

**Problem 12.1** *Kramer's equation*

Consider the Itô diffusion  $\{(X_t, V_t) : \Omega \rightarrow \mathbb{R}^{n+n}\}_{t \in \mathbb{R}}$  defined via Langevin's equations for a molecule or colloid of mass  $M$  in a force field  $F(x)$ :

$$dX_t = V_t dt, \quad dV_t = [-\gamma V_t + M^{-1} F(X_t)] dt + \sigma dW_t;$$

$\{W_t\}$  denotes the  $n$ -dimensional Wiener process,  $\gamma$  is a phenomenological friction coefficient, and  $\sigma$  parametrises the strength of the random force.

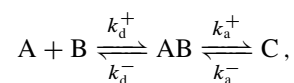
- Determine the Fokker–Planck equation for the probability density  $p_t(x, v)$  corresponding to this process. The result is known as *Kramer's equation*.
- Find the components  $j_t^{(x)}(x, v)$  and  $j_t^{(v)}(x, v)$  of the probability density current and identify reversible and purely irreversible contributions.
- Impose equilibrium conditions on the probability current(s). Solve for the equilibrium density using a product ansatz,  $p^{\text{eq}}(x, v) = q_x(x) q_v(v)$ . (What does this ansatz imply for the stochastic variables  $X_t$  and  $V_t$ ?)
  - Determine  $q_v$  first and interpret your result. Establish a relation between  $\sigma$  and  $\gamma$  in equilibrium.

Use that in statistical mechanics, temperature  $\mathcal{T}$  is defined in terms of Boltzmann's constant  $k_B$  and the average kinetic energy by  $n k_B \mathcal{T} / 2 = \mathbb{E}[M v^2 / 2]$ .

- Assume that the force is given by a potential,  $F(x) = -\partial_x U(x)$ , and solve for  $q_x$ . Interpret your overall result for  $p^{\text{eq}}(x, v)$ .

**Problem 12.2** *Diffusion-limited reaction kinetics*

The kinetics of the bi-molecular chemical reaction in solution,



is determined by *i*) the formation of an encounter complex  $AB$  followed by *ii*) the formation of an activated complex  $(AB)^*$ , which then decays to the product  $C$ . The latter aspect is addressed by Kramer's escape problem, which was discussed in the lecture. The first problem of spatial proximity of the reactants due to diffusion was solved by M. von Smoluchowski (1917), and extended by P. Debye (1942) to account for intermolecular forces.

We assume that the molecules  $A$  and  $B$  are present at concentrations  $c_A$  and  $c_B$ , respectively, and undergo free diffusion with diffusion constants  $D_A$  and  $D_B$ , ignoring any physical interactions between them. The complex  $AB$  is formed whenever the centres of an  $A$  and a  $B$  molecule are separated by less than a distance  $\sigma$ .

- a) Write down the Smoluchowski equation for the joint concentration field  $p_t(\mathbf{r}_A, \mathbf{r}_B)$ , i.e., the probability density for finding a molecule of each species  $\alpha \in \{A, B\}$  at  $\mathbf{r}_\alpha$  at time  $t$ . Show that the probability density  $p_t(r)$  for the separation  $r = |\mathbf{r}_A - \mathbf{r}_B|$  obeys

$$\partial_t p_t(r) = -\left(\partial_r + \frac{2}{r}\right)j_t(r), \quad j_t(r) := -(D_A + D_B)\partial_r p_t(r), \quad r \geq \sigma.$$

Justify the boundary conditions  $p_t(\sigma) = 0$  and  $p_t(r \rightarrow \infty) = c_A$ .

*Hint:* Substitute  $\mathbf{r} = \mathbf{r}_A - \mathbf{r}_B$  and  $R = (D_B \mathbf{r}_A + D_A \mathbf{r}_B)/(D_A + D_B)$ . Assume that there is only a single B molecule in the container at  $\mathbf{r} = 0$ .

- b) Solve this boundary value problem in the stationary case.  
c) Determine the rate constant  $k_d^+$  of the chemical reaction  $A + B \longrightarrow AB$ , which is defined by infinitesimal changes of the concentrations:

$$\frac{dc_{AB}}{dt} = k_d^+ c_A c_B \left( = -\frac{dc_A}{dt} = -\frac{dc_B}{dt} \right).$$

*Hint:* The number of AB complexes formed per unit time is given by the flux across *any* surface enclosing the reaction zone. Result:  $k_d^+ = 4\pi\sigma(D_A + D_B)$ .

- d) Argue that the dissociation rate  $k_d^-$  can be obtained by imposing the boundary conditions  $p_t(\sigma) = 3/4\pi\sigma^3$  and  $p_t(r \rightarrow \infty) = 0$ . Determine  $k_d^-$  and discuss the equilibrium constant  $K = k_d^+/k_d^-$ .