Problem Set 13 – Microhydrodynamics & fluctuations

Problem 1: Time-dependent density-density correlations

Consider a fixed configuration $\{\mathbf{R}_1, ..., \mathbf{R}_N\}$ of N spherical particles suspended in an isotropic, incompressible Newtonian fluid. The time-dependent density operator is given by $\hat{\rho}(\mathbf{r}, t) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{R}_i(t))$. We consider the correlation function

$$C(\mathbf{r} - \mathbf{r}', t - t') = \langle \delta\hat{\rho}(\mathbf{r}, t)\delta\hat{\rho}(\mathbf{r}', t')\rangle,$$

where $\langle ... \rangle$ denotes an equilibrium ensemble average and $\delta\hat{\rho}(\mathbf{r}, t) = \hat{\rho}(\mathbf{r}, t) - \langle\hat{\rho}(\mathbf{r}, t)\rangle$.

(a) Explain why C depends only on $\mathbf{r} - \mathbf{r}'$ and $t - t'$. Give a physical interpretation of $C(\mathbf{r} - \mathbf{r}', t - t')$ by considering how an out-of-equilibrium density profile $\rho(\mathbf{r}, t) = \overline{\hat{\rho}(\mathbf{r}, t)}$ relaxes in time within the linear-response regime. Here, the overline represents an out-of-equilibrium ensemble average.

(b) Introduce the Fourier transform $C(\mathbf{k}, t) = \int d\mathbf{k}\, C(\mathbf{r}, t)e^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}}$ and define the collective dynamical structure factor as $C(\mathbf{k}, t) = \bar{\rho}S_{\mathrm{c}}(\mathbf{k}, t)$ with $\bar{\rho} = N/V$. Show that

$$S_{\mathrm{c}}(\mathbf{k}, t) = \frac{1}{N}\sum_{i,j}\langle \exp\{\mathrm{i}\mathbf{k}\cdot[\mathbf{R}_i(t) - \mathbf{R}_j(0)]\}\rangle.$$

What happens to the $\mathbf{k} = \mathbf{0}$ mode?

(c) Within the framework of linear irreversible thermodynamics, we may presume that $\rho(\mathbf{r}, t)$ is governed by the generalised diffusion equation

$$\frac{\partial}{\partial t}\rho(\mathbf{r}, t) = -\nabla\cdot\mathbf{j}(\mathbf{r}, t), \quad \mathbf{j}(\mathbf{r}, t) = -\int d\mathbf{r}'\int_0^t dt'\, \boldsymbol{\mathfrak{D}}(\mathbf{r} - \mathbf{r}'; t - t')\cdot\nabla'\rho(\mathbf{r}', t').$$

Here, $\boldsymbol{\mathfrak{D}}(\mathbf{r} - \mathbf{r}'; t - t')$ is the collective diffusion kernel. Derive the differential equation for $S_{\mathrm{c}}(\mathbf{k}, t)$ and explain how it is an example of the Onsager regression hypothesis.

Problem 2: Gradient diffusion

The many-body Smoluchowski equation for N identical spherical particles of radius a is given by

$$\frac{\partial}{\partial t}P(\mathbf{R}^N, t) = \sum_{i,j}\frac{\partial}{\partial\mathbf{R}_i}\cdot\boldsymbol{D}_{ij}(\mathbf{R}^N)\cdot\left[\frac{\partial}{\partial\mathbf{R}_j}P(\mathbf{R}^N, t) + \beta P(\mathbf{R}^N, t)\frac{\partial}{\partial\mathbf{R}_j}\Phi(\mathbf{R}^N)\right],$$

where the interaction potentials are pair-wise additive $\Phi(\mathbf{R}^N) = \sum_{i<j}\phi(|\mathbf{R}_i - \mathbf{R}_j|)$ and $\boldsymbol{D}_{ij}$ denote diffusion tensors. Furthermore, $\beta = (k_{\mathrm{B}}T)^{-1}$.

(a) Consider the marginal probability distributions

$$P_1(\mathbf{r}, t) = \int d\mathbf{R}_2 ... \int d\mathbf{R}_N\, P(\mathbf{r}, \mathbf{R}_2, ..., \mathbf{R}_N, t),$$

$$P_2(\mathbf{r}, \mathbf{r}', t) = \int d\mathbf{R}_3 ... \int d\mathbf{R}_N\, P(\mathbf{r}, \mathbf{r}', \mathbf{R}_3, ..., \mathbf{R}_N, t),$$

$$P_3(\mathbf{r}, \mathbf{r}', \mathbf{r}''', t) = \int d\mathbf{R}_4 ... \int d\mathbf{R}_N\, P(\mathbf{r}, \mathbf{r}', \mathbf{r}'', \mathbf{R}_4, ..., \mathbf{R}_N, t).$$

Argue that the average number density is given by $\rho(\mathbf{r}, t) = NP_1(\mathbf{r}, t)$. Derive the differential equation that governs the behaviour of $\rho(\mathbf{r}, t)$ and show that there is a term coming from the self-diffusion tensor $\boldsymbol{D}_{ii}$ (no Einstein convention!) denoted by I_1 and a term coming from the cross-diffusion tensor $\boldsymbol{D}_{ij}$ with $i \neq j$ denoted by I_2.

(b) For sufficiently dilute systems we may assume that the $\boldsymbol{D}_{ij}$ consist only of one-body and two-body terms. We may parametrize them as follows

$$\boldsymbol{D}_{ii} = D_0 \left\{ \boldsymbol{I} + \sum_{j\neq i}^{N} \underbrace{[A_\mathrm{s}(R_{ij})\hat{\mathbf{R}}_{ij}\hat{\mathbf{R}}_{ij} + B_\mathrm{s}(R_{ij})(\boldsymbol{I} - \hat{\mathbf{R}}_{ij}\hat{\mathbf{R}}_{ij})]}_{\Delta\boldsymbol{D}(\mathbf{R}_{ij})} \right\},$$

$$\boldsymbol{D}_{ij} = D_0[A_\mathrm{c}(R_{ij})\hat{\mathbf{R}}_{ij}\hat{\mathbf{R}}_{ij} + B_\mathrm{c}(R_{ij})(\boldsymbol{I} - \hat{\mathbf{R}}_{ij}\hat{\mathbf{R}}_{ij})], \quad i \neq j.$$

What is D_0? Give an explicit expression.

(c) We first analyse I_1. Show that

$$\begin{aligned} I_1 =& (N-1)\beta\nabla\cdot\int d\mathbf{r}'\,[D_0\boldsymbol{I} + \Delta\boldsymbol{D}(\mathbf{r}-\mathbf{r}')]P_2(\mathbf{r},\mathbf{r}',t)\cdot\nabla\phi(|\mathbf{r}-\mathbf{r}'|) \\ &+ (N-1)(N-2)\beta\nabla\cdot\int d\mathbf{r}'\int d\mathbf{r}''\,\Delta\boldsymbol{D}(\mathbf{r}-\mathbf{r}')P_3(\mathbf{r},\mathbf{r}',\mathbf{r}'',t)\cdot\nabla\phi(|\mathbf{r}-\mathbf{r}''|). \qquad (1)\end{aligned}$$

Find a similar expression for I_2.

(d) We approximate $P_2(\mathbf{r},\mathbf{r}',t) \approx (1/N^2)\rho(\mathbf{r},t)\rho(\mathbf{r}',t)g(|\mathbf{r}-\mathbf{r}'|)$ with $g(r)$ the (equilibrium) radial distribution function. Argue that for dilute suspensions $g(r) \approx \exp[-\beta\phi(r)]$.

(e) Furthermore, we assume that the inhomogeneities in density are small and expand $\rho(\mathbf{r},t) = \bar{\rho} + \Delta\rho(\mathbf{r},t)$ with $\bar{\rho} = N/V$. Moreover, we may expand $\Delta\rho(\mathbf{r}') = \Delta\rho(\mathbf{r}) + (\mathbf{r}'-\mathbf{r})\cdot\nabla\Delta\rho(\mathbf{r},t)$. Argue why to linear order in the volume fraction $\varphi = (4/3)\pi a^3\bar{\rho}$, the term containing P_3 does not contribute.

(f) Show that

$$\frac{\partial}{\partial t}\rho(\mathbf{r},t) = D_0(1+\alpha_\nabla\varphi)\nabla^2\rho(\mathbf{r},t),$$

with

$$\begin{aligned}\alpha_\nabla = -\beta\int_0^\infty dx\,x^3 g(ax)\frac{dV(ax)}{dx} + \int_0^\infty dx\,x^2[A_\mathrm{s}(ax) + 2B_\mathrm{s}(ax)]g(ax) \\ - \int_0^\infty dx\,x^3\left[f(ax)g(ax) + A_\mathrm{c}(ax)\frac{dg(ax)}{dx}\right],\end{aligned}$$

where

$$f(ax) = x^2\frac{d}{dx}\left[\frac{A_\mathrm{c}(ax) - B_\mathrm{c}(ax)}{x^2}\right] + 4\frac{A_\mathrm{c}(ax) - B_\mathrm{c}(ax)}{x} + \frac{dB_\mathrm{c}(ax)}{dx}.$$

(g) Evaluate α_∇ for hard sphere interactions, i.e. $\phi(r) = 0$ for $r > a$ and $\phi(r) = \infty$ for $r < a$. You may use the approximate mobility functions

$$A_\mathrm{s}(ax) = -\frac{15}{4}x^{-4} + \frac{11}{2}x^{-6} + \mathcal{O}(x^{-8}), \quad B_\mathrm{s}(ax) = -\frac{17}{16}x^{-6} + \mathcal{O}(x^{-8}),$$

$$A_\mathrm{c}(ax) = \frac{3}{2}x^{-1} - x^{-3} + \frac{75}{4}x^{-7} + \mathcal{O}(x^{-9}), \quad B_\mathrm{c}(ax) = \frac{3}{4}x^{-1} + \frac{1}{2}x^{-3} + \mathcal{O}(x^{-9}).$$

You should find $\alpha_\nabla = 1.559....$