Problem Set 12 – Microhydrodynamics & fluctuations

Problem 1: Formal solution of the free Smoluchowski equation

Consider the one-dimensional diffusion equation for the probability density $P(x,t)$,

$$\frac{\partial P(x,t)}{\partial t} = \mathcal{D}P(x,t), \qquad \mathcal{D} = D\frac{\partial^2}{\partial x^2}, \qquad D > 0,$$

with initial condition $P(x,0) = P_0(x)$. Here D is the diffusion coefficient and $\mathcal{D}$ is the forward Smoluchowski operator.

(a) Show formally that the solution can be written as

$$P(x,t) = e^{t\mathcal{D}}P_0(x).$$

What is meant by the exponential of an operator?

(b) Taking $P_0(x) = \delta(x - x_0)$, define the Green's function by

$$G(x,t \mid x_0,0) = e^{t\mathcal{D}}\delta(x - x_0), \qquad t > 0.$$

Evaluate G explicitly, for example by Fourier transform, and show that

$$G(x,t \mid x_0,0) = \frac{1}{\sqrt{4\pi Dt}}\exp\left[-\frac{(x-x_0)^2}{4Dt}\right].$$

(c) Show that the conditional moments

$$\langle x(t) \mid x(0) = x_0\rangle = \int_{-\infty}^{\infty} x\, G(x,t \mid x_0,0)\,\mathrm{d}x,$$

and

$$\left\langle [x(t) - x_0]^2 \mid x(0) = x_0\right\rangle = \int_{-\infty}^{\infty} (x-x_0)^2 G(x,t \mid x_0,0)\,\mathrm{d}x$$

give the expected first and second moments.

(d) Expand the operator exponential for short times,

$$e^{t\mathcal{D}} = 1 + t\mathcal{D} + \frac{t^2}{2}\mathcal{D}^2 + \cdots,$$

and show that

$$P(x,t) = P_0(x) + t\mathcal{D}P_0(x) + \mathcal{O}(t^2).$$

Interpret this short-time expansion physically. What does the term $t\mathcal{D}P_0$ tell you about the initial evolution of a sharply localized distribution?
Hint: in this problem, $\mathcal{D}P_0 = D\,\partial_x^2 P_0$.

Problem 2: Adjoint Smoluchowski operator and correlation functions

Consider the one-particle Smoluchowski equation in d spatial dimensions,

$$\frac{\partial P(\boldsymbol{x},t)}{\partial t} = \mathcal{D}P(\boldsymbol{x},t),$$

with the Smoluchowski operator

$$\mathcal{D}P = -\nabla\cdot\big(\mu\boldsymbol{F}(\boldsymbol{x})P\big) + D\nabla^2 P, \qquad D = \mu k_B T,$$

where μ is a constant mobility and $\boldsymbol{F}(\boldsymbol{x})$ is a given force field. Let $A(\boldsymbol{x})$ be a smooth observable, and define its expectation value by

$$\langle A\rangle(t) = \int A(\boldsymbol{x})P(\boldsymbol{x},t)\,\mathrm{d}\boldsymbol{x}.$$

Assume throughout that all functions decay sufficiently fast at infinity, or that boundary conditions are such that boundary terms vanish when integrating by parts.

(a) Show that

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle A\rangle(t) = \int A(\boldsymbol{x})\,\mathcal{D}P(\boldsymbol{x},t)\,\mathrm{d}\boldsymbol{x}.$$

Use integration by parts to define the adjoint operator $\mathcal{D}^\dagger$ through the duality relation

$$\int A(\boldsymbol{x})\,(\mathcal{D}P)(\boldsymbol{x})\,\mathrm{d}\boldsymbol{x} = \int (\mathcal{D}^\dagger A)(\boldsymbol{x})\,P(\boldsymbol{x})\,\mathrm{d}\boldsymbol{x},$$

assuming that boundary terms vanish. Show that

$$\mathcal{D}^\dagger A = \mu\boldsymbol{F}\cdot\nabla A + D\nabla^2 A,$$

and conclude that

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle A\rangle = \left\langle \mathcal{D}^\dagger A\right\rangle.$$

Hint: treat the drift and diffusion terms separately.

(b) In this item, restrict to one spatial dimension and assume that the force derives from a potential,

$$F(x) = -V'(x).$$

Introduce $\beta = 1/k_BT$. Show that the forward Smoluchowski operator acting on a test function $\varphi(x)$ can be written in the factorized form

$$\mathcal{D}\varphi = D\frac{\partial}{\partial x}\left[e^{-\beta V}\frac{\partial}{\partial x}\left(e^{\beta V}\varphi\right)\right].$$

Show similarly that the adjoint operator can be written as

$$\mathcal{D}^\dagger\varphi = D\,e^{\beta V}\frac{\partial}{\partial x}\left[e^{-\beta V}\frac{\partial\varphi}{\partial x}\right].$$

Hint: start from the one-dimensional form

$$\mathcal{D}\varphi = -\frac{\partial}{\partial x}\left(\mu F(x)\varphi\right) + D\frac{\partial^2\varphi}{\partial x^2}, \qquad D = \mu k_BT.$$

(c) Let $P_0(\boldsymbol{x}) = P(\boldsymbol{x},0)$. Show formally that

$$P(\boldsymbol{x},t) = e^{t\mathcal{D}}P_0(\boldsymbol{x})$$

implies the duality relation

$$\int A\,e^{t\mathcal{D}}P_0\,\mathrm{d}\boldsymbol{x} = \int (e^{t\mathcal{D}^\dagger}A)\,P_0\,\mathrm{d}\boldsymbol{x}.$$

Hence derive

$$\langle A(t)\rangle = \int \left(e^{t\mathcal{D}^\dagger}A\right)(\boldsymbol{x})\,P_0(\boldsymbol{x})\,\mathrm{d}\boldsymbol{x}.$$

Hint: first prove the duality relation term by term for the power-series expansion of the exponential.

(d) Specialize to free diffusion, so that $\boldsymbol{F} = \boldsymbol{0}$ and

$$\mathcal{D}^\dagger = D\nabla^2.$$

Evaluate explicitly

$$e^{t\mathcal{D}^\dagger}x_i, \qquad e^{t\mathcal{D}^\dagger}(x_ix_j),$$

and use the result to recover the constancy of the mean position and the diffusive growth of the second moment for free Brownian motion without solving explicitly for $P(\boldsymbol{x},t)$. *Hint: compute $\nabla^2 x_i$ and $\nabla^2(x_ix_j)$ first.*

(e) Assume that the process starts from the initial distribution $P_0(\boldsymbol{x})$, and let $A(\boldsymbol{x})$ and $B(\boldsymbol{x})$ be two observables. Interpreting $B(0)$ as multiplication by $B(\boldsymbol{x})$ at the initial point (in the backward/Heisenberg picture), show that the two-time correlation function

$$\langle A(t)B(0)\rangle$$

can be written as

$$\langle A(t)B(0)\rangle = \int \big(e^{t\mathcal{D}^\dagger} A\big)(\boldsymbol{x})\, B(\boldsymbol{x})\, P_0(\boldsymbol{x})\, \mathrm{d}\boldsymbol{x}.$$

Problem 3: Many-particle Smoluchowski equation and its adjoint

Consider a system of N Brownian particles with configuration

$$\boldsymbol{X} = (\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N),$$

probability density $P(\boldsymbol{X}, t)$, configuration-dependent mobility blocks $\boldsymbol{\mu}_{ij}(\boldsymbol{X})$, and forces $\boldsymbol{F}_j(\boldsymbol{X})$. The many-particle Smoluchowski equation is

$$\frac{\partial P(\boldsymbol{X}, t)}{\partial t} = -\sum_{i=1}^{N} \nabla_i \cdot \left[\sum_{j=1}^{N} \boldsymbol{\mu}_{ij}(\boldsymbol{X}) \cdot \boldsymbol{F}_j(\boldsymbol{X})\, P - k_B T \sum_{j=1}^{N} \boldsymbol{\mu}_{ij}(\boldsymbol{X}) \cdot \nabla_j P \right].$$

For any smooth observable $A(\boldsymbol{X})$, define

$$\langle A \rangle (t) = \int A(\boldsymbol{X}) P(\boldsymbol{X}, t)\, \mathrm{d}\boldsymbol{X}, \qquad \mathrm{d}\boldsymbol{X} = \mathrm{d}\boldsymbol{x}_1 \cdots \mathrm{d}\boldsymbol{x}_N.$$

Again assume that boundary terms vanish under integration by parts.

(a) Write this equation in the operator form

$$\frac{\partial P}{\partial t} = \mathcal{D}P,$$

and identify explicitly the action of the many-particle Smoluchowski operator $\mathcal{D}$ on the density $P(\boldsymbol{X}, t)$.

(b) Show, by integration by parts, that

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle A \rangle = \left\langle \mathcal{D}^\dagger A \right\rangle,$$

with adjoint operator

$$\mathcal{D}^\dagger A = \sum_{i,j=1}^{N} \left[(\nabla_i A) \cdot \boldsymbol{\mu}_{ij}(\boldsymbol{X}) \cdot \boldsymbol{F}_j(\boldsymbol{X}) + k_B T\, \nabla_j \cdot \big(\boldsymbol{\mu}_{ij}(\boldsymbol{X}) \cdot \nabla_i A\big) \right].$$

Hint: keep the diffusion term in divergence form while integrating by parts; remember that $\boldsymbol{\mu}_{ij}(\boldsymbol{X})$ depends on configuration.

(c) Assume now that the forces derive from a many-particle potential,

$$\boldsymbol{F}_i(\boldsymbol{X}) = -\nabla_i \Phi(\boldsymbol{X}).$$

Show that the Boltzmann distribution

$$P_{\mathrm{eq}}(\boldsymbol{X}) \propto e^{-\Phi(\boldsymbol{X})/k_B T}$$

is stationary. *Hint: it is enough to show that the probability current vanishes identically.*

(d) Explain why the operator viewpoint is especially useful here, where $P(\boldsymbol{X}, t)$ lives in a $3N$-dimensional configuration space. In particular, comment on:

- the difficulty of solving directly for the full probability density $P(\boldsymbol{X}, t)$,
- the usefulness of $\mathcal{D}^\dagger$ for deriving evolution equations for selected observables.