HYDRODYNAMIC INTERACTIONS IN DYNAMICAL DENSITY FUNCTIONAL THEORY

Benjamin Goddard*[a)], Andreas Nold*, Petr Yatsyshin*, Nikos Savva*,
Greg Pavliotis** & Serafim Kalliadasis*
*Department of Chemical Engineering, Imperial College London, Exhibition Road, London, SW7 2AZ
**Department of Mathematics, Imperial College London, Exhibition Road, London, SW7 2AZ

Summary We study the dynamics of a colloidal fluid in the full position-momentum phase space, including hydrodynamic interactions, which strongly influence the non-equilibrium properties of the system. For large systems, the number of degrees of freedom prohibits direct simulation and a reduced model is necessary. Under standard assumptions, we derive a dynamical density functional theory (DDFT), which is a generalisation of many existing DDFTs, and shows good agreement with stochastic simulations.

DYNAMICS OF COLLOIDAL FLUIDS

Consider a large number N of identical, spherically symmetric colloidal particles of mass m suspended in a bath of many more much smaller and much lighter particles. This separation of scales allows the effects of the bath to be treated in a probabilistic way, leading to stochastic Newton's equations for the particles. For the $3N$-dimensional vectors $\mathbf{r}$ and $\mathbf{p}$, containing all particle positions and momenta respectively, and potential V:

$$\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t} = \frac{\mathbf{p}}{m}, \qquad \frac{\mathrm{d}\mathbf{p}}{\mathrm{d}t} = -\boldsymbol{\nabla}_{\mathbf{r}} V(\mathbf{r},t) - \boldsymbol{\Gamma}(\mathbf{r})\mathbf{p} + \mathbf{A}(\mathbf{r})\mathbf{f}(t). \tag{1}$$

The final two terms in (1) model the effects of the bath. The motion of colloidal particles cause flows in the bath, which in turn cause forces on the colloidal particles, called hydrodynamic interactions (HI), see Fig. 1. The momenta and forces are related by the $3N \times 3N$ positive-definite friction tensor $\boldsymbol{\Gamma}$. Collisions of bath particles with colloidal particles are described by the stochastic forces $\mathbf{f}$. The strength of these collisions is related to $\boldsymbol{\Gamma}$ via a generalized fluctutation-dissipation theorem, giving $\mathbf{A} = (mk_BT\boldsymbol{\Gamma})^{1/2}$, where T is the temperature and k_B is Boltzmann's constant. If an explict form for $\mathbf{A}$ is known (e.g. if HI are neglected and $\boldsymbol{\Gamma} = \gamma\mathbf{1}$, with γ the friction felt by a single isolated particle), then the numerical solution of (1) takes order N operations at each timestep. If $\mathbf{A}$ must be determined from $\boldsymbol{\Gamma}$, this is increased to order N^3. Hence HI are often neglected for numerical reasons, whilst physically they are important in all but very dilute systems as they decay only with the inverse of particle separation.

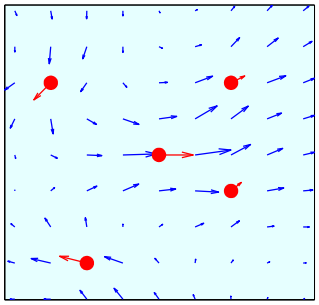

Figure 1. Bath fluid flows (blue) caused by colloidal motion (red).

When N is large, we are interested not in particular realizations of $\mathbf{r}$ and $\mathbf{p}$, given by (1), but in their joint probability distribution $f^{(N)}(\mathbf{r},\mathbf{p},t)$. Averaging (1) over the noise leads to the Kramers equation, a high-dimensional PDE:

$$\partial_t f^{(N)} + \frac{1}{m}\mathbf{p}\cdot\boldsymbol{\nabla}_{\mathbf{r}} f^{(N)} - \boldsymbol{\nabla}_{\mathbf{r}} V(\mathbf{r},t)\cdot\boldsymbol{\nabla}_{\mathbf{p}} f^{(N)} = \boldsymbol{\nabla}_{\mathbf{p}}\cdot[\boldsymbol{\Gamma}(\mathbf{r})(\mathbf{p} + mk_BT\boldsymbol{\nabla}_{\mathbf{p}})f^{(N)}]. \tag{2}$$

It is known rigorously that $f^{(N)}$ is a functional of the one-body position distribution $\rho(\mathbf{r}_1) = N\int \mathrm{d}\mathbf{p}\mathrm{d}\mathbf{r}' f^{(N)}(\mathbf{r},\mathbf{p},t)$, where $\mathrm{d}\mathbf{r}'$ denotes integration over all but $\mathbf{r}_1$, the position of the first particle. This motivates the derivation of a *dynamical density functional theory (DDFT)*, i.e. an equation of the form $\partial_t\rho(\mathbf{r}_1,t) = -\boldsymbol{\nabla}_{\mathbf{r}_1}\cdot\mathbf{a}(\mathbf{r}_1,t,[\rho])$, where $\mathbf{a}$ is a functional of ρ. Existing DDFTs have been formulated in the overdamped (high friction) regime [1], where inertial effects may be neglected, or ignore HI [2]. We present a general DDFT, of which existing formulations [1, 2] are special cases.

DERIVATION OF A DYNAMICAL DENSITY FUNCTIONAL THEORY

$$0 = \partial_t\rho(\mathbf{r}_1,t) + \boldsymbol{\nabla}_{\mathbf{r}_1}\cdot\big(\rho(\mathbf{r}_1,t)\mathbf{v}(\mathbf{r}_1,t)\big), \tag{3}$$

$$0 = \partial_t\big(\rho(\mathbf{r}_1,t)\mathbf{v}(\mathbf{r}_1,t)\big) + \gamma\rho(\mathbf{r}_1,t)\mathbf{v}(\mathbf{r}_1,t)$$

$$+ \frac{1}{m}\int \mathrm{d}\mathbf{r}'\boldsymbol{\nabla}_{\mathbf{r}_1} V(\mathbf{r},t)\rho^{(N)}(\mathbf{r},t) \tag{V}$$

$$+ \frac{N\gamma}{m}\sum_{j=1}^{N}\int \mathrm{d}\mathbf{p}\mathrm{d}\mathbf{r}'\tilde{\boldsymbol{\Gamma}}_{1j}(\mathbf{r})\mathbf{p}_j f^{(N)}(\mathbf{r},\mathbf{p},t) \tag{H}$$

$$+ \boldsymbol{\nabla}_{\mathbf{r}_1}\cdot\int \mathrm{d}\mathbf{p}_1\frac{\mathbf{p}_1\otimes\mathbf{p}_1}{m^2} f^{(1)}(\mathbf{r}_1,\mathbf{p}_1,t). \tag{K}$$

We denote the position and momentum of the jth particle by $\mathbf{r}_j$ and $\mathbf{p}_j$ and let $\boldsymbol{\Gamma}(\mathbf{r}) = \gamma[\mathbf{1} + \tilde{\boldsymbol{\Gamma}}(\mathbf{r})]$, where the HI tensor $\tilde{\boldsymbol{\Gamma}}$ is decomposed into 3×3 blocks $\tilde{\boldsymbol{\Gamma}}_{ij}$ [3]. By taking momentum moments of (2), we obtain an infinite hierarchy of equations. Truncating at the second equation gives a continuity equation (3), and the time evolution of the current. To close the second equation, it is necessary to deal with terms arising from many-body potentials (V), HI (H), and 'kinetic pressure' (K) effects. For (V), at equilibrium, there exists an exact functional identity $\int \mathrm{d}\mathbf{r}'\boldsymbol{\nabla}_{\mathbf{r}_1} V(\mathbf{r})\rho^{(N)}(\mathbf{r}) = \rho(\mathbf{r}_1,t)\boldsymbol{\nabla}_{\mathbf{r}_1}\frac{\delta\mathcal{F}[\rho]}{\delta\rho} - k_BT\boldsymbol{\nabla}_{\mathbf{r}_1}\rho(\mathbf{r}_1)$,

[a)] Corresponding author. E-mail: b.goddard@imperial.ac.uk

where $\mathcal{F}[\rho] = k_BT\int \mathrm{d}\mathbf{r}_1\rho(\mathbf{r}_1)\big[\ln\big(\Lambda^3\rho(\mathbf{r}_1)\big) - 1\big] + \mathcal{F}_{\mathrm{exc}}[\rho] + \int \mathrm{d}\mathbf{r}_1\rho(\mathbf{r}_1)V_1(\mathbf{r}_1)$ is the Helmholtz free energy functional. In general, $\mathcal{F}_{\mathrm{exc}}$ is unknown but has been well-studied at equilibrium and good approximations exist, e.g. [4]. We thus assume that this identity also holds out of equilibrium, in particular obtaining the correct equilibrium behaviour.

Since HI vanish at equilibrium there exists no analogous identity for (H). For ease of exposition, we assume that the HI are two-body: $\tilde{\mathbf{\Gamma}}_{ij}(\mathbf{r}) = \delta_{ij}\sum_{\ell\neq i}\mathbf{Z}_1(\mathbf{r}_i,\mathbf{r}_\ell) + (1-\delta_{ij})\mathbf{Z}_2(\mathbf{r}_i,\mathbf{r}_j)$. We also assume that $f^{(2)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2,t) \approx f^{(1)}(\mathbf{r}_1,\mathbf{p}_1,t)f^{(1)}(\mathbf{r}_1,\mathbf{p}_1,t)g(\mathbf{r}_1,\mathbf{r}_2,[\rho])$ for a *known* functional g. Again, this has been well-studied at equilibrium [5].

As (K) is analogous to the kinetic pressure tensor, there is no reason to expect it to be a simple functional of ρ and $\mathbf{v}$. However, for general $f^{(1)}$, we have $f^{(1)}(\mathbf{r}_1,\mathbf{p}_1,t) = f^{(1)}_{\mathrm{le}}(\mathbf{r}_1,\mathbf{p}_1,t) + f^{(1)}_{\mathrm{neq}}(\mathbf{r}_1,\mathbf{p}_1,t)$, where $f^{(1)}_{\mathrm{le}}(\mathbf{r}_1,\mathbf{p}_1,t) = (2\pi mk_BT)^{-3/2}\rho(\mathbf{r}_1,t)\exp\big(-|\mathbf{p}_1 - m\mathbf{v}(\mathbf{r}_1,t)|^2/(2mk_BT)\big)$ is the local-equilibrium part. The non-equilibrium part $f^{(1)}_{\mathrm{neq}}$ satisfies $\int \mathrm{d}\mathbf{p}_1\alpha(\mathbf{p}_1)f^{(1)}_{\mathrm{neq}}(\mathbf{r}_1,\mathbf{p}_1,t) = 0$ for $\alpha(\mathbf{p}_1)\in\{1,\mathbf{p}_1,|\mathbf{p}_1|^2\}$. Combining these three approximations gives

$$\partial_t\mathbf{v}(\mathbf{r}_1,t) + \big(\mathbf{v}(\mathbf{r}_1,t)\cdot\boldsymbol{\nabla}_{\mathbf{r}_1}\big)\mathbf{v}(\mathbf{r}_1,t) + \frac{1}{m}\boldsymbol{\nabla}_{\mathbf{r}_1}\frac{\delta\mathcal{F}[\rho]}{\delta\rho} + \frac{1}{\rho(\mathbf{r}_1,t)}\boldsymbol{\nabla}_{\mathbf{r}_1}\cdot\int \mathrm{d}\mathbf{p}_1\frac{\mathbf{p}_1\otimes\mathbf{p}_1}{m^2}f^{(1)}_{\mathrm{neq}}(\mathbf{r}_1,\mathbf{p}_1,t)$$
$$+\gamma\mathbf{v}(\mathbf{r}_1,t) + \gamma\int \mathrm{d}\mathbf{r}_2\rho(\mathbf{r}_2,t)g(\mathbf{r}_1,\mathbf{r}_2,[\rho])\big[\mathbf{Z}_1(\mathbf{r}_1,\mathbf{r}_2)\mathbf{v}(\mathbf{r}_1,t) + \mathbf{Z}_2(\mathbf{r}_1,\mathbf{r}_2)\mathbf{v}(\mathbf{r}_2,t)\big] = 0 \qquad (4)$$

which, along with the continuity equation (3), and under the additional assumption that the term containing $f^{(1)}_{\mathrm{neq}}$ may be neglected or approximated as a functional of ρ and $\mathbf{v}$, gives a DDFT. Neglecting this term can be rigorously motivated both close to local equilibrium, giving a generalised Navier-Stokes equation with non-local terms, and in the overdamped limit [3], recovering a Smoluchowski equation with a novel diffusion tensor. The terms involving $\mathbf{Z}_j$ in (4) are absent in previous DDFTs. The term involving $\mathbf{Z}_1$ combines with $\gamma\mathbf{v}$ to give an effective, density dependent friction coefficient, whilst that involving $\mathbf{Z}_2$ couples the velocities in a non-local way.

NUMERICAL SIMULATIONS

We consider 50 identical hard spheres of diameter 1 initially at equilibrium with spherically-symmetric external potential $V_1(r)$. The external potential is then instantaneously switched to $V_0(r)$ and then, at time $t = 0.5$, back to $V_1(r)$. Fig. 2 shows the mean radial position $\bar{r}$ and radial momentum $\bar{p}$ of the particles. We show eight simulations; DDFT as solid lines and stochastic simulation as squares. Red denotes the solution of (3) and (4) and the Euler-Maruyama solution of (1) without HI, i.e. $\mathbf{\Gamma} = \gamma\mathbf{1}$ (see also [2]). Purple is the corresponding overdamped DDFT [1] and Ermak-McCammon stochastic simulation [6]. Blue is as red, but the HI term is given by the inverse of the Rotne-Prager tensor for the stochastic simulation and by the 11-term Jeffrey-Onishi expansion for the DDFT [7]. These are not strictly equivalent and thus we expect only qualitative agreement. Finally, green is as purple but with the HI term given by the Rotne-Prager tensor for both DDFT and stochastic simulation. All simulations have $m = k_BT = 1$ and $\gamma = 8$.

The agreement in all cases is very good and clearly demonstrates the need to include both inertial effects and HI. In particular, neglecting inertia (purple/green) leads to a kink in the mean position, whilst its inclusion leads to smooth curves with a delay before the mean momentum changes sign. Further, there is a large quantitative difference from including HI; in particular, HI increase the effective friction of the system.

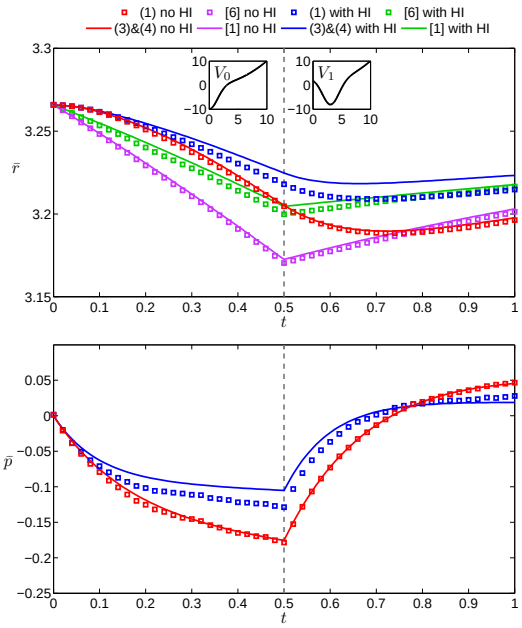

Figure 2. Comparison of DDFT and stochastic simulations; see text for details.

References

[1] U. M. B. Marconi and P. Tarazon, *J. Chem. Phys.* **110**, 8032 (1999); M. Rex and H. Löwen, *Eur. Phys. J. E* **28**, 139 (2009)
[2] A. J. Archer, *J. Chem. Phys.* **130**, 014509 (2009)
[3] B. D. Goddard, G. A. Pavliotis and S. Kalliadasis, *Submitted* (2011) http://arxiv.org/abs/1108.3185
[4] Y. Rosenfeld *Phys. Rev. Lett.* **63**, 980 (1989); R. Roth, R. Evans, A. Lang, and G. Kahl, *J. Phys. Condens. Matter* **14**, 12063 (2002)
[5] R. Evans *Adv. Phys.* **28**, 143 (1979); A. Trokhymchuk, I. Nezbeda, J. Jirsák and D. Henderson, *J. Chem. Phys.* **123**, 024501 (2005)
[6] D. L. Ermak and J. A. McCammon, *J. Chem. Phys.* **69**, 1351 (1978)
[7] J. Rotne and S. Prager, *J. Chem. Phys.* **50**, 4831 (1969); D. J. Jeffrey and Y. Onishi, *J. Fluid Mech.* **139**, 261 (1984)