}}_i = \boldsymbol{\lambda}\mathfrak{p}_i$, with $\boldsymbol{\lambda} = \mathfrak{m}^{-1/2}$, and $\mathfrak{f}_i = (\mathbf{F}_i, \mathbf{T}_i)$, along with the operators $\boldsymbol{\nabla}_{\mathfrak{r}_i} = \left(\frac{\partial}{\partial \mathbf{r}_i}, \frac{\partial}{\partial \boldsymbol{\Phi}_i}\right)^\top$ and $\boldsymbol{\nabla}_{\mathfrak{p}_i} = \left(\frac{\partial}{\partial \mathbf{p}_i}, \frac{\partial}{\partial \mathbf{L}_i}\right)^\top$, we can eventually rewrite equation (9) as,

$$\left\{\partial_t + \sum_{i=1}^{n}\left(\frac{\mathbf{p}_i^b}{m_b}\cdot\frac{\partial}{\partial\mathbf{r}_i^b} + \mathbf{f}_i\cdot\frac{\partial}{\partial\mathbf{p}_i^b}\right) + \sum_{i=1}^{N}\boldsymbol{\lambda}(\boldsymbol{\nabla}_{\mathfrak{r}_i}\cdot\tilde{\mathfrak{p}}_i + \mathfrak{f}_i\cdot\boldsymbol{\nabla}_{\tilde{\mathfrak{p}}_i})\right\}F^{(n+N)}(\tilde{\Gamma};\,t) = 0. \tag{13}$$

Now, we can use Zwanzig's projection technique to get the time-evolution equation for the N-particle distribution

$$f^{(N)}(t) = \int \mathrm{d}\mathbf{x}^n F^{(n+N)}(t), \tag{14}$$

from Liouville's equation [10–12, 15, 16]. For this purpose we define the projector operator over the fast phase-space variables (i.e. the bath phase-space coordinates [15])

$$\hat{\mathcal{P}}F^{(n+N)}(\Gamma;\,t) = \rho_n^{\dagger}(\mathbf{x}^n)\int \mathrm{d}\mathbf{x}^n\, F^{(n+N)}(\Gamma;\,t), \tag{15}$$

with $\rho_n^{\dagger}$ the equilibrium distribution of the bath particles in the instantaneous potential created by the colloidal particles. Thus, projecting Liouville's equation on the fast variables, taking the limit of massive colloidal particles (by letting $\boldsymbol{\lambda}\to\mathbf{0}$), and after considerable algebraic manipulations [11], we reach the time-evolution equation we were after:

$$\begin{aligned}\partial_t f^{(N)}(t) + \sum_{j=1}^{N}(\boldsymbol{\nabla}_{\mathfrak{r}_i}\cdot\boldsymbol{\mathfrak{m}}^{-1}\mathfrak{p}_i + \mathfrak{F}_i\cdot\boldsymbol{\nabla}_{\mathfrak{p}_i})f^{(N)}(t)\\ = \sum_{i,j=1}^{N}\boldsymbol{\nabla}_{\mathfrak{p}_i}\cdot\boldsymbol{\Gamma}_{ij}(\mathfrak{r}^N)(\mathfrak{p}_i + k_{\mathrm{B}}T\boldsymbol{\mathfrak{m}}\,\boldsymbol{\nabla}_{\mathfrak{p}_i})f^{(N)}(t).\end{aligned} \tag{16}$$

Here k_{B} is the Boltzmann constant and T the temperature imposed by the bath, $\mathfrak{F} = \langle\,\mathfrak{f}\rangle^{\dagger}$ denotes the solvent-averaged forces and torques, i.e.

$$\mathfrak{F}_i = \int \mathrm{d}\mathbf{x}^n\rho_n^{\dagger}(\mathbf{x}^n)\mathfrak{f}_i(\mathbf{r}_b^n,\,\mathbf{r}^N,\,\boldsymbol{\alpha}^N) \tag{17}$$

with $\langle.\rangle^{\dagger}$ representing the average over the fast variables, and

$$\boldsymbol{\Gamma}_{ij}(\mathfrak{r}^N) = \begin{pmatrix}\boldsymbol{\Gamma}_{ij}^{TT} & \boldsymbol{\Gamma}_{ij}^{TR}\\ \boldsymbol{\Gamma}_{ij}^{RT} & \boldsymbol{\Gamma}_{ij}^{RR}\end{pmatrix} = \beta\boldsymbol{\mathfrak{m}}^{-1}\int_0^{\infty}\mathrm{d}s\,\langle\,\mathfrak{f}_i(t)\otimes(\,\mathfrak{f}_j(t-s) - \mathfrak{F}_j)\rangle^{\dagger}. \tag{18}$$

where $\boldsymbol{\Gamma}_{ij}^{\mu\nu}$, $\mu,\,\nu\in\{T,\,R\}$, are the translational–rotational friction tensors, where $\beta = 1/k_{\mathrm{B}}T$. We may decompose the friction tensors as $\boldsymbol{\Gamma}_{ij}^{\mu\nu} = \gamma_{\mu\nu}\delta_{ij}\mathbf{1} + \gamma_{\mu\nu}\widetilde{\boldsymbol{\Gamma}}_{ij}^{\mu\nu}$, so that

$$\boldsymbol{\Gamma}_{ij} = \delta_{ij}\boldsymbol{\Upsilon} + \widetilde{\boldsymbol{\Upsilon}}_{ij}, \tag{19}$$

with the 6×6 tensor $\boldsymbol{\Upsilon} = (\gamma_{\mu\nu}\mathbf{1})$, where $\gamma_{\mu\nu}$ is the constant friction coefficient for an isolated particle and $\widetilde{\boldsymbol{\Upsilon}}_{ij} = (\gamma_{\mu\nu}\widetilde{\boldsymbol{\Gamma}}_{ij}^{\mu\nu})$, where $\widetilde{\boldsymbol{\Gamma}}_{ij}^{\mu\nu}$ are the translational–rotational hydrodynamic-interaction (HI) tensors. For the particular case of spheres far from walls, the components of the friction tensor are $\gamma_T = 6\pi\eta R_0/m$ and $\gamma_R = 8\pi\eta\,R_0^3/I = 20\pi\eta\,R_0/m$, whereas the mixed translational and rotational components vanish. Here R_0 is the radius of the colloidal particles and η is the dynamic viscosity [19].

2.2. Generalised LEs

The FPE we have just derived for arbitrarily shaped colloidal particles immersed in a bath, equation (16), can be transformed into a set of stochastic differential equations describing the temporal evolution of their dynamical variables [11, 17]

$$\begin{aligned}\dot{\mathfrak{r}}_i(t) &= \boldsymbol{\mathfrak{m}}^{-1}\mathfrak{p}_i(t)\\ \dot{\mathfrak{p}}_i(t) &= \mathfrak{F}_i - \sum_{j=1}^{N}\boldsymbol{\Gamma}_{ij}(\mathfrak{r}^N)\mathfrak{p}_j + \sum_{j=1}^{N}\mathbf{A}_{ij}\boldsymbol{\xi}_j(t),\end{aligned} \tag{20}$$

where $\boldsymbol{\xi}_j = (\,\mathbf{f}_j,\,\mathbf{t}_j)^{\top}$ is a six-dimensional Gaussian white noise representing the random forces, $\mathbf{f}_j$, and torques, $\mathbf{t}_j$, acting upon the jth particle, such that $\langle\xi_j^a(t)\rangle = 0$ and $\langle\xi_j^a(t)\xi_k^b(t')\rangle = 2\delta_{jk}\delta^{ab}\delta(t-t')$, where $\langle.\rangle$ refers to the average over an ensemble of the white-noise realisations. The strength of these random forces and torques is given by the tensor $\mathbf{A}_{jk}$ which obeys the fluctuation-dissipation relation,

$$k_{\mathrm{B}}T\boldsymbol{\mathfrak{m}}\,\boldsymbol{\Gamma}_{jk}(\mathfrak{r}^N) = \sum_{l=1}^{N}\mathbf{A}_{jl}(\mathfrak{r}^N)\mathbf{A}_{kl}(\mathfrak{r}^N). \tag{21}$$

Equation (20) represents the amalgamation of the translational and rotational LEs for a system of colloidal particles subject to HIs due to the bath. In some practical cases, however, the HIs due to the bath can be neglected. Hence, the stochastic dynamics of the colloidal particles is given by the LEs

$$\dot{\mathbf{r}}_i(t) = \mathfrak{m}^{-1}\mathbf{p}_i(t),$$
$$\dot{\mathbf{p}}_i(t) = \mathfrak{F}_i - \boldsymbol{\Upsilon}\mathbf{p}_i + \sqrt{k_B T \mathfrak{m}\boldsymbol{\Upsilon}}\ \boldsymbol{\xi}_i(t), \tag{22}$$

recalling that $\mathfrak{F}_i = (-\frac{\partial \mathcal{U}}{\partial \mathbf{r}_i}, -\frac{\partial \mathcal{U}}{\partial \boldsymbol{\Phi}_i} - (\mathbb{I}^{-1}\mathbf{L}_i) \times \mathbf{L}_i)$, where $\mathcal{U}(\mathbf{r}^N)$ is the solvent-averaged interaction-potential of mean force [50] that will be assumed to be of the form

$$\mathcal{U}(\mathbf{r}^N) = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1,j\neq i}^{N} V(\mathbf{r}_i - \mathbf{r}_j). \tag{23}$$

For simplicity, we assume that the system is in a very large container, so that the confining (external) potential $V_1(\mathbf{r})$ modelling the wall-particle interactions is zero inside the container and infinite outside. In these conditions the surface effects of the container can be considered negligible.

Our goal in this section is to derive the LEs for the microscopic number and momentum density fields

$$\hat{\rho}(\mathbf{r};\, t) = \sum_{i=1}^{N}\delta(\mathbf{r} - \mathbf{r}_i), \tag{24}$$

$$\hat{\mathbf{j}}(\mathbf{r};\, t) = \sum_{i=1}^{N}\mathbf{p}_i\delta(\mathbf{r} - \mathbf{r}_i), \tag{25}$$

where $\hat{\mathbf{j}} \equiv (\hat{\mathbf{j}}_T, \hat{\mathbf{j}}_R)^\top$, with $\hat{\mathbf{j}}_T(\mathbf{r};\, t) = \sum_{i=1}^{N}\mathbf{p}_i\delta(\mathbf{r} - \mathbf{r}_i)$ and $\hat{\mathbf{j}}_R(\mathbf{r};\, t) = \sum_{i=1}^{N}\mathbf{L}_i\delta(\mathbf{r} - \mathbf{r}_i)$ are the translational and angular (i.e. rotational) momentum density, respectively. Computing the time derivative of equations (24) and (25), and using equation (22), will result in a set of unclosed nonlinear stochastic equations that we refer to as *generalised* LEs. These constitute the starting point of any bottom-up derivation of the FH framework.

First, we can derive the time-evolution equation for the density field which results in the continuity equation,

$$\partial_t\hat{\rho}(\mathbf{r};\, t) = -\boldsymbol{\nabla}_{\mathbf{r}}\cdot(\mathfrak{m}^{-1}\hat{\mathbf{j}}(\mathbf{r};\, t)), \tag{26}$$

where we used the definition of $\hat{\mathbf{j}}$, given in equation (25). In a similar way, the time-evolution equation for the momentum density field can be obtained,

$$\frac{\partial}{\partial t}\hat{\mathbf{j}}(\mathbf{r};\, t) = -\boldsymbol{\nabla}_{\mathbf{r}}\cdot\sum_{i=1}^{N}(\mathfrak{m}^{-1}\mathbf{p}_i)\otimes\mathbf{p}_i\,\delta(\mathbf{r} - \mathbf{r}_i) + \sum_{i=1}^{N}\mathfrak{F}_i\,\delta(\mathbf{r} - \mathbf{r}_i) - \boldsymbol{\Upsilon}\hat{\mathbf{j}}(\mathbf{r};\, t) + \boldsymbol{\eta}(\mathbf{r};\, t), \tag{27}$$

where we have defined the local random fluctuations as

$$\boldsymbol{\eta}(\mathbf{r};\, t) = \sum_{i=1}^{N}\sqrt{k_{\mathrm{B}}T\ \mathfrak{m}\boldsymbol{\Upsilon}}\ \delta(\mathbf{r} - \mathbf{r}_i)\boldsymbol{\xi}_i(t). \tag{28}$$

We note that the noise term here can be rewritten in a much more useful way (as will be made apparent later). It is known that any noise with the structure shown in equation (28) can be rewritten (without changing the statistical properties) as long as the autocorrelation of the noise remains unchanged [51]. Hence, we can rewrite the local fluctuation term as [42]

$$\boldsymbol{\eta}(\mathbf{r};\, t) = \sqrt{k_{\mathrm{B}}T\ \mathfrak{m}\boldsymbol{\Upsilon}\ \hat{\rho}(\mathbf{r};\, t)}\ \boldsymbol{\xi}(\mathbf{r};\, t), \tag{29}$$

with $\boldsymbol{\xi}$ being a spatiotemporal Gaussian white noise satisfying $\langle\boldsymbol{\xi}(\mathbf{r};\, t)\boldsymbol{\xi}(\mathbf{r}';\, t')\rangle = 2\delta(t - t')\delta(\mathbf{r} - \mathbf{r}')\mathbf{1}$. Note that, hereinafter, we will interpret the fluctuations in the Itô sense, unless specified otherwise.

At this point, we need to discuss the stochasticity present in equations (26) and (27), the building blocks of the FH formalism, either microscopic, mesoscopic or macroscopic. The most evident source of randomness is due to the interaction between the particles under study and the constituent particles of the bath. Indeed, these unpredictable collisions result in the noise term appearing in equation (27). The second source of stochasticity is, however, more subtle. The equations derived so far can be understood as a convenient rewriting of the original LEs, which describe a unique trajectory in the phase space, $\Gamma(t) = \{\mathbf{r}_i,\, \mathbf{p}_i\}_1^N$, provided an initial condition at some earlier time, e.g. $t = 0$. However, for most practical purposes, we are not interested in following a single trajectory but an average over an ensemble of them. This ensemble can be readily determined in equilibrium, since we know its (canonical) distribution. Out of equilibrium, in general, the distribution representing the ensemble of systems will be time-dependent and one has to specify the ensemble at a given time, e.g. a distribution of initial conditions. If we want to study such an ensemble average we must carry out the following two steps [52]. First, we specify the values of the fluctuating forces and torques acting on the particles at any time. Second, such a fixed set of values can be considered as an external field acting on the colloidal particles and we can proceed with the average over an ensemble of initial conditions which gives rise to a *mesoscopic* FHE. Finally, if one is interested in a macroscopic picture, an average over the noise could be performed to obtain the (the expected) *macroscopic* FHE. Nevertheless, in a general non-equilibrium scenario, the expected dynamics resulting from sampling all possible realisations of the noise does not have to coincide with the most-likely one.

Indeed, our interest is obtaining the equation which governs the most likely path, i.e. the dynamics that is most likely to be observed, representing the maximum of the corresponding probability. For this purpose, one needs to derive the path probability associated with the mesoscopic FHE and, then, obtain the most likely dynamics. As we will discuss at the end of section 4, in the case of weak noise (i.e. when the deterministic fluxes govern the dynamics) the most-likely-path dynamics recovers previous DDFT equations. This should clarify the connection between DDFT and mesoscopic FH, with the former constituting the evolution law of the most-likely path obtained from the latter in the weak-noise limit (WNL). To set the notation, the FHE obtained when following individual trajectories, i.e. without performing any average, will be called the microscopic FHE in what follows.

3. Microscopic FH: generalising the Dean–Kawasaki model

In this section, we introduce the kinetic and internal energy functionals. This makes it possible to cast the generalised LEs (equation (27)) in a form resembling hydrodynamic equations, with an additional fluctuating term. It is noteworthy that these equations are often misleadingly referred to as the FHE for colloids. Nevertheless, as we discuss below, such equations still contain all the microscopic details, which is why we refer to them as the *microscopic* FHE. The following derivation reviews and generalises the Kawasaki model [41, 53] to describe general colloids. This generalisation can later be integrated over a finite time interval, yielding a time-evolution equation for the coarse-grained (and, hence, mesoscopic) density. At the end of this section, we show that the coarse-grained evolution equation exhibits the same general structure as Dean's equation [42], the overdamped counterpart of Kawasaki's equation. This result, however, represents a generalisation of Dean's original equation, which was derived for the microscopic density and not for a coarse-grained density [42].

In order to obtain a closed equation that depends only on the number and momentum density fields, $\hat{\rho}(\mathbf{r};\,t)$ and $\hat{\mathbf{j}}(\mathbf{r};\,t)$, we need to deal with the first and second term on the right-hand side of equation (27). We start with the term that involves the potential part of $\mathfrak{F}_i$, which can be easily rewritten as

$$\sum_{i=1}^{N}\boldsymbol{\nabla}_{\mathbf{r}_i}\mathcal{U}(\mathbf{r}^N)\delta(\mathbf{r}-\mathbf{r}_i)=\hat{\rho}(\mathbf{r};\,t)\int\mathrm{d}\mathbf{r}'\,\boldsymbol{\nabla}_{\mathbf{r}}V(\mathbf{r}-\mathbf{r}')\hat{\rho}(\mathbf{r}';\,t). \tag{30}$$

Next, the term involving the dyadic product can also be rewritten by using that

$$\begin{aligned}\sum_{i=1}^{N}(\mathbf{m}^{-1}\mathbf{p}_i)\otimes\mathbf{p}_i\,\delta(\mathbf{r}-\mathbf{r}_i)&=\frac{\sum_{i=1}^{N}\sum_{j=1}^{N}(\mathbf{m}^{-1}\mathbf{p}_i)\otimes\mathbf{p}_i\delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}-\mathbf{r}_j)}{\hat{\rho}(\mathbf{r};\,t)}\\&=\frac{(\mathbf{m}^{-1}\hat{\mathbf{j}}(\mathbf{r};\,t))\otimes\hat{\mathbf{j}}(\mathbf{r};\,t)}{\hat{\rho}(\mathbf{r};\,t)}.\end{aligned} \tag{31}$$

This same argument can be applied to the part of the second term in equation (27) that involves the intrinsic torques, giving

$$\mathbf{T}_m(\mathbf{r};\,t)=-\sum_{i=1}^{N}(\mathbb{I}^{-1}\mathbf{L}_i)\times\mathbf{L}_i\,\delta(\mathbf{r}-\mathbf{r}_i)=-\frac{(\mathbb{I}^{-1}\hat{\mathbf{j}}_R(\mathbf{r};\,t))\times\hat{\mathbf{j}}_R(\mathbf{r};\,t)}{\hat{\rho}(\mathbf{r};\,t)}, \tag{32}$$

where $\mathbf{T}_m(\mathbf{r};\,t)$ stands for the the microscopic torque field. For the sake of convenience, we introduce the definition $\hat{\mathbf{T}}(\mathbf{r};\,t)=(\mathbf{0},\,\mathbf{T}_m(\mathbf{r};\,t))^{\top}$ that will be useful below.

Note that equations (31) and (32) are not completely mathematically rigorous unless the Dirac delta function is understood in a more physical sense. Such an interpretation relies on the assumption that we can discretise the phase space into finite cells, small enough such that no more than one particle can occupy the same spatial cell. Under such circumstances, the Dirac delta function can be understood in terms of a Kronecker delta divided by the volume of a cell. This is a reliable approximation if we are considering systems of interacting particles with a repulsive hard core. A more detailed discussion of how to discretise the phase space can be found elsewhere [53]. We will make use of this interpretation in what follows only when there is no other way to get a clear connection with a well-known expression or term. For instance, it was necessary above to rewrite the first term in equation (27) in the same way as the kinetic stress tensor of classical (mesoscopic) FH [36].

Substituting equations (29)–(32) into the fluctuating momentum-moment equation (27) gives

$$\partial_t \hat{\mathbf{j}}(\mathbf{r};\, t) = -\boldsymbol{\nabla}_{\mathbf{r}} \cdot \left(\frac{(\mathbf{m}^{-1}\hat{\mathbf{j}}(\mathbf{r};\, t)) \otimes \hat{\mathbf{j}}(\mathbf{r};\, t)}{\hat{\rho}(\mathbf{r};\, t)} \right) - \hat{\rho}(\mathbf{r};\, t) \int \mathrm{d}\mathbf{r}'\, \boldsymbol{\nabla}_{\mathbf{r}} V(\mathbf{r} - \mathbf{r}') \hat{\rho}(\mathbf{r}';\, t) + \hat{\mathbf{T}}(\mathbf{r};\, t) - \boldsymbol{\Upsilon} \hat{\mathbf{j}}(\mathbf{r};\, t) + \sqrt{k_{\mathrm{B}} T\, \mathbf{m}\boldsymbol{\Upsilon}\, \hat{\rho}(\mathbf{r};\, t)}\; \boldsymbol{\xi}(\mathbf{r};\, t), \tag{33}$$

where the terms in the right-hand-side have been written to emphasise the connection with those appearing in classical conservation laws for both the linear and angular momenta [54]. The first (and nonlinear) term can be identified with the kinetic stress tensor. The second and third terms correspond to the body forces acting on the system of particles. Finally, the last two terms describe the bath forces acting on the particles, with the first representing the dissipation and the second the fluctuation. Inserting the definition of the kinetic and internal energy functionals

$$\mathcal{H}_K[\phi,\, \boldsymbol{\pi}] = \frac{1}{2} \int \mathrm{d}\mathbf{r}\, \frac{\boldsymbol{\pi}(\mathbf{r})^2}{\phi(\mathbf{r})}, \tag{34}$$

$$\mathcal{H}_U[\phi] = \frac{1}{2} \iint \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\, V(\mathbf{r} - \mathbf{r}')(\phi(\mathbf{r})\phi(\mathbf{r}') - \delta(\mathbf{r} - \mathbf{r}')\phi(\mathbf{r})), \tag{35}$$

equation (33) can be rewritten as

$$\partial_t \hat{\mathbf{j}}(\mathbf{r};\, t) = -\boldsymbol{\nabla}_{\mathbf{r}} \cdot \left(\frac{(\mathbf{m}^{-1}\hat{\mathbf{j}}(\mathbf{r};\, t)) \otimes \hat{\mathbf{j}}(\mathbf{r};\, t)}{\hat{\rho}(\mathbf{r};\, t)} \right) + \hat{\mathbf{T}}(\mathbf{r};\, t) - \hat{\rho}(\mathbf{r};\, t) \left[\boldsymbol{\nabla}_{\mathbf{r}} \frac{\delta \mathcal{H}_U[\hat{\rho}]}{\delta \hat{\rho}(\mathbf{r},\, t)} \right] - \boldsymbol{\Upsilon} \left[\frac{\delta \mathcal{H}_K[\hat{\rho},\, \hat{\mathbf{j}}]}{\delta \hat{\mathbf{j}}(\mathbf{r},\, t)} \right] + \sqrt{k_{\mathrm{B}} T \mathbf{m}\boldsymbol{\Upsilon}\hat{\rho}(\mathbf{r};\, t)}\; \boldsymbol{\xi}(\mathbf{r};\, t). \tag{36}$$

In the absence of a thermal bath, i.e. with $\boldsymbol{\Upsilon} = \mathbf{0}$, equations (26) and (36) are the canonical equations for the deterministic number and momentum fields. In fact, in the canonical situation, the Hamiltonian of the system $\mathcal{H}[\hat{\rho},\, \hat{\mathbf{j}}] = \mathcal{H}_U[\hat{\rho}] + \mathcal{H}_K[\rho,\, \hat{\mathbf{j}}]$ is conserved and corresponds to the total energy.

Consider now the PDF for observing a given configuration $\{\hat{\rho},\, \hat{\mathbf{j}}\}$ at time t,

$$f([\hat{\rho},\, \hat{\mathbf{j}}];\, t) = \langle \delta[\rho - \hat{\rho}_t] \delta[\mathbf{j} - \hat{\mathbf{j}}_t] \rangle \tag{37}$$

with the average $\langle . \rangle$ carried out over $\{\boldsymbol{\xi}(\mathbf{r};\, t)\}_{\mathbf{r}}$ and the delta functional defined by

$$\delta[\rho - \hat{\rho}_t] \delta[\mathbf{j} - \hat{\mathbf{j}}_t] = \prod_{\mathbf{r}} \delta[\rho(\mathbf{r}) - \hat{\rho}(\mathbf{r};\, t)] \delta[\mathbf{j}(\mathbf{r}) - \hat{\mathbf{j}}(\mathbf{r};\, t)]. \tag{38}$$

The time-evolution equation governing the dynamics of $f([\hat{\rho},\, \hat{\mathbf{j}}];\, t)$ can be formally derived by following standard arguments [41, 53]. Such an equation has the structure of an FPE and it has been presented elsewhere for spherical particles [25, 41, 53]. The functional FPE is out of the scope of the present study, but it is worth mentioning that there exists a stationary solution given by

$$f_{\mathrm{eq}}[\rho,\, \mathbf{j}] = \mathcal{Z}^{-1} \exp(-\beta \mathcal{H}[\rho,\, \mathbf{j}]), \tag{39}$$

which is a field representation of the canonical Gibbs distribution, with $\beta = 1/k_{\mathrm{B}}T$ and $\mathcal{Z}$ the canonical partition function. This is the reason for introducing the energy functionals in equations (34) and (35): they make it possible to understand the microscopic FHEs (26) and (33) for the fields as the dynamics associated with the canonical ensemble. In that sense, it is not surprising to see that the Hamiltonian function involved so far does not include any entropic contribution, unlike in the mesoscopic case. This is due to the fact that equation (33) describes the exact dynamics of a given microstate in the phase space, i.e. a unique trajectory in the space, $\{\hat{\rho}(\mathbf{r}),\, \hat{\mathbf{j}}(\mathbf{r})\}$. It is only after coarse graining the description that some information is lost, which will finally produce the typical entropic contribution $\rho(\mathbf{r})\log \rho(\mathbf{r})$. Remarkably, the structure of the entropic contribution will turn out to be the same if we coarse grain the evolution of the density field (as usually done to study the overdamped limit [53]) or the general formalism (by averaging the FHEs with some nonequilibrium distribution), as discussed in section 4.

3.1. Generalised Dean equation for the coarse-grained density

In many physical situations, colloidal fluids are subject to strong dissipation due to the bath. This allows a substantial simplification of the formalism developed above, eventually yielding a time-evolution equation for the microscopic density field $\hat{\rho}(t)$. In the strong damping limit, the density field relaxes much slower than the momentum density, which relaxes on a typical time scale $\tau = \|\mathbf{m}^{-1}\boldsymbol{\Upsilon}\|^{-1} \to 0$. Hence, the unsteady acceleration vanishes rapidly so that $\partial_t \hat{\mathbf{j}}(\mathbf{r};\, t) \to \mathbf{0}$ for $t > \tau$. Under such circumstances, it is customary to integrate the evolution equations (26) and (33) over a (mesoscopic) time interval $[t,\, t + \Delta t]$ with $\tau/\Delta t \to 0$

and then take the continuous limit $\Delta t \to 0$ to finally get the evolution equation for the coarse-grained density field [53]

$$\begin{aligned}\partial_t \widetilde{\rho}(\mathbf{r};\, t) &= \boldsymbol{\nabla}_{\mathbf{r}} \cdot \left(\zeta^{-1} \widetilde{\rho}(\mathbf{r};\, t) \left(\left[\boldsymbol{\nabla}_{\mathbf{r}} \frac{\delta \mathcal{H}_U[\widetilde{\rho}]}{\delta \widetilde{\rho}(\mathbf{r},\, t)} \right] + \frac{k_{\mathrm{B}} T}{\widetilde{\rho}(\mathbf{r};\, t)} \boldsymbol{\nabla}_{\mathbf{r}} \widetilde{\rho}(\mathbf{r};\, t) \right) \right) \\ &\quad + \boldsymbol{\nabla}_{\mathbf{r}} \cdot \sqrt{k_{\mathrm{B}} T \zeta^{-1} \widetilde{\rho}(\mathbf{r};\, t)}\ \boldsymbol{\xi}(\mathbf{r};\, t) \\ &= \boldsymbol{\nabla}_{\mathbf{r}} \cdot \left(\zeta^{-1} \widetilde{\rho}(\mathbf{r};\, t) \left[\boldsymbol{\nabla}_{\mathbf{r}} \frac{\delta \widetilde{\mathcal{H}}[\widetilde{\rho}]}{\delta \widetilde{\rho}(\mathbf{r};\, t)} \right] + \sqrt{k_{\mathrm{B}} T \zeta^{-1} \widetilde{\rho}(\mathbf{r};\, t)}\, \boldsymbol{\xi}(\mathbf{r};\, t) \right), \end{aligned} \tag{40}$$

where we define

$$\widetilde{\rho}(\mathbf{r};\, t_n) = \lim_{\tau/\Delta t \to 0} \hat{\rho}(\mathbf{r};\, t_n), \qquad t_n = n \Delta t \ (n = 1,\, 2,\, \ldots). \tag{41}$$

Here $\zeta = \mathbf{m}\boldsymbol{\Upsilon}$ and $\widetilde{\mathcal{H}}[\rho] = \mathcal{H}_U[\rho] + \mathcal{H}_{id}[\rho]$, where $\mathcal{H}_{\mathrm{id}}[\rho] = k_{\mathrm{B}} T \int \mathrm{d}\mathbf{r} \rho(\mathbf{r})(\log(\rho(\mathbf{r})) - 1)$ resembles the ideal-gas contribution to the free energy function in classical DFT. For systems of smooth spherical particles, where the friction tensor $\boldsymbol{\Upsilon}$ reduces to the translational component, we recover the Dean–Kawasaki model[5] [41, 42, 55]. However, the strength of the rotational–translational coupling increases rapidly as the distance of the particles from a wall decreases [11, 19, 56]. For that reason, such a coupling must be taken into account near walls even for the spherically-symmetric case, which makes equation (40) an indispensable generalisation of the state of the art.

When the number of colloidal particles is sufficiently low (the so-called weak-solution limit) we find that $\widetilde{\mathcal{H}}[\widetilde{\rho}] \simeq \mathcal{H}_{\mathrm{id}}[\widetilde{\rho}]$, so that the generalised Dean–Kawasaki equation (40) becomes,

$$\partial_t \widetilde{\rho}(\mathbf{r};\, t) \simeq \boldsymbol{\nabla}_{\mathbf{r}} \cdot (k_{\mathrm{B}} T \zeta^{-1} \boldsymbol{\nabla}_{\mathbf{r}} \widetilde{\rho}(\mathbf{r};\, t)) + \boldsymbol{\nabla}_{\mathbf{r}} \cdot \sqrt{k_{\mathrm{B}} T \zeta^{-1} \widetilde{\rho}(\mathbf{r};\, t)}\, \boldsymbol{\xi}(\mathbf{r};\, t) \tag{42}$$

which is a generalised diffusion equation with noise. Here, we naturally identify $\mathbf{D} = k_{\mathrm{B}} T \zeta^{-1}$ as the diffusion tensor, which fulfils the generalised Einstein relationships [11, 19, 49]

$$\begin{aligned} \beta \mathbf{D}_{\mathrm{TT}} &= (\zeta_{\mathrm{TT}} - \zeta_{\mathrm{TR}} \zeta_{\mathrm{RR}}^{-1} \zeta_{\mathrm{RT}})^{-1} \\ \beta \mathbf{D}_{\mathrm{TR}} &= -(\zeta_{\mathrm{TT}} - \zeta_{\mathrm{TR}} \zeta_{\mathrm{RR}}^{-1} \zeta_{\mathrm{RT}})^{-1} \zeta_{\mathrm{TR}} \zeta_{\mathrm{RR}}^{-1} \equiv (\zeta_{\mathrm{RT}} - \zeta_{\mathrm{TT}} \zeta_{\mathrm{TR}}^{-1} \zeta_{\mathrm{RR}})^{-1} \\ \beta \mathbf{D}_{\mathrm{RT}} &= -(\zeta_{\mathrm{TT}} - \zeta_{\mathrm{TR}} \zeta_{\mathrm{RR}}^{-1} \zeta_{\mathrm{RT}})^{-1} \zeta_{\mathrm{RT}} \zeta_{\mathrm{TT}}^{-1} \equiv (\zeta_{\mathrm{TR}} - \zeta_{\mathrm{RR}} \zeta_{\mathrm{RT}}^{-1} \zeta_{\mathrm{TT}})^{-1} \\ \beta \mathbf{D}_{\mathrm{RR}} &= (\zeta_{\mathrm{RR}} - \zeta_{\mathrm{RT}} \zeta_{\mathrm{TT}}^{-1} \zeta_{\mathrm{TR}})^{-1}. \end{aligned} \tag{43}$$

In the special case when the translational and rotational motions are fully decoupled, $\mathbf{D}_{\mathrm{TR}} = \mathbf{D}_{\mathrm{RT}} \equiv \mathbf{0}$, equation (42) exhibits the classical Laplacian structure for the drift term.

4. Mesoscopic fluctuating DDFT: beyond Dean–Kawasaki

In what follows we derive the dynamical law of the relevant observable quantities for a general colloidal fluid in contact with a thermal bath. These are the continuum fields accounting for the local density and momentum, which can be understood as the ensemble averages of the corresponding microscopic fields introduced before. While the fluctuating equation (36) governing the microscopic fields is quite appealing, it is not useful for describing the observable momenta of the colloidal fluid, since it still depends on all positions and momenta of the constituent particles. Recall that the fields given by equations (24) and (25) are sums of Dirac's deltas, implicitly involving all positions and momenta. Indeed, equation (36) can be seen just as a more convenient representation of the original LEs (22). However, more often than not, the microscopic FHE is heuristically used as the dynamical law governing the temporal evolution of the mesoscopic fields describing the sate of the system. Here we introduce the formal step required to get a mesoscopic FH description by carrying out an ensemble average of the generalised DK equation. Such a procedure allows us to introduce a proper free-energy functional that will be shown to exhibit the same properties as the equilibrium energy functional of DFT [21, 22]. Eventually, this makes possible to connect our result with the DDFT formalism. The schematic in figure 1 offers a diagrammatic representation of the whole derivation and the possible connections of our framework with previous FH equations.

First of all, we need to introduce a nonequilibrium distribution, $f(\Gamma;\, t)$, to describe the nonequilibrium ensemble under consideration. With this, the local mesoscopic density and mean velocity are defined by

[5] It is worth mentioning that Dean's original derivation of equation (40) does not involve the mesoscopic coarse-grained density $\widetilde{\rho}$ but the microscopic density $\hat{\rho}$. Indeed, Dean's equation results from the use of Itô's lemma [51] on $\hat{\rho}$, which is a function of all particles' positions evolving according to LEs.

$$\left\langle \begin{matrix} \hat{\rho}(\mathfrak{r};\,t) \\ \hat{\mathbf{j}}(\mathfrak{r};\,t) \end{matrix} \right\rangle = \int \mathrm{d}\Gamma \begin{pmatrix} \hat{\rho}(\mathfrak{r};\,t) \\ \hat{\mathbf{j}}(\mathfrak{r};\,t) \end{pmatrix} f(\Gamma;\,t) = \begin{pmatrix} 1 \\ \mathfrak{m}\mathfrak{v}(\mathfrak{r};\,t) \end{pmatrix} \rho(\mathfrak{r};\,t). \tag{44}$$

Consider the decomposition $f(\Gamma;\,t) = f_{\mathrm{leq}}(\Gamma;\,t) + f_{\mathrm{neq}}(\Gamma;\,t)$, taking into account both local-equilibrium and nonequilibrium effects. The first term represents a regime in which the system has reached a local-equilibrium state. In this scenario the probability distribution can be constructed using the equilibrium canonical distribution

$$\begin{aligned} f_{\mathrm{eq}}(\Gamma) &= \mathcal{Z}^{-1}\exp(-\beta H(\Gamma)) \\ &= \mathcal{Z}^{-1}\exp\left(-\beta \int \mathrm{d}\mathfrak{r} \sum_{i=1}^{N} \frac{1}{2}\left\{\left((\mathfrak{m}^{-1}\mathfrak{p}_i)\cdot\mathfrak{p}_i + \sum_{j\neq i}^{N} V(\mathfrak{r}_i - \mathfrak{r}_j)\right)\right\}\delta(\mathfrak{r} - \mathfrak{r}_i)\right) \end{aligned} \tag{45}$$

by referring the linear and angular momenta to a comoving reference frame with local velocity $\mathfrak{v}(\mathfrak{r};\,t)$, in which the fluid seems to be at rest. The local-equilibrium distribution is given by equation (45) with the substitution $\mathfrak{p}_i \mapsto \mathfrak{p}_i' = \mathfrak{p}_i - \mathfrak{m}\mathfrak{v}(\mathfrak{r};\,t)$ [5, 11, 48, 57, 58], and $f_{\mathrm{leq}}(\Gamma';\,t) = \mathcal{Z}^{-1}\exp(-\beta H(\Gamma'))$, with the prime symbol indicating the comoving reference frame, the local-equilibrium linear and angular momenta defined by

$$\mathbf{j}_{\mathrm{leq}}(\mathfrak{r};\,t) = \langle \hat{\mathbf{j}}(\mathfrak{r};\,t)\rangle_{\mathrm{leq}} \tag{46}$$

and $\hat{\rho}'(\mathfrak{r};\,t) = \hat{\rho}(\mathfrak{r};\,t)$. On the other hand, the nonequilibrium term must satisfy:

$$\int \mathrm{d}\mathfrak{p}^N \begin{pmatrix} 1 \\ \hat{\mathbf{j}}(\mathfrak{r};\,t) \end{pmatrix} f_{\mathrm{neq}}(\Gamma;\,t) = \begin{pmatrix} 0 \\ \mathbf{0} \end{pmatrix}. \tag{47}$$

Using equations (47) and (46) it is readily found that $\mathbf{j}(\mathfrak{r};\,t) = \mathbf{j}_{\mathrm{leq}}(\mathfrak{r};\,t) = \mathfrak{m}\mathfrak{v}(\mathfrak{r};\,t)\rho(\mathfrak{r};\,t)$, since f_{neq} only contributes to higher moments, such as the kinetic stress tensor, or the local torque density.

Applying now $\langle . \rangle = \langle . \rangle_{\mathrm{leq}} + \langle . \rangle_{\mathrm{neq}}$ on both sides of equations (26) and (27) yields the desired FHE for the coarse-grained fields $\rho(\mathfrak{r};\,t)$ and $\mathbf{j}(\mathfrak{r};\,t)$. Starting with the continuity equation we get its coarse-grained counterpart,

$$\partial_t \rho(\mathfrak{r};\,t) + \boldsymbol{\nabla}_{\mathfrak{r}}\cdot(\mathfrak{m}^{-1}\mathbf{j}(\mathfrak{r};\,t)) = 0. \tag{48}$$

Continuing with the momentum equation (27) we get,

$$\begin{aligned} &\partial_t \mathbf{j}(\mathfrak{r};\,t) + \boldsymbol{\nabla}_{\mathfrak{r}}\cdot\left\langle \sum_{i=1}^{N}(\mathfrak{m}^{-1}\mathfrak{p}_i)\otimes\mathfrak{p}_i\delta(\mathfrak{r}-\mathfrak{r}_i)\right\rangle - \left\langle \sum_{i=1}^{N}\mathfrak{F}_i\delta(\mathfrak{r}-\mathfrak{r}_i)\right\rangle \\ &\quad = \langle \boldsymbol{\Upsilon}\hat{\mathbf{j}}\rangle + \sqrt{k_{\mathrm{B}}T\mathfrak{m}\boldsymbol{\Upsilon}\rho(\mathfrak{r};\,t)}\;\boldsymbol{\xi}(\mathfrak{r};\,t). \end{aligned} \tag{49}$$

Using the properties of the canonical distribution we can rewrite the second and third term on the left-hand side of the latter equation in a more convenient way. First,

$$\boldsymbol{\nabla}_{\mathfrak{r}}\cdot\left\langle \sum_{i=1}^{N}(\mathfrak{m}^{-1}\mathfrak{p}_i)\otimes\mathfrak{p}_i\delta(\mathfrak{r}-\mathfrak{r}_i)\right\rangle = k_{\mathrm{B}}T\boldsymbol{\nabla}_{\mathfrak{r}}\rho(\mathfrak{r};\,t) + \boldsymbol{\nabla}_{\mathfrak{r}}\cdot\overline{\overline{\boldsymbol{\Pi}}}(\mathfrak{r};\,t), \tag{50}$$

where we have introduced the definition of the kinetic stress tensor:

$$\overline{\overline{\boldsymbol{\Pi}}}(\mathfrak{r};\,t) = [\mathfrak{v}(\mathfrak{r};\,t)\otimes\mathfrak{m}\mathfrak{v}(\mathfrak{r};\,t)]\rho(\mathfrak{r};\,t) + \left\langle \sum_{i=1}^{N}(\mathfrak{m}^{-1}\mathfrak{p}_i)\otimes\mathfrak{p}_i\delta(\mathfrak{r}-\mathfrak{r}_i)\right\rangle_{\mathrm{neq}} \tag{51}$$

$$= \overline{\overline{\boldsymbol{\Pi}}}_{\mathrm{leq}}(\mathfrak{r};\,t) + \overline{\overline{\boldsymbol{\Pi}}}_{\mathrm{neq}}(\mathfrak{r};\,t) \tag{52}$$

with the first term embodying the local-equilibrium stress due to translational, rotational and coupled velocities. Second,

$$-\left\langle \sum_{i=1}^{N}\mathfrak{F}_i\delta(\mathfrak{r}-\mathfrak{r}_i)\right\rangle = \int \mathrm{d}\mathfrak{r}'\;\boldsymbol{\nabla}_{\mathfrak{r}}V(\mathfrak{r}-\mathfrak{r}')\langle\hat{\rho}(\mathfrak{r};\,t)\hat{\rho}(\mathfrak{r}';\,t)\rangle_{\mathrm{leq}} - \boldsymbol{\mathfrak{T}}(\mathfrak{r};\,t), \tag{53}$$

where $\boldsymbol{\mathfrak{T}}(\mathfrak{r};\,t) = \langle\hat{\mathbf{T}}(\mathfrak{r};\,t)\rangle_{\mathrm{neq}}$ is the non-inertial local torque, which vanishes in the local-equilibrium limit. To close the derivation, we shall define the functional:

$$\mathcal{F}[\rho(\mathfrak{r};\,t)] = k_{\mathrm{B}}T\int \mathrm{d}\mathfrak{r}\;\rho(\mathfrak{r};\,t)(\log(\Lambda^3\rho(\mathfrak{r};\,t)) - 1) + \mathcal{F}_{\mathrm{exc}}[\rho(\mathfrak{r};\,t)] \tag{54}$$

with Λ being the de Broglie wavelength (which will turn out to be irrelevant) and $\mathcal{F}_{\mathrm{exc}}[\rho(\mathfrak{r};\,t)]$ satisfying the relationship,

$$\frac{\delta \mathcal{F}_{\rm exc}[\rho]}{\delta \rho(\mathbf{r};\, t)} = \left\langle \frac{\delta \mathcal{H}_U[\hat{\rho}]}{\delta \hat{\rho}(\mathbf{r};\, t)} \right\rangle_{\rm leq}. \tag{55}$$

It can be shown that the functional derivative of $\mathcal{F}[\rho]$ fulfils,

$$\rho(\mathbf{r};\, t)\boldsymbol{\nabla}_{\mathbf{r}} \frac{\delta \mathcal{F}[\rho]}{\delta \rho(\mathbf{r};\, t)} = k_{\rm B}T \boldsymbol{\nabla}_{\mathbf{r}} \rho(\mathbf{r};\, t) + \int {\rm d}\mathbf{r}'\ \boldsymbol{\nabla}_{\mathbf{r}} V(\mathbf{r}-\mathbf{r}')\rho^{(2)}(\mathbf{r},\, \mathbf{r}';\, t), \tag{56}$$

where we introduced the definition $\rho^{(2)}(\mathbf{r},\, \mathbf{r}';\, t) = \langle \hat{\rho}(\mathbf{r};\, t)\hat{\rho}(\mathbf{r}';\, t)\rangle_{\rm leq}$. In particular, if the averages are taken at equilibrium, equation (56) recovers the first equation of the Yvon–Born–Green hierarchy [48, 59], as reported in previous derivations of DDFT [4, 5, 11]. For this reason, the functional $\mathcal{F}[\rho]$ can be identified as the classical Helmholtz free-energy functional [21, 22] where the first term on the right-hand side of equation (54) accounts for the ideal gas contribution and the last one is the excess over-ideal term containing the contribution due to interactions. Upon substitution of equations (50)–(56) into (49), and using equation (48), the mesoscopic fluctuating DDFT equation is finally obtained,

$$\begin{aligned} &\partial_t \rho(\mathbf{r};\, t) + \boldsymbol{\nabla}_{\mathbf{r}} \cdot (\mathbf{m}^{-1}\mathbf{j}(\mathbf{r};\, t)) = 0 \\ &\partial_t \mathbf{j}(\mathbf{r};\, t) + \boldsymbol{\nabla}_{\mathbf{r}} \cdot \overline{\overline{\boldsymbol{\Pi}}} - \boldsymbol{\mathfrak{T}}(\mathbf{r};\, t) \\ &+ \rho(\mathbf{r};\, t)\boldsymbol{\nabla}_{\mathbf{r}} \frac{\delta \mathcal{F}[\rho]}{\delta \rho(\mathbf{r};\, t)} = -\boldsymbol{\Upsilon}\mathbf{j}(\mathbf{r};\, t) + \sqrt{k_{\rm B}T\mathbf{m}\boldsymbol{\Upsilon}\rho(\mathbf{r};\, t)}\ \boldsymbol{\xi}(\mathbf{r};\, t), \end{aligned} \tag{57}$$

which constitutes the main result of this work. To understand the connection between the fluctuating DDFT (57) and the fluctuating Navier–Stokes (NS) equations of Landau and Lifshitz [36], we need to discuss first the connection between local pressure and the free-energy functional. Under the local-equilibrium approximation, the term involving the functional derivative of the free-energy functional can be related to the local pressure as follows [22, 52],

$$\boldsymbol{\nabla}_{\mathbf{r}} p(\mathbf{r};\, t) = \rho(\mathbf{r};\, t)\boldsymbol{\nabla}_{\mathbf{r}} \frac{\delta \mathcal{F}[\rho]}{\delta \rho(\mathbf{r};\, t)}, \tag{58}$$

by using, e.g., the Gibbs–Duhem equation for an isothermal and single-component system, ${\rm d}p = \rho {\rm d}\mu$, along with the Euler–Lagrange equation of DFT, $\mu = \delta\mathcal{F}[\rho]/\delta\rho$. This allows us to rewrite equation (57) as,

$$\begin{aligned} &\partial_t \rho(\mathbf{r};\, t) + \boldsymbol{\nabla}_{\mathbf{r}} \cdot (\mathbf{m}^{-1}\mathbf{j}(\mathbf{r};\, t)) = 0 \\ &\partial_t \mathbf{j}(\mathbf{r};\, t) + \boldsymbol{\nabla}_{\mathbf{r}} \cdot \boldsymbol{\Pi}(\mathbf{r};\, t) = -\boldsymbol{\Upsilon}\mathbf{j}(\mathbf{r};\, t) + \sqrt{k_{\rm B}T\mathbf{m}\boldsymbol{\Upsilon}\rho(\mathbf{r};\, t)}\ \boldsymbol{\xi}(\mathbf{r};\, t), \end{aligned} \tag{59}$$

where $\boldsymbol{\Pi}(\mathbf{r};\, t) = \boldsymbol{\sigma}(\mathbf{r};\, t) + \overline{\overline{\boldsymbol{\Pi}}}_{\rm leq}(\mathbf{r};\, t)$, with $\boldsymbol{\sigma}(\mathbf{r};\, t) = p(\mathbf{r};\, t)\mathbf{1}$ the complete stress tensor [54]. Equation (59) comprises indeed a generalised version of the fluctuating NS equation for isothermal systems under local-equilibrium conditions. What is more, equation (57) can be transformed into (59) by inserting $\boldsymbol{\sigma}(\mathbf{r};\, t) = p(\mathbf{r};\, t)\mathbf{1} + \overline{\overline{\boldsymbol{\Pi}}}_{\rm neq}(\mathbf{r};\, t)$, if the relationship given in equation (58) is assumed to hold and the torque $\boldsymbol{\mathfrak{T}}$ is neglected. This shows that the mesoscopic fluctuating DDFT derived here is consistent with the phenomenological FH formalism of Landau and Lifshitz. Indeed, our derivation endows the FH framework with the originally missing connection between the microscopic and mesoscopic dynamics, which sheds light on the structure and origin of the noise term, besides also generalising FH to more realistic colloids. Figure 1 depicts a diagrammatic representation of these connections.

One can also connect the mesoscopic fluctuating DDFT with previous macroscopic DDFTs for arbitrary-shape colloids [11, 29, 30]. To do that, we consider the local-equilibrium approximation in equation (57) and multiply it by $\mathbf{m}^{-1}$ on both sides, resulting

$$\begin{aligned} &\partial_t(\rho(\mathbf{r};\, t)\boldsymbol{\mathfrak{v}}(\mathbf{r};\, t)) + \boldsymbol{\nabla}_{\mathbf{r}} \cdot [(\boldsymbol{\mathfrak{v}}(\mathbf{r};\, t) \otimes \boldsymbol{\mathfrak{v}}(\mathbf{r};\, t))\rho(\mathbf{r};\, t)] + \mathbf{m}^{-1}\rho(\mathbf{r};\, t)\boldsymbol{\nabla}_{\mathbf{r}} \frac{\delta \mathcal{F}[\rho]}{\delta \rho(\mathbf{r};\, t)} \\ &= -(\mathbf{m}^{-1}\boldsymbol{\Upsilon}\mathbf{m})\rho(\mathbf{r};\, t)\boldsymbol{\mathfrak{v}}(\mathbf{r};\, t) + \mathbf{m}^{-1}\sqrt{k_{\rm B}T\mathbf{m}\boldsymbol{\Upsilon}\rho(\mathbf{r};\, t)}\ \boldsymbol{\xi}(\mathbf{r};\, t). \end{aligned} \tag{60}$$

Making use of equation (48) together with the identity,

$$\boldsymbol{\nabla}_{\mathbf{r}} \cdot [(\boldsymbol{\mathfrak{v}}(\mathbf{r};\, t) \otimes \boldsymbol{\mathfrak{v}}(\mathbf{r};\, t))\rho(\mathbf{r};\, t)] = \boldsymbol{\mathfrak{v}}(\mathbf{r};\, t)\boldsymbol{\nabla}_{\mathbf{r}} \cdot (\boldsymbol{\mathfrak{v}}(\mathbf{r};\, t)\rho(\mathbf{r};\, t)) + \rho(\mathbf{r};\, t)(\boldsymbol{\mathfrak{v}}(\mathbf{r};\, t) \cdot \boldsymbol{\nabla}_{\mathbf{r}})\boldsymbol{\mathfrak{v}}(\mathbf{r};\, t), \tag{61}$$

we get

$$\begin{aligned} &\partial \rho(\mathbf{r};\, t) + \boldsymbol{\nabla}_{\mathbf{r}} \cdot (\rho(\mathbf{r};\, t)\boldsymbol{\mathfrak{v}}(\mathbf{r};\, t)) = 0 \\ &\rho(\mathbf{r};\, t)\mathcal{D}_t \boldsymbol{\mathfrak{v}}(\mathbf{r};\, t) + \mathbf{m}^{-1}\rho(\mathbf{r};\, t)\boldsymbol{\nabla}_{\mathbf{r}} \frac{\delta \mathcal{F}[\rho]}{\delta \rho(\mathbf{r};\, t)} \\ &+(\boldsymbol{\Upsilon}_{\parallel} + \boldsymbol{\Upsilon}_{\perp}\boldsymbol{\epsilon})\rho(\mathbf{r};\, t)\boldsymbol{\mathfrak{v}}(\mathbf{r};\, t) = \mathbf{m}^{-1}\sqrt{k_{\rm B}T\mathbf{m}\boldsymbol{\Upsilon}\rho(\mathbf{r};\, t)}\ \boldsymbol{\xi}(\mathbf{r};\, t), \end{aligned} \tag{62}$$

where we used the material derivative $\mathcal{D}_t = (\partial_t + \boldsymbol{\mathfrak{v}}(\mathbf{r};\, t) \cdot \boldsymbol{\nabla}_{\mathbf{r}})$ and introduced the definitions: $\boldsymbol{\Upsilon}_{\parallel} = {\rm diag}(\gamma_{\rm TT}\mathbf{1},\, \gamma_{\rm RR}\mathbf{1})$, $\boldsymbol{\Upsilon}_{\perp} = {\rm diag}(\gamma_{\rm TR}\mathbf{1},\, \gamma_{\rm RT}\mathbf{1})$, and $\boldsymbol{\epsilon} = {\rm adiag}(m^{-1}\mathbb{I},\, m\mathbb{I}^{-1})$ the anti-diagonal block matrix with submatrices, $(\boldsymbol{\epsilon})_{1,2} = m^{-1}\mathbb{I}$, $(\boldsymbol{\epsilon})_{2,1} = m\mathbb{I}^{-1}$ and $(\boldsymbol{\epsilon})_{1,1} = (\boldsymbol{\epsilon})_{2,2} = \mathbf{0}$. Interestingly, if we remove the noise

in equation (62), we recover a special case of the DDFT equation derived by Durán-Olivencia *et al* [11] for pairwise interacting particles without HIs. Hence, the mesoscopic FHE (57), or equivalently equation (62), provides an extension of the generalised DDFT equation to fluctuation-driven processes, e.g. phase transitions. We will come back to this point of connecting DDFT with our FHE at the end of this section.

Finally, having developed the general framework, we want to compare the coarse-grained microscopic FHE (40) presented in the previous section with the mesoscopic FH that we have just discussed. To do that we need to take the limit of strong dissipation in equation (60) (or (62)). In this limit, as discussed before, the momentum current will be small enough so that the quadratic term with $\mathbf{j}(\mathbf{r};\,t)$ (or $\mathfrak{v}(\mathbf{r};\,t)$) can be neglected. This assumption considerably simplifies the equations:

$$\begin{aligned}\partial_t\rho(\mathbf{r};\,t) + \boldsymbol{\nabla}_{\mathbf{r}}\cdot(\mathbf{m}^{-1}\mathbf{j}(\mathbf{r};\,t)) &= 0\\ \partial_t\mathbf{j}(\mathbf{r};\,t) + \rho(\mathbf{r};\,t)\boldsymbol{\nabla}_{\mathbf{r}}\frac{\delta\mathcal{F}[\rho]}{\delta\rho(\mathbf{r};\,t)} &= -\boldsymbol{\Upsilon}\mathbf{j}(\mathbf{r};\,t) + \sqrt{k_{\mathrm{B}}T\mathbf{m}\boldsymbol{\Upsilon}\rho(\mathbf{r};\,t)}\;\boldsymbol{\xi}(\mathbf{r};\,t).\end{aligned} \tag{63}$$

Given the linearity of equation (63), we can use $\partial_t^2\rho(\mathbf{r};\,t)(\mathbf{m}\boldsymbol{\Upsilon})^{-1}$ and $\partial_t\rho(\mathbf{r};\,t)\mathbf{1}$ to eliminate the momentum. We then neglect the second-order time derivative of the density (in agreement with the overdamped hypothesis), giving

$$\partial_t\rho(\mathbf{r};\,t) = \boldsymbol{\nabla}_{\mathbf{r}}\cdot\left(\boldsymbol{\zeta}^{-1}\rho(\mathbf{r};\,t)\boldsymbol{\nabla}_{\mathbf{r}}\frac{\delta\mathcal{F}[\rho]}{\delta\rho(\mathbf{r};\,t)}\right) + \boldsymbol{\nabla}_{\mathbf{r}}\cdot(\sqrt{k_{\mathrm{B}}T\boldsymbol{\zeta}^{-1}\rho(\mathbf{r};\,t)}\;\boldsymbol{\xi}(\mathbf{r};\,t)), \tag{64}$$

which again has the form of a DK model. At a first glance, equations (40) and (64) seem to be exactly the same, and that is true of the overall structure. However, although the ideal contribution is exactly equivalent in both equations, the excess energy is not. The product $\widetilde{\rho}(\mathbf{r};\,t)\widetilde{\rho}(\mathbf{r}';\,t)$ present inside $\mathcal{H}_U[\rho]$ is not in general equal to the pairwise distribution function shown in the expression for $\mathcal{F}_{\mathrm{exc}}$. Assuming $\widetilde{\rho}(\mathbf{r};\,t) = \rho(\mathbf{r};\,t)$ is equivalent to ignoring all the correlations between particles [21, 48, 59], i.e. to imposing the crude approximation:

$$\rho^{(2)}(\mathbf{r},\,\mathbf{r}';\,t) \simeq \rho(\mathbf{r};\,t)\rho(\mathbf{r}';\,t). \tag{65}$$

In short, the microscopic and mesoscopic derivations only converge when the correlations between particles are negligible. Hence, equation (40) will only represent a good approximation for nearly homogeneous states, but fails to describe most interesting cases such as liquid–vapour interfaces, phase transitions or fluids in confined geometries, to name a few examples, where correlations play a crucial role. Therefore, the mesoscopic route provides a more general framework where the free-energy in equation (64) includes the proper interparticle correlations.

As we already pointed out for the underdamped case, if one (artificially) removes the noise in equation (64), the overdamped DDFT equation for orientable colloids [11] (with the same definition of $\boldsymbol{\zeta}$) is recovered. Indeed, as we already discussed after deriving equation (42), we can naturally identify $\mathbf{D} = k_{\mathrm{B}}T\boldsymbol{\zeta}^{-1}$ as the diffusion tensor which satisfies the generalised Einstein relationships (43). In this regard, equation (64) provides a generalisation of the DDFT equations derived by Rex *et al* [29] and Wittkowski and Löwen [30] for systems of orientable particles.

The formal connection with previous DDFT equations would require addressing some technical issues involving the most-likely path, as we mentioned at the end of section 2. The probability for a path of the generic SPDE [60, 61]: $\partial_t\boldsymbol{\phi}(\mathbf{r};\,t) = F[\boldsymbol{\phi}] + \sigma[\boldsymbol{\phi}]\boldsymbol{\xi}(\mathbf{r};\,t)$, with F being a general functional and σ an operator acting on the noise $\boldsymbol{\xi}$, is given by: $\mathbb{P}[\boldsymbol{\phi}] \sim \exp\left(-\frac{1}{2}\int_0^T\mathcal{L}\mathrm{d}t\right)$, with $\mathcal{L} = ||\partial_t\boldsymbol{\phi} - F[\boldsymbol{\phi}]||_{(\sigma\sigma^*)^{-1}}$ in the WNL, with σ^* being the adjoint of σ and $||.||_{(\sigma\sigma^*)^{-1}}$ is the weighted norm consistent with the L^2_m-inner product, which is defined as $\langle u,\,v\rangle = \int\mathrm{d}\mathbf{r}m(\mathbf{r})u(\mathbf{r})v(\mathbf{r})$, with $m = (\sigma\sigma^*)^{-1}$. The most likely path is the deterministic solution $\overline{\boldsymbol{\phi}}(\mathbf{r};\,t)$ that minimises the Lagrangian $\mathcal{L}$. Therefore, in the WNL, we can obtain that the most-likely solution is the one which fulfils: $\partial_t\overline{\boldsymbol{\phi}}(\mathbf{r};\,t) = F[\overline{\boldsymbol{\phi}}]$. Hence, the dynamics of the most-likely observed solution in the WNL is given by the deterministic part of the SPDE. This formally justifies why our framework recovers previous DDFTs by (artificially) removing the noise term, given that the DDFTs we refer to are valid in near-equilibrium conditions where the WNL is applicable. However, it is important to highlight that the meaning of $\rho(\mathbf{r};\,t)$ and $\mathbf{j}(\mathbf{r};\,t)$ in our formalism is not the same as in DDFT. The DDFT equation involves the most-likely solution, $\overline{\rho}(\mathbf{r};\,t)$ and $\overline{\mathbf{j}}(\mathbf{r};\,t)$. Hopefully, this point also sheds light on the discussion in the literature about the compatibility of DDFT and fluctuations. Indeed, it should now be clear that there is no much sense in (artificially) adding noise to a DDFT equation, as it already contains the information of fluctuations. This also reveals the importance of a bottom-up derivation, which avoids not only confusion but also the misuse of the equations. For instance, one should not expect to describe the observed dynamics with DDFT in a regime where fluctuations are considerably important (the 'strong noise limit'). In this case, the appropriate Lagrangian should be derived and minimised accordingly. This very interesting point, however, goes beyond the scope of this work.

5. Concluding remarks

We have introduced a bottom-up derivation of FH to describe general soft-matter systems out of equilibrium. This extends the application of FH to systems of arbitrarily shaped particles where local orientation plays a key role, e.g. the fundamental study of perfectly-rough spheres [7], loaded spherocylinders [7, 8], nematic solutions [62, 63], the study of biological processes such as protein adsorption and trapping, antibody-antigen interaction, biochemical assembly by monomer aggregation or polymerisation [19]. Furthermore, many processes require the consideration of fluctuations in order to correctly capture and elucidate their dynamics. Phase transformations such as liquid-crystal transitions [43, 44, 63, 64, 65], and biological processes such as bone formation [66, 67] or *in vivo* protein crystallisation [68, 69], are clear examples of that need. We believe that the FH formalism developed here can be utilised to tackle all these problems and more.

Our work introduces, for the first time, a fluctuating DDFT for general colloidal fluids, which in itself is a generalisation of previous deterministic DDFTs [11, 29, 30]. Indeed, we have shown that the naturally emerging free-energy functional for the mesoscopic FH exhibits the *same* properties as the equilibrium free-energy functional of DFT [21, 22]. This is in contrast with the free-energy functional obtained by following the 'classical' procedure outlined by Kawasaki [41] and Dean [42], which only coincides with equilibrium DFT derivation when the correlations between particles can be neglected, i.e. $\rho^{(2)}(\mathfrak{r}, \mathfrak{r}') \sim \rho(\mathfrak{r})\rho(\mathfrak{r}')$. What is more, our work shows the connection between fluctuating DDFT and the Landau–Lifshitz FH formalism, demonstrating that our framework recovers the (phenomenological) stochastic NS equation of an isothermal system. Thus, the derivation presented here establishes a formal connection between the microscopic dynamics of the constituent particles and the time evolution of the mesoscopic continuum fields defining the dynamical state of a real system. Moreover, we have demonstrated the generality and versatility of our framework by showing how it recovers the deterministic governing equations of selected paradigmatic model systems throughout the derivation, namely spherically symmetric colloids, loaded spheres and purely arbitrary-shape particles. This framework can be applied to further generalise FH to describe active soft-matter systems, which are naturally out of equilibrium. For that purpose one should include the self-propulsion forces and torques characteristic of active media. This could be readily achieved by including an additional term $\mathfrak{F}_i^A(\mathfrak{r}; t)$ inside the solvent-averaged interaction forces and torques $\mathfrak{F}_i$. We are currently studying how such forces and torques affect the energy functional involved and the resultant FHE.

Finally, we believe that our results will motivate further analytical studies on the role of particle orientation both in passive and active matter. An interesting extension of the framework developed here would be to study the effects of torsional DoF present in flexible-chain molecules [70] and multiple-particle species [31]. A natural application of our formalism would also be the study of nucleation by generalising the mesoscopic nucleation theory by Lutsko [52]. This would allow us to evaluate the impact of the coupling between translational and rotational DoF on characteristic quantities, such as the nucleation barrier and rate. But also effects of walls [71, 72] and confinement [73, 74–77], which in general should lead to definite orientation in the first particle layers near a solid substrate which in turn can induce anisotropy of both equilibrium and transport properties. Orientation coupled with layering can also cause formation of new phases in the fluid with the extreme form of the substrate-induced ordering being 'surface freezing', i.e. formation of a crystalline phase above the bulk freezing point. Of particular interest would also be nonlinear dynamics problems, for example nonlinear phenomena of spontaneous symmetry breaking and pattern formation due to orientation at the microscale, responsible for self-organisation on the mesoscopic level. We shall examine these and related questions in future studies.

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