Problem Set 14 – Microhydrodynamics & fluctuations

Problem 1: Time-dependent correlation functions

Let $A(t) = A(\mathbf{X}(t))$ and $B(t) = B(\mathbf{X}(t'))$ be two time-dependent observables with $t > t'$ that depend on the general phase space trajectory $\mathbf{X}(t)$. In this exercise we are interested in the time-dependent correlation function

$$C_{AB}(t,t') = \langle A(t)B(t')\rangle = \int d\mathbf{X}_0\, P_0(\mathbf{X}_0)A(\mathbf{X}(t))B(\mathbf{X}(t')), \quad t > t',$$

given that $\mathbf{X}(t=0) = \mathbf{X}_0$. The angular brackets denote a general ensemble average (not necessarily an equilibrium one!) and $P_0(\mathbf{X}_0)$ denotes the phase space probability distribution at $t = 0$, i.e. $P_0(\mathbf{X}) = P(\mathbf{X}, t = 0)$, where $P(\mathbf{X}, t)$ evolves according to

$$\frac{\partial}{\partial t}P(\mathbf{X},t) = \mathcal{D}P(\mathbf{X},t),$$

for a general linear operator $\mathcal{D}$.

(a) Explain why we have to specify the condition $t > t'$.

(b) Show that

$$C_{AB}(t,t') = \int d\mathbf{X} \int d\mathbf{X}'\, P(\mathbf{X},t;\mathbf{X}',t')A(\mathbf{X})B(\mathbf{X}'), \quad t > t',$$

with $P(\mathbf{X},t;\mathbf{X}',t')$ the joint probability distribution function for finding the system at phase-space point $\mathbf{X}$ at time t *and* at phase-space point $\mathbf{X}'$ at time t'. Give an explicit expression for this quantity in terms of P_0.

(c) By expressing $P(\mathbf{X},t;\mathbf{X},t') = P(\mathbf{X},t|\mathbf{X}',t')P(\mathbf{X}',t')$, where $P(\mathbf{X},t|\mathbf{X}',t')$ is the conditional probability distribution of finding a phase-space point $\mathbf{X}$ at time t given that at time t' the system is in $\mathbf{X}'$, show that

$$C_{AB}(t,t') = \int d\mathbf{X}\, P(\mathbf{X},t')B(\mathbf{X})e^{\mathcal{L}(t-t')}A(\mathbf{X}), \quad t > t',$$

and write down an expression for $\mathcal{L}$ in terms of $\mathcal{D}$.

(d) Show that in equilibrium $C_{AB}(t,t') = C_{AB}(t-t')$ and explain the physical rationale behind it.

Problem 2: Self-diffusion of a hard-sphere suspension

We will now apply the results from Problem 1 to self-diffusion of spheres in three spatial dimensions. We focus only on the translational sector, i.e. $\mathbf{X}(t) = \{\mathbf{R}_1(t), ..., \mathbf{R}_N(t)\}$. We choose for our our probe particle the Brownian trajectory $\mathbf{R}_1(t)$. The spheres interact via direct forces governed by the interaction potential $\Phi(\mathbf{R}^N) = \sum_{i<j}\phi(|\mathbf{R}_i - \mathbf{R}_j|)$ and hydrodynamic interactions via the many-body mobility tensors $\boldsymbol{\mu}^{\mathrm{tt}}_{ij}(\mathbf{X})$.

(a) Write down an expression for $\mathcal{D}$ and from it derive an expression for $\mathcal{L}$.

(b) The normalised mean-squared displacement is

$$W(t) = \frac{1}{6}\langle|\mathbf{R}_1(t) - \mathbf{R}_1(0)|^2\rangle,$$

where now angular brackets denote an equilibrium ensemble average. Define the time-dependent self-diffusion coefficient as $D_{\mathrm{s}}(t) = \partial_t W(t)$. Show that the long-time self-diffusion coefficient $D_{\mathrm{s}}^{\mathrm{l}} = \lim_{t\to\infty} D_{\mathrm{s}}(t)$ is given by

$$D_{\mathrm{s}}^{\mathrm{l}} = D_{\mathrm{s}}^{\mathrm{s}} + \langle \mathbf{U}_1 \cdot \mathcal{L}^{-1}\mathbf{U}_1 \rangle,$$

with $D_{\mathrm{s}}^{\mathrm{s}} = \lim_{t\to 0} D_{\mathrm{s}}(t)$ and $\mathbf{U}_1 = \mathcal{L}\mathbf{R}_1$.

(c) Derive an expression for $D_{\mathrm{s}}^{\mathrm{s}}$ in terms of $\boldsymbol{\mu}_{ij}(\mathbf{X})$. Give a physical interpretation for $D_{\mathrm{s}}^{\mathrm{s}}$.

(d) Explain why $\mathbf{U}_1$ is sometimes called the Smoluchowski velocity and why it is only well-defined in the probabilistic sense.

For dilute suspensions, it can be shown that $D_{\mathrm{s}}^{\mathrm{l}} = D_0[1 + (\lambda_{\mathrm{s}} + \lambda_{\mathrm{l}})\varphi]$, with φ the total volume fraction of spheres. We can express the coefficients λ_{s} and λ_{l} in terms of the pair hydrodynamic functions

$$\boldsymbol{\mu}_{11}^{\mathrm{tt}}(\mathbf{R}_1, \mathbf{R}_2) = \mu_0[\boldsymbol{I} + A_{11}(r)\hat{\mathbf{r}}\hat{\mathbf{r}} + B_{11}(r)(\boldsymbol{I} - \hat{\mathbf{r}}\hat{\mathbf{r}})], \quad \boldsymbol{\mu}_{12}^{\mathrm{tt}}(\mathbf{R}_1, \mathbf{R}_2) = \mu_0[A_{12}(r)\hat{\mathbf{r}}\hat{\mathbf{r}} + B_{12}(r)(\boldsymbol{I} - \hat{\mathbf{r}}\hat{\mathbf{r}})],$$

with $\mu_0 = 1/(6\pi\eta a)$ and $D_0 = k_{\mathrm{B}}T\mu_0$. Furthermore, $\mathbf{r} = \mathbf{R}_2 - \mathbf{R}_1$.

(e) Show that for a system with general pair potential $\phi(r)$ where $\phi(r) = \infty$ for $r < 2a$ that

$$\lambda_{\mathrm{S}} = 8\int_1^\infty dx\, x^2 g(x)[A_{11}(x) + 2B_{11}(x)],$$

with $x = r/(2a)$. Furthermore, $g(r) = \exp[-\beta\phi(r)]$ is the radial distribution function for a dilute system.

(f) Derive the long-time correction

$$\lambda_{\mathrm{l}} = 4\int_1^\infty dx\, x^2 f(x) g(x) \left[W(x) - \frac{1}{2}\beta\frac{d\phi}{dx}G(x)\right],$$

where

$$G(x) = 1 + A_{11}(x) - A_{12}(x), \quad H(x) = 1 + B_{11}(x) - B_{12}(x),$$

and

$$W(x) = \frac{G(x) - H(x)}{x} + \frac{1}{2}\frac{d}{dx}G(x).$$

Show that the function f follows from the two-body Smoluchowski equation and is determined by the differential equation for $x > 1$

$$\frac{1}{x^2}\frac{d}{dx}\left[x^2 G(x)\frac{d}{dx}f(x)\right] - \beta\frac{d\phi(x)}{dx}G(x)\frac{d}{dx}f(x) - \frac{2H(x)}{x^2}f(x) = 4W(x) - 2\beta\frac{d\phi(x)}{dx}G(x),$$

with boundary conditions

$$\left[G(x)\frac{d}{dx}f(x)\right]_{x=1} = 0, \quad \lim_{x\to\infty} f(x) = 0.$$

(g) Consider now a hard-sphere system. Show that in the absence of hydrodynamic interactions that $D_{\mathrm{s}}^{\mathrm{l}} = D_0(1 - 2\varphi)$. What is the expression for $D_{\mathrm{s}}^{\mathrm{s}}$?

(h) Suppose we treat the hydrodynamic interactions within the Rotne-Prager-Yamakawa approximation. Will the result for $D_{\mathrm{s}}^{\mathrm{l}}$ change? What about $D_{\mathrm{s}}^{\mathrm{s}}$? Explain your answer.