

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. $\mathbf{X}(t) = \{\mathbf{R}_1(t), \dots, \mathbf{R}_N(t)\}$. We choose for 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 $\boldsymbol{\mu}_{ij}^{\text{tt}}(\mathbf{X})$.

- (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 $D_s(t) = \partial_t W(t)$. Show that the short-time self-diffusion coefficient $D_s^s = \lim_{t \rightarrow 0} D_s(t)$ is given by

$$D_s^s = \frac{k_B T}{3} \text{tr} \langle \boldsymbol{\mu}_{11}(\mathbf{X}) \rangle.$$

For dilute suspensions, it can be shown that $D_s^s = D_0(1 + \lambda_s \varphi)$, 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

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

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

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

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

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

The long-time self-diffusion coefficient is given by $D_s^l = \lim_{t \rightarrow \infty} D_s(t)$. It can be shown for dilute suspensions (not required here) that $D_s^l = D_0[1 + (\lambda_s + \lambda_l)\varphi]$, where

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

where

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

and

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

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

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

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

(e) Suppose we treat the hydrodynamic interactions within the Rotne-Prager-Yamakawa approximation. Will the result for D_s^l change? What about D_s^s ? Explain your answer.