Nonequilibrium soft and active matter

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The aim of this course is to introduce how some recent methods of statistical Physics can be used to model the complex dynamics of soft and active systems. Active systems are made of interacting agents able to extract energy stored in the environment to produce directed motion. The local conversion of energy into mechanical work drives the system far from equilibrium, yielding dynamics and phases without any equivalent in passive systems. Using some minimal models of passive and active systems, this course illustrates how to distinguish equilibrium and nonequilibrium features of the dynamics, and how to rationalize the emergence of collective behaviors.

Although the lecture notes are self-contained, below is a list of references for further reading:

- N. G. Van Kampen, *Stochastic processes in physics and chemistry*, North-Holland Personal Library (2007)
- C. Gardiner, *Stochastic methods*, Springer (2009)
- P. M. Chaikin, T. C. Lubensky, *Principles of condensed matter physics*, Cambridge University Press (2000)
- D. T. Limmer, *Statistical mechanics and stochastic thermodynamics: A textbook on modern approaches in and out of equilibrium*, Oxford University Press (2024)
- U. Seifert, *Stochastic thermodynamics, fluctuation theorems and molecular machines*, Rep. Prog. Phys. 75, 126001 (2012)
- É. Fodor, M. C. Marchetti, *The statistical physics of active matter: From self-catalytic colloids to living cells*, Physica A 504, 106 (2018)
- É. Fodor, R. L. Jack, M. E. Cates, *Irreversibility and biased ensembles in active matter: Insights from stochastic thermodynamics*, Annu. Rev. Condens. Matter Phys. 13, 215 (2022)

Contents

1 Stochastic dynamics and Langevin equation

In this Section, we consider how to model the stochastic motion of a colloid in a viscous solvent. We introduce the seminal Langevin equation, and analyze the statistics of position and velocity in some simple cases.

1.1 Colloid in a viscous solvent

Let us consider a colloid with micrometer size ($\ell \approx 1$ μm) immersed in a solvent with viscosity ν. The dynamics of the colloid and the surrounding solvent molecules follows some complex many-body interactions. Following the seminal approach of Paul Langevin (1872-1946), we will adopt an effective description of the colloid dynamics, which deliberately avoids describing the details of the collisions between solvent molecules and colloids. Langevin's approach assumes that such collisions only result into two effects:

- a fluctuating force $\boldsymbol{\eta}$, modeled as a source of noise independent of the colloid position, with the following properties: (i) Gaussian statistics, due to the many collisions between colloids and solvent molecules, (ii) no average drift $\langle \eta_\alpha(t) \rangle = 0$ for any spatial component α, where $\langle \cdot \rangle$ denotes an average over noise realizations, and (iii) instantaneous correlations given by

$$\langle \eta_\alpha(t) \eta_\beta(0) \rangle = 2B \delta_{\alpha\beta} \delta(t), \tag{1}$$

  where B is the noise amplitude,

- a drag force $-\gamma \dot{\mathbf{x}}$ which hinders the motion of colloid, proportional and opposite to colloid velocity, where $\gamma \sim \nu \ell$ is the damping coefficient.

Applying Newton's law to the colloid, we obtain the *underdamped Langevin equation*:

$$\boxed{m\ddot{\mathbf{x}} = -\nabla U - \gamma \dot{\mathbf{x}} + \boldsymbol{\eta},} \tag{2}$$

where m is the colloid's mass, and U is an external potential. In short, by discarding the degrees of freedom associated with the solvent molecules, we use stochastic dynamics with an explicit Gaussian white noise to describe the colloid dynamics.

1.2 Steady-state properties

The energy of the colloid E is given by the sum of kinetic K and potential U contributions:

$$E(\mathbf{x}, \mathbf{v}) = K(\mathbf{v}) + U(\mathbf{x}), \quad K(\mathbf{v}) = m\mathbf{v}^2/2, \tag{3}$$

where $\mathbf{v} = \dot{\mathbf{x}}$. Given that position and velocity are stochastic, the energy E itself fluctuates. The solvent molecules here act as a thermostat at fixed temperature T, namely a reservoir which exchanges energy with the colloid through collisions. Equilibrium statistical mechanics then enforces that the steady state follows the Boltzmann distribution:

$$P_s(\mathbf{x}, \mathbf{v}) = \frac{1}{Z} \exp\big[-E(\mathbf{x}, \mathbf{v})/T \big], \quad Z = \iint d\mathbf{x} d\mathbf{v} \exp\big[-E(\mathbf{x}, \mathbf{v})/T \big], \tag{4}$$

where the Boltzmann constant is set to unity ($k_\mathrm{B} = 1$), and Z is the partition function.

We evaluate the average kinetic energy in steady state as

$$\langle K(\mathbf{v}) \rangle_s = \iint d\mathbf{x} d\mathbf{v} K(\mathbf{v}) \exp\big[-E(\mathbf{x}, \mathbf{v})/T \big] \Big/ \iint d\mathbf{x}' d\mathbf{v}' \exp\big[-E(\mathbf{x}', \mathbf{v}')/T \big]. \tag{5}$$

Here, the average over noise realizations $\langle \cdot \rangle$ is equivalent to the average with respect to the steady-state statistics $\langle \cdot \rangle_s$. Integrating Eq. (5) over $\mathbf{x}$ and $\mathbf{x}'$ yields the *equipartition theorem*:

$$\langle K(\mathbf{v}) \rangle_s = \int d\mathbf{v} K(\mathbf{v}) \exp\big[-K(\mathbf{v})/T \big] \Big/ \int d\mathbf{v}' \exp\big[-K(\mathbf{v}')/T \big] = \frac{dT}{2}, \tag{6}$$

where d is the spatial dimension, and we have used the properties of Gaussian integrals [see TD1]:

$$\int d\mathbf{x} e^{-\mathbf{x}^2/(2a)} = (2\pi a)^{d/2}, \quad \int \mathbf{x}^2 d\mathbf{x} e^{-\mathbf{x}^2/(2a)} = da(2\pi a)^{d/2}. \tag{7}$$

From Eq. (6), we can define the typical velocity scale given by $v^* = \sqrt{T/m}$. We then evaluate the *Reynolds number*, which compares inertial and viscous effects in the underdamped Langevin equation [Eq. (2)], defined as

$$\mathrm{Re} = \frac{mv^*}{\gamma \ell} = \frac{\sqrt{mT}}{\nu \ell^2}. \tag{8}$$

For a micrometer polysterene bead in water at room temperature, we get $\ell \sim 1\,\mu$m, $m = \rho \ell^3 \sim 10^3 \times (10^{-6})^3\,$kg, $\nu = 10^{-3}\,$N.s/m^2, and $T = 10^{-21}\,$J, from which we deduce $\mathrm{Re} \sim 10^{-3}$. Then, it is indeed legitimate to neglect internal effects in such a case, leading us to consider the *overdamped Langevin equation*:

$$\boxed{\gamma \dot{\mathbf{x}} = -\nabla U + \boldsymbol{\eta}.} \tag{9}$$

In what follows, we will consider either the underdamped [Eq. (2)] or the overdamped [Eq. (9)] version of the Langevin equation.

1.3 Relaxation towards steady state

In this Section, we demonstrate how the Langevin equation can be used to predict the statistics beyond steady state. Specifically, we are interested in characterizing the relaxation of the colloid's position and velocity in some simple cases.

1.3.1 Velocity statistics

We want to evaluate the statistics of the colloid's velocity in the absence of potential ($U = 0$). Considering the underdamped Langevin equation [Eq. (2)], the velocity obeys a linear dynamics:

$$m\dot{\mathbf{v}} + \gamma \mathbf{v} = m \exp(-t/\tau_m) \frac{d}{dt}\Big[\exp(t/\tau_m)\mathbf{v}(t)\Big] = \boldsymbol{\eta}, \tag{10}$$

where $\tau_m = m/\gamma$ is a typical relaxation time. Equation (10) can be straightforwardly integrated as

$$\mathbf{v}(t) = \mathbf{v}(0)\exp(-t/\tau_m) + \frac{1}{m}\int_0^t \exp((t'-t)/\tau_m)\boldsymbol{\eta}(t')dt'. \tag{11}$$

Given that the velocity $\mathbf{v}$ is linearly related to the Gaussian noise $\boldsymbol{\eta}$, it follows that $\mathbf{v}$ also has Gaussian statistics [see TD1].

From Eq. (11), we deduce that the average velocity relaxes towards a vanishing value, as expected from the absence of any drift:

$$\langle v_\alpha(t)\rangle = \langle v_\alpha(0)\rangle \exp(-t/\tau_m) \underset{t \gg \tau_m}{\longrightarrow} 0. \tag{12}$$

We can express the velocity correlations as

$$\langle v_\alpha(t) v_\beta(0)\rangle = \langle v_\alpha(0) v_\beta(0)\rangle \exp(-t/\tau_m) + \frac{1}{m}\int_0^t \exp((t'-t)/\tau_m)\langle \eta_\alpha(t') v_\beta(0)\rangle dt'. \tag{13}$$

Causality enforces that $\langle \eta_\beta(t') v_\beta(0)\rangle = 0$ for $t' > 0$. Indeed, a noise realization at a given time t' only affects the realizations of velocity at later times $t > t'$, while it does not affect the velocity at earlier times $t < t'$. It follows that

$$\langle v_\alpha(t) v_\beta(0)\rangle = \langle v_\alpha(0) v_\beta(0)\rangle \exp(-|t|/\tau_m), \tag{14}$$

where we have assumed that correlations are symmetric with respect to t. Finally, we evaluate the variance of velocity as

$$\begin{aligned}\langle \mathbf{v}(t)^2\rangle &= \langle \mathbf{v}(0)^2\rangle \exp(-2t/\tau_m) + \frac{1}{m^2}\iint_0^t \exp((t'+t''-2t)/\tau_m)\langle \boldsymbol{\eta}(t')\cdot\boldsymbol{\eta}(t'')\rangle dt''dt' \\ &= \langle \mathbf{v}(0)^2\rangle \exp(-2t/\tau_m) + \frac{2Bd}{m^2}\int_0^t \exp(2(t'-t)/\tau_m)dt', \\ &= \langle \mathbf{v}(0)^2\rangle \exp(-2t/\tau_m) + \frac{Bd}{\gamma m}\Big[1-\exp(-2t/\tau_m)\Big] \underset{t\gg\tau_m}{\longrightarrow} \frac{Bd}{\gamma m},\end{aligned} \tag{15}$$

where we have used again $\langle \eta_\alpha(t')v_\beta(0)\rangle = 0$ for $t' > 0$ by causality. At large times, the variance must coincide with the steady-state value given by the equipartition theorem [Eq. (6)], from which we deduce

$$\boxed{B = T\gamma.} \tag{16}$$

The noise amplitude B and the damping coefficient γ are related through the temperature T. This important result is a version of the *fluctuation-dissipation theorem*. It emphasizes that the noise term and the viscous force in the Langevin equation both stem from the same physical mechanism, namely collisions between the solvent molecules and the colloid.

1.3.2 Position statistics

We want to characterize the typical deviation of the colloid's position from its initial value. To this end, we introduce the *mean-squared displacement* (MSD):

$$\langle \Delta\mathbf{x}^2(t)\rangle = \big\langle [\mathbf{x}(t)-\mathbf{x}(0)]^2\big\rangle. \tag{17}$$

Given that $\int_0^t \mathbf{v}(t')dt' = \mathbf{x}(t)-\mathbf{x}(0)$, the MSD is directly related to the velocity correlations as

$$\langle \Delta\mathbf{x}^2(t)\rangle = \iint_0^t \langle \mathbf{v}(t')\cdot\mathbf{v}(t'')\rangle dt'dt''. \tag{18}$$

Let us first evaluate the MSD for the underdamped Langevin equation [Eq. (2)] in the absence of any potential ($U = 0$). Using the invariance of the dynamics under time translation, we deduce

$$\langle \mathbf{v}(t')\cdot\mathbf{v}(t'')\rangle = \langle \mathbf{v}(t'-t'')\cdot\mathbf{v}(0)\rangle = (Td/m)\exp(-|t'-t''|/\tau_m), \tag{19}$$

where we have used Eq. (14), and we have assumed that the dynamics is initially at steady state, namely $\langle \mathbf{v}(0)^2\rangle = \langle \mathbf{v}^2\rangle_s = dT/m$. After substituting Eq. (19) into the expression of the MSD in Eq. (18), we perform the time integration as

$$\begin{aligned}\langle \Delta\mathbf{x}^2(t)\rangle &= \frac{dT}{m}\int_0^t dt'\left[\int_0^{t'}\exp(-(t'-t'')/\tau_m) + \int_{t'}^t \exp(-(t''-t')/\tau_m)\right]dt'' \\ &= \frac{dT}{\gamma}\int_0^t dt'\Big[1-\exp(-t'/\tau_m)-\exp(-(t-t')/\tau_m)+1\Big],\end{aligned} \tag{20}$$

yielding

$$\boxed{\langle \Delta\mathbf{x}^2(t)\rangle = \frac{2dT}{\gamma}t - \frac{2dT\tau_m}{\gamma}\Big[1-\exp(-t/\tau_m)\Big].} \tag{21}$$

At small time ($t \ll \tau_m$), the MSD follows a ballistic regime dominated by inertia: $\langle \Delta\mathbf{x}^2(t)\rangle \sim (dT/m)t^2$. At large times ($t \gg \tau_m$), we get instead a diffusive regime: $\langle \Delta\mathbf{x}^2(t)\rangle \sim (2dT/\gamma)t$, for which we can express the diffusion coefficient as $D = T/\gamma$, in agreement with *Einstein's relation*.

We want now to evaluate the MSD from the overdamped Langevin equation [Eq. (9)] in the presence of a harmonic potential ($U = k\mathbf{x}^2/2$). In this case, the colloid's position obeys a linear dynamics:

$$\gamma\dot{\mathbf{x}} = -k\mathbf{x} + \boldsymbol{\eta}, \tag{22}$$

which we integrate as

$$\mathbf{x}(t) = \mathbf{x}(0)\exp(-t/\tau_\gamma) + \frac{1}{\gamma}\int_0^t \exp(-(t-t')/\tau_\gamma)\boldsymbol{\eta}(t')dt', \tag{23}$$

where $\tau_\gamma = \gamma/k$ is a typical relaxation time. Substituting Eq. (23) into the definition of the MSD [Eq. (17)], we readily deduce the expression of the MSD as

$$\langle \Delta\mathbf{x}^2(t)\rangle = \langle \mathbf{x}(0)^2\rangle\Big[\exp(-t/\tau_\gamma)-1\Big]^2 + \frac{1}{\gamma^2}\iint_0^t \exp(-(2t-t'-t'')/\tau_\gamma)\langle\boldsymbol{\eta}(t')\cdot\boldsymbol{\eta}(t'')\rangle dt'dt'', \tag{24}$$

where we have used again $\langle \eta_\alpha(t')x_\beta(0)\rangle = 0$ for $t' > 0$ by causality. The second term in Eq. (24) is an integral similar to that obtained when computing the velocity variance for a free particle [Eq. (15)]. After integration, we get

$$\boxed{\langle \Delta\mathbf{x}^2(t)\rangle = \frac{2dT}{k}\Big[1-\exp(-t/\tau_\gamma)\Big],} \tag{25}$$

where we have assumed that the system is initially in steady state: $\langle \mathbf{x}(0)^2\rangle = \langle \mathbf{x}^2\rangle_s = dT/k$. At small times ($t \ll \tau_\gamma$), the MSD is diffusive: $\langle \Delta\mathbf{x}^2(t)\rangle \sim (2dT/\gamma)t$. At large times ($t \gg \tau_\gamma$), we get instead a saturation: $\langle \Delta\mathbf{x}^2(t)\rangle \to 2dT/k$, which illustrates the confinement of the colloid.

2 Probability distribution and stochastic calculus

In this Section, we consider how to describe the time-evolution of the probability distribution for a stochastic dynamics. Using this tool, we examine how the standard rules of calculus can be extended to stochastic variables.

2.1 Master equation

Let us first consider a generic dynamics where the position $\mathbf{x}(t)$ is a *Markov process*. We denote by $P(\mathbf{x}, t+\Delta t|\mathbf{x}_0, 0)$ the probability distribution to observe a realization $\mathbf{x}(t) = \mathbf{x}$ given that the position was initially at $\mathbf{x}(0) = \mathbf{x}_0$. This probability obeys the *Chapman-Kolmogorov relation*:

$$P(\mathbf{x}, t+\Delta t|\mathbf{x}_0, 0) = \int d\mathbf{x}' P(\mathbf{x}, t+\Delta t|\mathbf{x}', t) P(\mathbf{x}', t|\mathbf{x}_0, 0). \tag{26}$$

For small time intervals Δt, we express $P(\mathbf{x}, t+\Delta t|\mathbf{x}', t)$ in terms of the transfer rate $W(\mathbf{x}', \mathbf{x}-\mathbf{x}')$ to move from position $\mathbf{x}'$ to $\mathbf{x}$:

$$P(\mathbf{x}, t+\Delta t|\mathbf{x}', t') = W(\mathbf{x}', \mathbf{x}-\mathbf{x}')\Delta t + \left[1 - \Delta t \int d\mathbf{x}'' W(\mathbf{x}', \mathbf{x}''-\mathbf{x}')\right]\delta(\mathbf{x}-\mathbf{x}') + o(\Delta t). \tag{27}$$

Substituting Eq. (27) into Eq. (26), we deduce

$$\begin{aligned} &P(\mathbf{x}, t+\Delta t|\mathbf{x}_0, 0) \\ &\quad = \left[1 - \Delta t \int d\mathbf{x}'' W(\mathbf{x}, \mathbf{x}''-\mathbf{x})\right] P(\mathbf{x}, t|\mathbf{x}_0, 0) + \Delta t \int d\mathbf{x}' W(\mathbf{x}', \mathbf{x}-\mathbf{x}') P(\mathbf{x}', t|\mathbf{x}_0, 0) + o(\Delta t). \end{aligned} \tag{28}$$

Taking the limit of small time interval ($\Delta t \to 0$), we obtain the *Master equation* ruling the dynamics of $P(\mathbf{x}, t) = P(\mathbf{x}, t|\mathbf{x}_0, 0)$:

$$\boxed{\partial_t P(\mathbf{x}, t) = \int \left[P(\mathbf{x}', t) W(\mathbf{x}', \mathbf{x}-\mathbf{x}') - P(\mathbf{x}, t) W(\mathbf{x}, \mathbf{x}'-\mathbf{x})\right] d\mathbf{x}'.} \tag{29}$$

Since the Master equation is linear for the probability P, it has a unique stationary solution P_s. In equilibrium, this solution is found by imposing that the all probability fluxes in the rhs of Eq. (29) vanish, yielding

$$P_s(\mathbf{x}') W(\mathbf{x}', \mathbf{x}-\mathbf{x}') = P_s(\mathbf{x}) W(\mathbf{x}, \mathbf{x}'-\mathbf{x}). \tag{30}$$

The equilibrium condition in Eq. (30) is known as the *local detailed balance*. It enforces that the ratio of probabilities to be at distinct positions is given by the corresponding ratio of transfer rates between these positions.

2.2 Fokker-Planck equation

We want to demonstrate that, when the position increment $\mathbf{u} = \mathbf{x} - \mathbf{x}'$ is small, the Master equation [Eq. (29)] reduces to a simpler partial differential equation. In this regime, we assume that the transfer rate $W(\mathbf{x}', \mathbf{x}-\mathbf{x}') = W(\mathbf{x}-\mathbf{u}, \mathbf{u})$ weakly depends on the starting point $\mathbf{x}-\mathbf{u}$, yet strongly depends on the step length $\mathbf{u}$. Indeed, transitions get typically rejected if the step length exceeds a given relaxation length. As a result, we expand W only with respect to its first argument:

$$\begin{aligned} P(\mathbf{x}', t) W(\mathbf{x}', \mathbf{x}-\mathbf{x}') &= P(\mathbf{x}-\mathbf{u}, t) W(\mathbf{x}-\mathbf{u}, \mathbf{u}) \\ &= P(\mathbf{x}, t) W(\mathbf{x}, \mathbf{u}) - \mathbf{u} \cdot \partial_{\mathbf{x}}(P(\mathbf{x}, t) W(\mathbf{x}, \mathbf{u})) + \frac{\mathbf{u}^2}{2} \partial^2_{\mathbf{xx}}(P(\mathbf{x}, t) W(\mathbf{x}, \mathbf{u})) + o(\mathbf{u}^2). \end{aligned} \tag{31}$$

Substituting Eq. (31) in the Master equation [Eq. (29)] yields

$$\begin{aligned} \partial_t P(\mathbf{x}, t) &= \int \left[P(\mathbf{x}-\mathbf{u}, t) W(\mathbf{x}-\mathbf{u}, \mathbf{u}) - P(\mathbf{x}, t) W(\mathbf{x}, -\mathbf{u})\right] d\mathbf{u} \\ &= \int \Big[P(\mathbf{x}, t)(W(\mathbf{x}, \mathbf{u}) - W(\mathbf{x}, -\mathbf{u})) - \mathbf{u} \cdot \partial_{\mathbf{x}}(P(\mathbf{x}, t) W(\mathbf{x}, \mathbf{u})) \\ &\qquad + \frac{\mathbf{u}^2}{2} \partial^2_{\mathbf{xx}}(P(\mathbf{x}, t) W(\mathbf{x}, \mathbf{u})) + o(\mathbf{u}^2)\Big] d\mathbf{u}. \end{aligned} \tag{32}$$

Using $\int W(\mathbf{x},\mathbf{u})d\mathbf{u} = \int W(\mathbf{x},-\mathbf{u})d\mathbf{u}$, and ignoring contributions of order $\mathbf{u}^2$ in Eq. (32), we get the *Fokker-Planck equation*:

$$\boxed{\partial_t P(\mathbf{x},t) = -\partial_{\mathbf{x}}\cdot(\mathbf{a}_1(x)P(\mathbf{x},t)) + \frac{1}{2}\partial^2_{\mathbf{xx}}(a_2(\mathbf{x})P(\mathbf{x},t)),} \tag{33}$$

where

$$\mathbf{a}_1(\mathbf{x}) = \int \mathbf{u}W(\mathbf{x},\mathbf{u})d\mathbf{u}, \quad a_2(\mathbf{x}) = \int \mathbf{u}^2 W(\mathbf{x},\mathbf{u})d\mathbf{u}. \tag{34}$$

To provide a physical meaning to the coefficients $\mathbf{a}_1$ and a_2, let us consider a small position displacement $[\mathbf{x},\mathbf{x}+\mathbf{u}]$ during small time interval $[t,t+\Delta t]$. The initial position is fixed, so that there is not any uncertainty on the probability distribution at time t, namely $P(\mathbf{x}+\mathbf{u},t) = \delta(\mathbf{u})$. Therefore, we can express the average displacement as

$$\begin{aligned}\langle\mathbf{u}\rangle &= \int \mathbf{u}P(\mathbf{x}+\mathbf{u},t+\Delta t)d\mathbf{u}\\ &= \int \mathbf{u}P(\mathbf{x}+\mathbf{u},t)d\mathbf{u} + \Delta t\int \mathbf{u}\partial_{\mathbf{u}}\cdot\Big[-\mathbf{a}_1(\mathbf{x}+\mathbf{u})P(\mathbf{x}+\mathbf{u},t)\\ &\quad + \frac{1}{2}\partial_{\mathbf{u}}(a_2(\mathbf{x}+\mathbf{u})P(\mathbf{x}+\mathbf{u},t))\Big]d\mathbf{u} + o(\Delta t),\end{aligned} \tag{35}$$

where we have substituted Eq. (33) evaluated at small Δt, yielding

$$\begin{aligned}\langle\mathbf{u}\rangle &= \Delta t\int\Big[-\mathbf{a}_1(\mathbf{x}+u)P(\mathbf{x}+\mathbf{u},t) + \frac{1}{2}\partial_{\mathbf{u}}(a_2(\mathbf{x}+\mathbf{u})P(\mathbf{x}+\mathbf{u},t))\Big]d\mathbf{u} + o(\Delta t)\\ &= \mathbf{a}_1(\mathbf{x})\Delta t - (\Delta t/2)\Big[a_2(\mathbf{x}+\mathbf{u})P(\mathbf{x}+\mathbf{u},t)\Big]^{|\mathbf{u}|=\infty}_{|\mathbf{u}|=-\infty} + o(\Delta t)\\ &= \mathbf{a}_1(x)\Delta t + o(\Delta t),\end{aligned} \tag{36}$$

where we have used integration by parts in the first line, $P(\mathbf{x}+\mathbf{u},t) = \delta(\mathbf{u})$ in the second one, and $P(\pm\infty,t) = 0$ in the third one. Likewise, following the same series of steps, let us evaluate

$$\begin{aligned}\langle\mathbf{u}^2\rangle &= \int \mathbf{u}^2 P(\mathbf{x}+\mathbf{u},t)d\mathbf{u} + \Delta t\int \mathbf{u}^2\partial_{\mathbf{u}}\cdot\Big[-\mathbf{a}_1(\mathbf{x}+\mathbf{u})P(\mathbf{x}+\mathbf{u},t)\\ &\quad + \frac{1}{2}\partial_{\mathbf{u}}(a_2(\mathbf{x}+\mathbf{u})P(\mathbf{x}+\mathbf{u},t))\Big]d\mathbf{u} + o(\Delta t)\\ &= -\Delta t\int 2\mathbf{u}\cdot\Big[-\mathbf{a}_1(\mathbf{x}+\mathbf{u})P(\mathbf{x}+\mathbf{u},t) + \frac{1}{2}\partial_{\mathbf{u}}(a_2(\mathbf{x}+\mathbf{u})P(\mathbf{x}+\mathbf{u},t))\Big]d\mathbf{u} + o(\Delta t)\\ &= a_2(x)d\Delta t + o(\Delta t).\end{aligned} \tag{37}$$

Overall, Eqs. (36) and (37) demonstrate that there is a straightforward connection between the statistics of u and the coefficients $\{\mathbf{a}_1, a_2\}$.

2.3 Connection to stochastic dynamics

In this Section, we show that there is a direct correspondence between the Langevin equation, giving the stochastic dynamics of positions, and the Fokker-Planck equation, describing the corresponding dynamics of its probability distribution.

2.3.1 Additive Langevin equation

Let us consider the overdamped Langevin equation [Eq. (9)], where now time is discretized as $t_n = n\Delta t$ in terms of a small time interval Δt. The noise statistics can be written as

$$\langle\eta_\alpha(t_n)\eta_\beta(t_m)\rangle = 2\gamma T\delta_{\alpha\beta}\delta((n-m)\Delta t) = 2\gamma T\delta_{\alpha\beta}\delta_{nm}/\Delta t, \tag{38}$$

where $\delta_{nm} = 1$ if $n = m$, and $\delta_{nm} = 0$ otherwise. Therefore, we cast the noise term $\boldsymbol{\eta}(t_n)$ in terms of the Gaussian variable $\boldsymbol{\eta}_n$ as

$$\boldsymbol{\eta}(t_n) = \boldsymbol{\eta}_n/\sqrt{\Delta t}, \quad \langle\eta_{n\alpha}\rangle = 0, \quad \langle\eta_{n\alpha}\eta_{m\beta}\rangle = 2\gamma T\delta_{\alpha\beta}\delta_{nm}. \tag{39}$$

For a fixed initial position $\mathbf{x}_n = \mathbf{x}(t_n)$, the position displacement reads

$$\mathbf{u} = \mathbf{x}_{n+1} - \mathbf{x}_n = (1/\gamma)\Big[- \Delta t \nabla U(\mathbf{x}_n) + \sqrt{\Delta t}\boldsymbol{\eta}_n\Big] + o(\Delta t), \tag{40}$$

yielding

$$\begin{aligned} \langle \mathbf{u} \rangle &= -(\Delta t/\gamma)\nabla U(\mathbf{x}_n) + o(\Delta t), \\ \langle \mathbf{u}^2 \rangle &= (1/\gamma)^2 \Delta t \langle \boldsymbol{\eta}_n \cdot \boldsymbol{\eta}_n \rangle + o(\Delta t) = (2Td/\gamma)\Delta t + o(\Delta t), \end{aligned} \tag{41}$$

where we have used that initial position $\mathbf{x}(t_n)$ is fixed, so that $\langle \nabla U(\mathbf{x}_n) \rangle = \nabla U(\mathbf{x}_n)$. In practice, higher-order terms $\langle \mathbf{u}^n \rangle$ are negligible compared to Δt for $n > 2$, which justifies *a posteriori* truncating the expansion to order $\mathbf{u}^2$ in Eq. (32).

Combining Eq. (41) with the results in Sec. 2.2, it directly follows that the Fokker-Planck equation associated with the overdamped Langevin equation [Eq. (9)] takes the form

$$\partial_t P = (1/\gamma)\partial_{\mathbf{x}} \cdot (P\nabla U + T\partial_{\mathbf{x}} P). \tag{42}$$

In equilibrium, the steady-state follows by imposing that the probability flux in the rhs of Eq. (42) vanishes: $P_s \nabla U = -T\partial_{\mathbf{x}} P_s$. The solution is given by the Boltzmann distribution $P_s \sim \exp(-U/T)$, which is independent of the damping coefficient γ. Considering now a set of Langevin equations with a generic drift term $\mathbf{A}(\{\mathbf{x}_k\})$ for the variables $\{\mathbf{x}_k\}$, the corresponding Fokker-Planck equation reads

$$\boxed{\begin{aligned} \dot{\mathbf{x}}_i &= \mathbf{A}(\{\mathbf{x}_k\}) + \boldsymbol{\eta}_i, \quad \langle \eta_{i\alpha}(t)\eta_{j\beta}(0)\rangle = 2B_i\delta_{ij}\delta_{\alpha\beta}\delta(t), \\ \partial_t P &= \sum_i \partial_{\mathbf{x}_i} \cdot \Big[- \mathbf{A}(\{\mathbf{x}_k\})P + B_i \partial_{\mathbf{x}_i} P\Big]. \end{aligned}} \tag{43}$$

In particular, applying the correspondence in Eq. (43) to the underdamped Langevin equation [Eq. (2)] yields the following Fokker-Planck equation:

$$\partial_t P = -\partial_{\mathbf{x}} \cdot (\mathbf{v}P) + (1/m)\partial_{\mathbf{v}} \cdot \Big[(\gamma\mathbf{v} + \nabla U)P + (T/m)\partial_{\mathbf{v}} P\Big], \tag{44}$$

which admits the Maxwell-Boltzmann distribution $P_s \sim \exp[-(m\mathbf{v}^2/2 + U)/T]$ as its stationary solution, as expected.

2.3.2 Multiplicative Langevin equation

Let us now consider the case where the noise term in the Langevin equation is multiplied by the function $C(\mathbf{x}(t))$:

$$\dot{\mathbf{x}} = \mathbf{A}(\mathbf{x}(t)) + C(\mathbf{x}(t))\boldsymbol{\xi}(t), \quad \langle \xi_\alpha(t)\xi_\beta(0)\rangle = 2\delta_{\alpha\beta}\delta(t). \tag{45}$$

This type of multiplicative Langevin equation arises, for instance, when considering the dynamics of a colloid close to a wall [see TD2]. For a fixed initial position $\mathbf{x}_n$, we express the position displacement as

$$\mathbf{u} = \mathbf{x}_{n+1} - \mathbf{x}_n = \Delta t \mathbf{A}(\mathbf{x}_a) + \sqrt{\Delta t} C(\mathbf{x}_a)\boldsymbol{\xi}_n + o(\Delta t), \quad \langle \xi_{n\alpha}\xi_{m\beta}\rangle = 2\delta_{\alpha\beta}\delta_{nm}, \tag{46}$$

where we have introduced $\mathbf{x}_a = (1-a)\mathbf{x}_n + a\mathbf{x}_{n+1}$, which distinguishes various conventions for time discretisation in terms of the parameter $0 < a < 1$. We expand the drift term and the multiplicative factor in Eq. (46) as

$$\begin{aligned} A(\mathbf{x}_a)\Delta t &= A(\mathbf{x}_n)\Delta t + o(\Delta t) \\ \sqrt{\Delta t} C(\mathbf{x}_a) &= \sqrt{\Delta t} C(\mathbf{x}_n) + a\sqrt{\Delta t}(\mathbf{x}_{n+1} - \mathbf{x}_n) \cdot \nabla C(\mathbf{x}_n) + o(\mathbf{x}_{n+1} - \mathbf{x}_n) \\ &= \sqrt{\Delta t} C(\mathbf{x}_n) + a\sqrt{\Delta t}\Big[\Delta t \mathbf{A}(\mathbf{x}_n) + \sqrt{\Delta t} C(\mathbf{x}_n)\boldsymbol{\xi}_n + o(\Delta t)\Big] \cdot \nabla C(\mathbf{x}_n) + o(\Delta t) \\ &= \sqrt{\Delta t} C(\mathbf{x}_n) + a\Delta t C(\mathbf{x}_n)\boldsymbol{\xi}_n \cdot \nabla C(\mathbf{x}_n) + o(\Delta t), \end{aligned} \tag{47}$$

yielding

$$\mathbf{u} = \Delta t\Big[\mathbf{A}(\mathbf{x}_n) + aC(\mathbf{x}_n)(\boldsymbol{\xi}_n \cdot \nabla C(\mathbf{x}_n))\boldsymbol{\xi}_n\Big] + \sqrt{\Delta t} C(\mathbf{x}_n)\boldsymbol{\xi}_n + o(\Delta t). \tag{48}$$

We then deduce

$$\begin{aligned}\langle \mathbf{u} \rangle &= \Delta t \Big[\mathbf{A}(\mathbf{x}_n) + 2aC(\mathbf{x}_n)\nabla C(\mathbf{x}_n) \Big] + o(\Delta t), \\ \langle \mathbf{u}^2 \rangle &= 2C(\mathbf{x}_n)^2 d\Delta t + o(\Delta t),\end{aligned} \tag{49}$$

and the corresponding Fokker-Planck equation follows as

$$\boxed{\partial_t P = \partial_{\mathbf{x}} \cdot \Big[-(\mathbf{A} + 2aC\nabla C)P + \partial_{\mathbf{x}}(C^2 P) \Big].} \tag{50}$$

The term $2aC\nabla C$ in the rhs of Eq. (50) is called the *spurious drift*. In contrast with the case of the additive Langevin equation, one now needs to prescribe the convention of time discretisation (set by a) to ensure a unique correspondence with the Fokker-Planck equation. Some popular discretisation schemes are given by the Stratonovitch ($a = 1/2$), the Itô ($a = 0$), and the anti-Itô ($a = 1$) conventions.

2.4 Stochastic calculus

Let us examine how the rules of differential calculus can be extended to stochastic variables. To this end, we consider the following additive Langevin equation:

$$\dot{\mathbf{x}} = \mathbf{A}(\mathbf{x}) + \boldsymbol{\eta}, \quad \langle \eta_\alpha(t)\eta_\beta(0) \rangle = 2B\delta_{\alpha\beta}\delta(t). \tag{51}$$

We want to evaluate the time derivative of an arbitrary function $f(\mathbf{x}(t))$. First, using the Fokker-Planck equation [Eq. (43)], we get

$$\begin{aligned}\langle \dot{f}(\mathbf{x}(t)) \rangle &= \int d\mathbf{x} f(\mathbf{x}) \partial_t P(x,t) \\ &= \int d\mathbf{x} f(\mathbf{x}) \partial_{\mathbf{x}} \cdot \Big[-\mathbf{A}(\mathbf{x})P(x,t) + B\partial_{\mathbf{x}} P(x,t) \Big] \\ &= -\int d\mathbf{x} \nabla f \cdot \Big[-\mathbf{A}(\mathbf{x})P(x,t) + B\partial_{\mathbf{x}} P(x,t) \Big] \\ &= \langle \mathbf{A}(\mathbf{x}) \cdot \nabla f \rangle + B\langle \nabla^2 f \rangle,\end{aligned} \tag{52}$$

where we have used some integration by parts. Using the Langevin equation in Eq. (51), we should expect to obtain the same result. Assuming that the standard chain rule extends to stochastic variables, we get

$$\langle \dot{f} \rangle = \langle \dot{\mathbf{x}} \cdot \nabla f \rangle = \langle (\mathbf{A}(\mathbf{x}) + \boldsymbol{\eta}) \cdot \nabla f \rangle. \tag{53}$$

While the first term in the rhs of Eq. (53) does not suffer from any ambiguity, we need to specify the scheme for time discretisation when evaluating the second term. To this end, as in Sec. 2.3, we consider a time-discretized version of the dynamics for $\mathbf{x}_n = \mathbf{x}(n\Delta t)$ and $\boldsymbol{\eta}_n = \sqrt{\Delta t}\boldsymbol{\eta}(n\Delta t)$, given in terms of the small time interval Δt. Introducing the generic convention $\mathbf{x}_a = (1-a)\mathbf{x}_n + a\mathbf{x}_{n+1}$ ($0 < a < 1$), we get

$$\begin{aligned}\langle \boldsymbol{\eta}(t) \cdot \nabla f(\mathbf{x}(t)) \rangle &= \langle \boldsymbol{\eta}_n \cdot \nabla f(\mathbf{x}_a) \rangle / \sqrt{\Delta t} \\ &= \langle \boldsymbol{\eta}_n \cdot \nabla f(\mathbf{x}_n) \rangle / \sqrt{\Delta t} + a\langle \eta_n \eta_n \nabla^2 f(\mathbf{x}_n) \rangle + o(\Delta t^0),\end{aligned} \tag{54}$$

where we have used the same series of steps as in Eq. (47). Causality enforces that $\boldsymbol{\eta}_n$ and $f(\mathbf{x}_n)$ are uncorrelated at small Δt, yielding

$$\langle \boldsymbol{\eta}(t) \cdot \nabla f(\mathbf{x}(t)) \rangle = 2aB\langle \nabla^2 f(\mathbf{x}(t)) \rangle. \tag{55}$$

To ensure that the result obtained with the Langevin equation [Eqs. (53) and (55)] is consistent with that obtained with the Fokker-Planck equation [Eq. (52)], one needs to choose the Stratonovitch convention ($a = 1/2$). In other words, the Stratonovitch convention is the only one which conserves the standard chain rule for stochastic variables. Alternatively, choosing the Itô convention ($a = 0$) requires to adapt the standard chain rule using *Itô's lemma*:

$$\boxed{\langle \dot{f} \rangle = \langle \dot{\mathbf{x}} \cdot \nabla f \rangle + B\langle \nabla^2 f \rangle}. \tag{56}$$

This lemma actually extends to describe the stochastic dynamics of an arbitrary function $f(\mathbf{x}(t))$ by considering Eq. (56) without the averaging. In practice, either convention (Stratonovitch or Itô) can be used for stochastic calculus, provided that they are complemented with the appropriate rule of calculus (respectively, the standard chain rule or Itô's lemma).

3 Generalized Langevin equation

In this Section, we show that the Langevin equation is relevant to describe a broad class of systems, even beyond the case of colloids in a solvent, by considering the dynamics of a tracer particle in contact with a thermal bath.

3.1 Tracer in a thermal bath

We consider the dynamics of a tracer with position $\mathbf{x}$ surrounded by a bath of N particles with positions $\{\mathbf{r}_i\}$. We assume that tracer and bath particles interact through the harmonic potential $V(\mathbf{x}, \{\mathbf{r}_k\}) = (1/2)\sum_i k_i(\mathbf{x} - \mathbf{r}_i)^2$. The dynamics then reads

$$m\ddot{\mathbf{x}} = -\nabla U - \sum_{i=1}^{N} k_i(\mathbf{x} - \mathbf{r}_i), \quad m_i\ddot{\mathbf{r}}_i = -k_i(\mathbf{r}_i - \mathbf{x}), \tag{57}$$

where m and m_i respectively denote the masses of the tracer and bath particles. We integrate the bath dynamics as

$$\mathbf{r}_i(t) = \mathbf{r}_i(0)\cos(\omega_i t) + \dot{\mathbf{r}}_i(0)\sin(\omega_i t)/\omega_i + \omega_i \int_0^t dt' \mathbf{x}(t')\sin(\omega_i(t - t')), \tag{58}$$

where $\omega_i = \sqrt{k_i/m_i}$ is the oscillation frequency of the bath particles. Integrating by parts the last term in the rhs of Eq. (58) yields

$$\begin{aligned}\omega_i \int_0^t dt' \mathbf{x}(t')\sin(\omega_i(t - t')) &= \Big[\mathbf{x}(t')\cos(\omega_i(t - t'))\Big]_0^t - \int_0^t dt' \dot{\mathbf{x}}(t')\cos(\omega_i(t - t')) \\ &= \mathbf{x}(t) - \mathbf{x}(0)\cos(\omega_i t) - \int_0^t \dot{\mathbf{x}}(t')\cos(\omega_i(t - t'))dt'.\end{aligned} \tag{59}$$

Substituting Eqs. (58) and (59) into the tracer dynamics [Eq. (57)], we then get

$$\begin{aligned}m\ddot{\mathbf{x}} &= -\nabla U - \int_0^t \dot{\mathbf{x}}(t')K(t - t')dt' + \boldsymbol{\eta}, \quad K(t) = \sum_{i=1}^{N} k_i\cos(\omega_i t), \\ \boldsymbol{\eta}(t) &= -\sum_{i=1}^{N} k_i\Big[(\mathbf{x}(0) - \mathbf{r}_i(0))\cos(\omega_i t) - \dot{\mathbf{r}}_i(0)\sin(\omega_i t)/\omega_i\Big].\end{aligned} \tag{60}$$

Therefore, integrating the positions of bath particles leads to a damping term opposed to the velocity of the tracer. In contrast with the underdamped Langevin equation [Eq. (2)], the damping term is no longer instantaneous, since it now features the memory kernel K.

In the regime of a large number of bath particles ($N \gg 1$), the expression of the kernel can be simplified. Assuming that all bath particles have the same mass ($m_i = \bar{m}$), we get

$$K(t) \underset{N\gg 1}{\longrightarrow} \bar{m}\int \omega^2 g(\omega)\cos(\omega t)d\omega, \tag{61}$$

where g is the distribution of oscillation frequencies. Choosing $g(\omega) \sim 1/\omega^2$ yields $K(t) \sim \delta(t)$, for which one recovers an instantaneous damping force. Instead, considering $g(\omega) \sim \omega^{-2}/(1 + (\omega\tau)^2)$ leads to $K(t) \sim \exp(-t/\tau)$: such a kernel describes a Maxwell fluid with a finite relaxation time τ. In general, one can tailor the distribution g to reproduce the damping of a large class of viscoelastic materials.

3.2 Averaging over initial conditions

We assume that the initial positions and velocities are sampled according to their equilibrium statistics, given by the Maxwell-Boltzmann distribution:

$$P_s(\{\dot{\mathbf{r}}_k, \mathbf{r}_k\}) = \frac{1}{Z}\exp\Big[-\frac{1}{2T}\sum_i \Big(m_i\dot{\mathbf{r}}_i^2 + k_i(\mathbf{x} - \mathbf{r}_i)^2\Big)\Big], \tag{62}$$

where Z is the partition function. Given that the term $\boldsymbol{\eta}$ in Eq. (60) is a linear combination of $\{\mathbf{x}(0), \mathbf{r}_i(0), \dot{\mathbf{r}}_i(0)\}$, which are all Gaussian variables [Eq. (62)], it follows that $\boldsymbol{\eta}$ can be regarded as a noise term with Gaussian statistics. In practice, one readily gets that $\langle \eta_\alpha(t) \rangle = 0$, where the average is here evaluated with respect to the distribution in Eq. (62), and the correlations read

$$\begin{aligned} \langle \eta_\alpha(t)\eta_\beta(t') \rangle = \sum_{i,j=1}^{N} k_i k_j \Big\langle \Big[(x_\alpha(0) - r_{i\alpha}(0)) \cos(\omega_i t) - \dot{r}_{i\alpha}(0) \sin(\omega_i t)/\omega_i \Big] \\ \times \Big[(x_\beta(0) - r_{j\beta}(0)) \cos(\omega_j t') - \dot{r}_{j\beta}(0) \sin(\omega_j t')/\omega_j \Big] \Big\rangle. \end{aligned} \tag{63}$$

Using the following results

$$\begin{aligned} k_i k_j \langle (x_\alpha(0) - r_{i\alpha}(0))(x_\beta(0) - r_{j\beta}(0)) \rangle &= \delta_{ij}\delta_{\alpha\beta} k_i T, \\ (k_i k_j/\omega_i\omega_j) \langle \dot{r}_{i\alpha}(0) \dot{r}_{j\beta}(0)) \rangle &= \delta_{ij}\delta_{\alpha\beta} k_i T, \\ \langle \dot{r}_{i\alpha}(0)(x_\beta(0) - r_{j\beta}(0)) \rangle &= 0, \end{aligned} \tag{64}$$

we deduce

$$\langle \eta_\alpha(t)\eta_\beta(t') \rangle = T\delta_{\alpha\beta} \sum_{i=1}^{N} k_i \Big[\cos(\omega_i t)\cos(\omega_i t') + \sin(\omega_i t)\sin(\omega_i t') \Big] = T\delta_{\alpha\beta} \sum_{i=1}^{N} k_i \cos(\omega_i (t - t')). \tag{65}$$

We identify in Eq. (65) the expression of the memory kernel K [Eq. (60)], so that we can now express the tracer dynamics in a closed form:

$$\boxed{m\ddot{\mathbf{x}} = -\nabla U - \int_0^t \dot{\mathbf{x}}(t') K(t - t') dt' + \boldsymbol{\eta}, \quad \langle \eta_\alpha(t)\eta_\beta(0) \rangle = T\delta_{\alpha\beta} K(|t|).} \tag{66}$$

The dynamics in Eq. (66) is known as the *generalized Langevin equation* in its underdamped version. As in the original underdamped Langevin equation [Eq. (2)], the noise correlations are directly related to the features of the damping force: this is another version of the fluctuation-dissipation theorem [Eq. (16)]. Although the original dynamics for tracer and bath particles [Eq. (57)] is Markovian, this is no longer true for the tracer dynamics in Eq. (66), since the noise does not have instantaneous correlations. Therefore, there is not any simple Fokker-Planck equation associated with the generalized Langevin equation.

4 Path probability and linear response theory

In this Section, we introduce a description of stochastic dynamics, equivalent to the Langevin equation [Sec. 1] and the Fokker-Planck equation [Sec. 2], in terms of the path probability of trajectories. We examine how this tool can be applied to predict the response of the system to a weak perturbation.

4.1 Onsager-Machlup action

We want to obtain a representation of stochastic dynamics in terms of the probability to observe a given trajectory. To this end, we consider the version of the overdamped Langevin equation [Eq. (9)] with discrete time $t_n = n\Delta t$. As detailed in Sec. 2.3, the position displacement then reads

$$\mathbf{x}_{n+1} - \mathbf{x}_n = -\frac{1}{\gamma}\Big[\Delta t \nabla U((1-a)\mathbf{x}_n + a\mathbf{x}_{n+1}) + \sqrt{\Delta t}\boldsymbol{\eta}_n\Big] + o(\Delta t), \quad \langle \eta_{n\alpha}\eta_{m\beta}\rangle = 2\gamma T\delta_{\alpha\beta}\delta_{nm}, \tag{67}$$

where $0 < a < 1$ distinguishes various conventions of time discretisation. For an additive Langevin equation, such a convention does not affect the form of the corresponding Fokker-Planck equation [Eq. (43)], yet it changes the probability of trajectories, as detailed below.

We denote by $P(\mathbf{x}_{n+1}|\mathbf{x}_n)$ the probability to observe the position $\mathbf{x}_{n+1}$ at time t_{n+1} given that it was $\mathbf{x}_n$ at time t_n. It is related to the probability $P(\boldsymbol{\eta}_n)$ to observe the noise realization $\boldsymbol{\eta}_n$ at time t_n:

$$P(\mathbf{x}_{n+1}|\mathbf{x}_n)d\mathbf{x}_{n+1} = P(\boldsymbol{\eta}_n)d\boldsymbol{\eta}_n. \tag{68}$$

From the discretized dynamics [Eq. (67)], we evaluate the Jacobian as

$$\begin{aligned} d\eta_{n,\alpha}/dx_{n+1,\beta} &= \delta_{\alpha\beta}(\gamma/\sqrt{\Delta t})\Big[1 + (a\Delta t/\gamma)(d/dx_\alpha)^2 U + o(\Delta t)\Big] \\ &= (\gamma/\sqrt{\Delta t})\exp\Big[\delta_{\alpha\beta}(a\Delta t/\gamma)(d/dx_\alpha)^2 U + o(\Delta t)\Big]. \end{aligned} \tag{69}$$

Given that the noise has Gaussian statistics: $P(\boldsymbol{\eta}_n) \sim \exp(-\boldsymbol{\eta}_n^2/(4\gamma T))$, we then deduce

$$P(\mathbf{x}_{n+1}|\mathbf{x}_n) \sim \exp\Big[-\frac{\Delta t}{4\gamma T}\Big(\gamma\frac{\mathbf{x}_{n+1}-\mathbf{x}_n}{\Delta t} + \nabla U\Big)^2 + \frac{a\Delta t}{\gamma}\nabla^2 U + o(\Delta t)\Big]. \tag{70}$$

Finally, using the Chapman-Kolmogorov relation [Eq. (26)] given by

$$P(\mathbf{x}_{n+1}|\mathbf{x}_0) = \int d\mathbf{x}_1 P(\mathbf{x}_{n+1}|\mathbf{x}_1)P(\mathbf{x}_1|\mathbf{x}_0) = \int \prod_{i=0}^{n} d\mathbf{x}_i P(\mathbf{x}_{i+1}|\mathbf{x}_i), \tag{71}$$

we obtain the expression of the *path probability* $\mathcal{P}[\mathbf{x}] = \lim_{\Delta t\to 0} P(\mathbf{x}_n|\mathbf{x}_0)$ as:

$$\boxed{\mathcal{P}[\mathbf{x}] = \int_{\mathbf{x}(0)=\mathbf{x}_0}^{\mathbf{x}(t)=\mathbf{x}_n} \mathcal{N}\exp(-\mathcal{S}[\mathbf{x}])\mathcal{D}\mathbf{x}, \quad \mathcal{S}[\mathbf{x}] = \int_0^t dt'\Big[\frac{1}{4\gamma T}(\gamma\dot{\mathbf{x}} + \nabla U)^2 - \frac{a}{\gamma}\nabla^2 U\Big],} \tag{72}$$

where the normalization factor $\mathcal{N}$ ensures that $\int d\mathbf{x}_n P(\mathbf{x}_n|\mathbf{x}_0) = 1$. The functional $\mathcal{S}[\mathbf{x}]$ is called the *Onsager-Machlup action*, and it depends on the whole trajectory of position. This action contains the same information about the trajectory statistics as the overdamped Langevin equation [Eq. (9)], and depends explicitly on the discretization convention.

4.2 Time-reversal symmetry

We want to characterize the time-reversal symmetry of stochastic dynamics. To this end, we consider the time-reversal operation applied on a given trajectory $[\mathbf{x}]$, going from time $t' = 0$ to $t' = t$. Considering an arbitrary function $f(\mathbf{x}(t), \dot{\mathbf{x}}(t))$, this operation is defined as

$$t' \to t - t', \quad f(\mathbf{x}(t'), \dot{\mathbf{x}}(t')) \to f(\mathbf{x}(t-t'), -\dot{\mathbf{x}}(t-t')). \tag{73}$$

To compare the path probabilities for the forward and reversed trajectories, we evaluate the Onsager-Machlup actions [Eq. (72)] with Stratonovitch convention ($a = 1/2$). Indeed, this choice

ensures that the forward and reversed trajectories are compared for the same set of time-points in the discretized version of the dynamics. Applying the time-reversal operation [Eq. (73)] to Eq. (72), we get

$$\mathcal{S}[\mathbf{x}_R] = \int_0^t dt' \left[\frac{1}{4\gamma T}(-\gamma\dot{\mathbf{x}} + \nabla U)^2 - \frac{1}{2\gamma}\nabla^2 U \right], \tag{74}$$

where we have changed variable as $t' \to t - t'$, from which we deduce

$$\mathcal{S}[\mathbf{x}] - \mathcal{S}[\mathbf{x}_R] = \frac{1}{T}\int_0^t dt' \dot{\mathbf{x}} \cdot \nabla U = \frac{U(\mathbf{x}(t)) - U(\mathbf{x}(0))}{T}, \tag{75}$$

where we have used the chain rule $\dot{U} = \dot{\mathbf{x}} \cdot \nabla U$ within Stratonovitch convention [see Sec. 2.4].

Considering some arbitrary functions $f(\mathbf{x}(t))$ and $g(\mathbf{x}(t))$, we evaluate the following correlation:

$$\langle f(\mathbf{x}(t_1))g(\mathbf{x}(t_2))\rangle = \int d\mathbf{x}_n d\mathbf{x}_0 P_s(\mathbf{x}_0) \int_{\mathbf{x}(0)=\mathbf{x}_0}^{\mathbf{x}(t)=\mathbf{x}_n} \mathcal{N} \exp(-\mathcal{S}[\mathbf{x}]) f(\mathbf{x}(t_1))g(\mathbf{x}(t_2))\mathcal{D}\mathbf{x}, \tag{76}$$

where P_s denotes the steady-state probability distribution, assuming that the system is initially fully relaxed. Introducing the change of path associated with time reversal [Eq. (73)], we get

$$\begin{aligned}
&\langle f(\mathbf{x}(t_1))g(\mathbf{x}(t_2))\rangle \\
&= \int d\mathbf{x}_n d\mathbf{x}_0 P_s(\mathbf{x}_0) \int_{\mathbf{x}(0)=\mathbf{x}_n}^{\mathbf{x}(t)=\mathbf{x}_0} \mathcal{N} \exp\left[-\mathcal{S}[\mathbf{x}] + \frac{U(\mathbf{x}(t)) - U(\mathbf{x}(0))}{T} \right] f(\mathbf{x}(t-t_1))g(\mathbf{x}(t-t_2))\mathcal{D}\mathbf{x} \\
&= \int d\mathbf{x}_n d\mathbf{x}_0 P_s(\mathbf{x}_n) \int_{\mathbf{x}(0)=\mathbf{x}_n}^{\mathbf{x}(t)=\mathbf{x}_0} \mathcal{N} \exp(-\mathcal{S}[\mathbf{x}]) f(\mathbf{x}(t-t_1))g(\mathbf{x}(t-t_2))\mathcal{D}\mathbf{x} \\
&= \langle f(\mathbf{x}(t-t_1))g(\mathbf{x}(t-t_2))\rangle,
\end{aligned} \tag{77}$$

where we have used Eq. (75) in the first line, and $P_s \sim \exp(-U/T)$ in the second line. With a similar series of steps, one can also show: $\langle f(\mathbf{x}(t_1))g(\mathbf{x}(t_2))\dot{\mathbf{x}}(t_2)\rangle = -\langle f(\mathbf{x}(t-t_1))g(\mathbf{x}(t-t_2))\dot{\mathbf{x}}(t-t_2)\rangle$. Choosing $t_1 = t$ and $t_2 = 0$, we finally deduce the *Onsager reciprocal relations*:

$$\boxed{\langle f(\mathbf{x}(t))g(\mathbf{x}(0))\rangle = \langle f(\mathbf{x}(0))g(\mathbf{x}(t))\rangle, \quad \langle f(\mathbf{x}(t))g(\mathbf{x}(0))\dot{\mathbf{x}}(0)\rangle = -\langle f(\mathbf{x}(0))g(\mathbf{x}(t))\dot{\mathbf{x}}(t)\rangle.} \tag{78}$$

Such relations are the essential property of equilibrium dynamics. They state that, in steady state, one cannot distinguish the statistics of trajectories running either forward or reversed in time.

4.3 Linear response theory

We want to evaluate the effect of a weak perturbation on the overdamped Langevin dynamics [Eq. (9)]. To this end, we consider the perturbation $U(\mathbf{x}) \to U(\mathbf{x}) - h(t)g(\mathbf{x})$, and we introduce the linear response function R as

$$\langle f(\mathbf{x}(t))\rangle = \int_0^t dt' h(t')R(t-t') + o(h), \tag{79}$$

where we have assumed that $\langle f(\mathbf{x})\rangle$ vanishes in the unperturbed dynamics. Equivalently, one can define the response using the functional derivative:

$$R(t) = \left. \frac{\delta\langle f(\mathbf{x}(t))\rangle}{\delta h(0)} \right|_{h\to 0}, \tag{80}$$

where we have used the property $\delta h(t)/\delta h(0) = \delta(t)$. We express the average in the lhs of Eq. (79) in terms of the path probability:

$$\langle f(\mathbf{x}(t))\rangle = \int d\mathbf{x} d\mathbf{x}_0 P_s(\mathbf{x}_0) \int_{\mathbf{x}(0)=\mathbf{x}_0}^{\mathbf{x}(t)=\mathbf{x}_n} \mathcal{N} \exp(-\mathcal{S}[\mathbf{x}]) f(\mathbf{x}(t))\mathcal{D}\mathbf{x}, \tag{81}$$

yielding

$$R(t) = \int d\mathbf{x}_n d\mathbf{x}_0 P_s(\mathbf{x}_0) \int_{\mathbf{x}(0)=\mathbf{x}_0}^{\mathbf{x}(t)=\mathbf{x}_n} \mathcal{N} \frac{\delta}{\delta h(0)} \Big[\exp(-\mathcal{S}[\mathbf{x}])\mathbf{x} \Big]_{h\to 0} f(\mathbf{x}(t))\mathcal{D}, \tag{82}$$

where we have assumed that $\mathcal{N}$ is independent of the perturbation h, consistently with $\langle f(\mathbf{x})\rangle_{h=0} = 0$. We evaluate the functional derivative in Eq. (82) as

$$\begin{aligned}\frac{\delta}{\delta h(0)}\Big[\exp(-\mathcal{S}[\mathbf{x}])\Big]_{h\to 0} &= -\exp(-\mathcal{S}[\mathbf{x}])\int_0^t dt' \frac{\delta}{\delta h(0)}\left[\frac{1}{4\gamma T}(\gamma\dot{\mathbf{x}}+\nabla(U-h(t)g))^2 - \frac{1}{2\gamma}\nabla^2(U-h(t)g)\right]_{h\to 0} \\ &= \frac{\exp(-\mathcal{S}[\mathbf{x}])}{2\gamma}\left[\frac{1}{T}\nabla g(\mathbf{x}(0))\cdot(\gamma\dot{\mathbf{x}}(0)+\nabla U(\mathbf{x}(0))) - (\nabla^2 g\nabla^2 U)(\mathbf{x}(0))\right].\end{aligned} \tag{83}$$

Substituting Eq. (83) in Eq. (82), we deduce

$$R(t) = \frac{1}{2\gamma T}\langle f(\mathbf{x}(t))\nabla g(\mathbf{x}(0))\cdot(\gamma\dot{\mathbf{x}}(0)+\nabla U(\mathbf{x}(0)))\rangle - \frac{1}{2\gamma}\langle f(\mathbf{x}(t))(\nabla^2 g\nabla^2 U)(\mathbf{x}(0))\rangle. \tag{84}$$

To simplify further the expression of the response, we consider the time-symmetrised version:

$$\begin{aligned}R(t)-R(-t) = &\frac{1}{2T}\langle f(\mathbf{x}(t))\nabla g(\mathbf{x}(0))\cdot\dot{\mathbf{x}}(0) - f(\mathbf{x}(-t))\nabla g(\mathbf{x}(0))\cdot\dot{\mathbf{x}}(0)\rangle \\ &+\frac{1}{2\gamma T}\langle f(\mathbf{x}(t))(\nabla g\cdot\nabla U)(\mathbf{x}(0)) - f(\mathbf{x}(-t))(\nabla g\cdot\nabla U)(\mathbf{x}(0))\rangle \\ &-\frac{1}{2\gamma}\langle f(\mathbf{x}(t))(\nabla^2 g\nabla^2 U)(\mathbf{x}(0)) - f(\mathbf{x}(-t))(\nabla^2 g\nabla^2 U)(\mathbf{x}(0))\rangle.\end{aligned} \tag{85}$$

Using the time-translational invariance: $\langle f(\mathbf{x}(t_1))g(\mathbf{x}(t_2))\rangle = \langle f(\mathbf{x}(t_1-t_2))g(\mathbf{x}(0))\rangle$, and Onsager reciprocal relations [Eq. (78)], we then deduce

$$R(t)-R(-t) = \frac{1}{T}\langle f(\mathbf{x}(t))\nabla g(\mathbf{x}(0))\cdot\dot{\mathbf{x}}(0)\rangle = -\frac{1}{T}\frac{d}{dt}\langle f(\mathbf{x}(t))g(\mathbf{x}(0))\rangle. \tag{86}$$

Causality enforces that $R(t) = 0$ for $t < 0$, from which we finally get

$$\boxed{R(t) = -\frac{H(t)}{T}\frac{d}{dt}\langle f(\mathbf{x}(t))g(\mathbf{x}(0))\rangle,} \tag{87}$$

where H is the Heaviside function, defined such that $H(t) = 1$ for $t > 0$, and $H(t) = 0$ for $t < 0$. The relation between response and correlation functions in Eq. (87) is another version of the *fluctuation-dissipation theorem*. It states that the response to an external perturbation is encoded in the correlations of unperturbed dynamics. Importantly, the correlation of interest here only involves the perturbation (g) and the response observable (f): one can measure this correlation without knowing the expression of the potential U.

5 Stochastic thermodynamics

The aim of this Section is to introduce the definition of some energetic quantities, specifically heat and work, associated with stochastic dynamics. Importantly, we show that the time-reversal invariance of equilibrium dynamics enforces a specific symmetry on the distribution of these quantities.

5.1 Heat and work

We consider an overdamped Langevin equation [Eq. (9)] where the potential $U(\mathbf{x}(t), \alpha(t))$ now depends on a control parameter α, which can be varied in time by an external operator, and the non-conservative force $\mathbf{F}$ is applied to the colloid:

$$\gamma\dot{\mathbf{x}} = -\partial_{\mathbf{x}}U + \mathbf{F} + \boldsymbol{\eta}, \quad \langle \eta_\alpha(t)\eta_\beta(0)\rangle = 2\gamma T\delta_{\alpha\beta}\delta(t). \tag{88}$$

The dynamics can be driven out of equilibrium by two factors: (i) changing the control parameter α in time, and/or (ii) applying the non-conservative force. The Onsager-Machlup actions associated with the dynamics in Eq. (88), for the forward $\mathcal{S}[\mathbf{x}]$ and reversed $\mathcal{S}[\mathbf{x}_R]$ trajectories [Eq. (73)], read

$$\begin{aligned}\mathcal{S}[\mathbf{x}] &= \int_0^t dt' \left[\frac{1}{4\gamma T}(\gamma\dot{\mathbf{x}} + \partial_{\mathbf{x}}U - \mathbf{F})^2 - \frac{1}{2\gamma}\nabla^2 U\right],\\ \mathcal{S}[\mathbf{x}_R] &= \int_0^t dt' \left[\frac{1}{4\gamma T}(-\gamma\dot{\mathbf{x}} + \partial_{\mathbf{x}}U - \mathbf{F})^2 - \frac{1}{2\gamma}\nabla^2 U\right].\end{aligned} \tag{89}$$

The stochastic heat $\mathcal{Q}$ is defined as a work applied by the colloid on the surrounding thermostat. Given that the thermostat exerts the damping force $-\gamma\dot{\mathbf{x}}$ and the noise $\boldsymbol{\eta}$ on the colloid, the heat follows as

$$\mathcal{Q} = \int_0^t \dot{\mathbf{x}} \cdot (\gamma\dot{\mathbf{x}} - \boldsymbol{\eta})dt', \tag{90}$$

where we have used Stratonovitch convention [see Sec. 2.4]. Substituting the dynamics [Eq. (88)] in this definition of heat, we get

$$\mathcal{Q} = \int_0^t \dot{\mathbf{x}} \cdot (-\partial_{\mathbf{x}}U + \mathbf{F})dt'. \tag{91}$$

When the control parameter α is constant, the first term in Eq. (91) vanishes on average, since $\langle \dot{\mathbf{x}} \cdot \nabla U\rangle = \langle \dot{U}\rangle = 0$, so that the average heat coincides with the power of the non-conservative force: $\langle \mathcal{Q}\rangle = \int_0^t dt' \langle \dot{\mathbf{x}} \cdot \mathbf{F}\rangle$, as expected from standard thermodynamics. In the absence of $\mathbf{F}$, we recover that the average heat is zero: the work provided by the noise $\boldsymbol{\eta}$ is exactly compensated by the one dissipated by the damping force $-\gamma\dot{\mathbf{x}}$.

Interestingly, evaluating the action difference from Eq. (89), it appears that the expression in Eq. (91) can be connected to the time-reversal symmetry breakdown of the nonequilibrium dynamics as

$$\mathcal{Q} = T(\mathcal{S}[\mathbf{x}_R] - \mathcal{S}[\mathbf{x}]) = T\ln\left(\mathcal{P}[\mathbf{x}]/\mathcal{P}[\mathbf{x}_R]\right). \tag{92}$$

The expression in Eq. (92) illustrates that the heat coincides the *Kullback-Leibler divergence* between the forward $\mathcal{P}[\mathbf{x}]$ and reversed $\mathcal{P}[\mathbf{x}_R]$ path probabilities [Eq. (72)]. In particular, it enforces that the average heat $\langle \mathcal{Q}\rangle = \int d\mathbf{x}_0 d\mathbf{x}_n P_s(\mathbf{x}_0)\mathcal{P}[\mathbf{x}]\ln(\mathcal{P}[\mathbf{x}]/\mathcal{P}[\mathbf{x}_R])$ is always positive.

When α varies in time, the stochastic work associated with such a protocol is defined in terms of the change of the potential energy U induced by the perturbation:

$$\mathcal{W} = \int_0^t (\dot{\alpha}\partial_\alpha U + \dot{\mathbf{x}} \cdot \mathbf{F})dt'. \tag{93}$$

Using the chain rule, valid for Stratonovitch convention [see Sec. 2.4], to express the variation of potential energy ΔU as

$$\Delta U = \int_0^t dt'\dot{U} = \int_0^t dt'(\dot{\mathbf{x}} \cdot \partial_{\mathbf{x}} + \dot{\alpha}\partial_\alpha)U, \tag{94}$$

we readily deduce the *first law of thermodynamics*:

$$\boxed{\Delta U = U(\mathbf{x}(t),\alpha(t)) - U(\mathbf{x}(0),\alpha(0)) = \mathcal{W} - \mathcal{Q}.} \tag{95}$$

Importantly, Eq. (95) enforces that change of potential energy can be separated into work and heat contributions for each trajectory, namely at a stochastic level. Averaging over noise realizations, we recover the usual first law of thermodynamics.

For a quasistatic protocol, the operator drives the parameter α so slowly that the system effectively goes through a series of steady states. In such a case, the averaged work [Eq. (93)] can be written as

$$\langle \mathcal{W} \rangle_{qs} = \int_0^t \dot{\alpha}(t') \langle \partial_\alpha U \rangle_s dt' = \int_{\alpha(0)}^{\alpha(t)} \langle \partial_\alpha U \rangle_s d\alpha. \tag{96}$$

In the absence of non-conservative force, the steady-state average can be written in terms of the free energy F as

$$\langle \partial_\alpha U \rangle_s = \frac{\int d\mathbf{x} \exp(-U/T) \partial_\alpha U}{\int d\mathbf{x}' \exp(-U/T)} = \frac{dF}{d\alpha}, \quad F = -T \ln \left[\int d\mathbf{x} \exp(-U/T) \right], \tag{97}$$

yielding

$$\langle \mathcal{W} \rangle_{qs} = F(\alpha(t)) - F(\alpha(0)) = \Delta F. \tag{98}$$

The averaged work only depends on the initial and final points of the protocol for a quasistatic protocol, it is independent of the whole trajectory $\alpha(t)$ between these points. When driving the parameter α not so slowly, the averaged work now explicitly depends on the details of the trajectory [see TD5].

5.2 Fluctuation theorems

We want to characterize the distribution of heat and work. Let us first consider the case where $\dot{\alpha} = 0$, such that $\mathcal{W} = 0$, for which the difference of actions [Eq. (89)] reads

$$\mathcal{S}[\mathbf{x}] - \mathcal{S}[\mathbf{x}_R] = \frac{1}{T} \int_0^t dt' \dot{\mathbf{x}} \cdot (\nabla U - \mathbf{F}) = \frac{\Delta U}{T} - \frac{1}{T} \int_0^t dt' \dot{\mathbf{x}} \cdot \mathbf{F}. \tag{99}$$

We evaluate the distribution of heat [Eq. (91)] as

$$P(\mathcal{Q}) = \int d\mathbf{x}_n d\mathbf{x}_0 P_s(\mathbf{x}_0) \int_{\mathbf{x}(0)=\mathbf{x}_0}^{\mathbf{x}(t)=\mathbf{x}_n} \mathcal{N} \exp(-\mathcal{S}[\mathbf{x}]) \, \delta\left(\mathcal{Q} - \int_0^t dt' \dot{\mathbf{x}} \cdot \mathbf{F} \right) \mathcal{D}\mathbf{x}. \tag{100}$$

Introducing the change of path corresponding to time reversal [Eq. (73)], we get

$$\begin{aligned} P(\mathcal{Q}) &= \int d\mathbf{x}_n d\mathbf{x}_0 P_s(\mathbf{x}_0) \int_{\mathbf{x}(0)=\mathbf{x}_n}^{\mathbf{x}(t)=\mathbf{x}_0} \mathcal{N} \exp\left(-\mathcal{S}[\mathbf{x}] + \frac{\Delta U}{T} - \frac{1}{T} \int_0^t dt' \dot{\mathbf{x}} \cdot \mathbf{F} \right) \\ &\quad \times \delta\left(\mathcal{Q} + \int_0^t dt' \dot{\mathbf{x}} \cdot \mathbf{F} \right) \mathcal{D}\mathbf{x}. \\ &= \int d\mathbf{x}_n d\mathbf{x}_0 P_s(\mathbf{x}_n) \int_{\mathbf{x}(0)=\mathbf{x}_n}^{\mathbf{x}(t)=\mathbf{x}_0} \mathcal{N} \exp\left(-\mathcal{S}[\mathbf{x}] + \frac{\mathcal{Q}}{T} \right) \delta\left(\mathcal{Q} + \int_0^t dt' \dot{\mathbf{x}} \cdot \mathbf{F} \right) \mathcal{D}\mathbf{x}. \end{aligned} \tag{101}$$

where we have used Eq. (99) and $P_s \sim e^{-U/T}$, yielding the *fluctuation theorem*:

$$\boxed{P(\mathcal{Q}) = P(-\mathcal{Q}) \exp(\mathcal{Q}/T)}. \tag{102}$$

This result straightforwardly extends to the case $\dot{\alpha} \neq 0$. Integrating Eq. (102) with respect to $\mathcal{Q}$, and using the change of variable $\mathcal{Q} \to -\mathcal{Q}$ in the rhs, we readily deduce the *integral fluctuation theorem*:

$$1 = \langle \exp(-\mathcal{Q}/T) \rangle. \tag{103}$$

Finally, using Jensen's inequality, which states that $\langle f(\mathcal{Q})\rangle > f(\langle\mathcal{Q}\rangle)$ for any convex function f, we obtain the *second law of thermodynamics*:

$$\langle\mathcal{Q}\rangle \geq 0. \tag{104}$$

The fluctuation theorem [Eq. (102)] should be regarded as a consequence of the statistical invariance of the equilibrium dynamics under time-reversal. Such an invariance enforces a specific symmetry on the distribution of heat in the presence of a non-conservative force. Specifically, observing a given realisation $\mathcal{Q}$ is exponentially more probable than observing its negative counterpart $-\mathcal{Q}$. In particular, although negative heat values are possible, they are much rarer than their positive counterparts.

Let us now consider the case where $\mathbf{F} = \mathbf{0}$, for which the difference of actions [Eq. (89)] reads

$$\mathcal{S}[\mathbf{x}] - \mathcal{S}[\mathbf{x}_R] = \frac{1}{T}\int_0^t dt'\dot{\mathbf{x}}\cdot\partial_{\mathbf{x}}U = \frac{\Delta U}{T} - \frac{1}{T}\int_0^t dt'\dot{\alpha}\partial_\alpha U. \tag{105}$$

We evaluate the distribution of work [Eq. (93)] as

$$P(\mathcal{W}) = \int d\mathbf{x}_n d\mathbf{x}_0 P_s(\mathbf{x}_0,\alpha(0))\int_{\mathbf{x}(0)=\mathbf{x}_0}^{\mathbf{x}(t)=\mathbf{x}_n}\mathcal{N}\exp(-\mathcal{S}[\mathbf{x}])\,\delta\Big(\mathcal{W} - \int_0^t dt'\dot{\alpha}\partial_\alpha U\Big)\mathcal{D}\mathbf{x}. \tag{106}$$

Introducing the change of path corresponding to time reversal [Eq. (73)] complemented with $f(\alpha(t'),\dot{\alpha}(t')) \to f(\alpha(t-t'),-\dot{\alpha}(t-t'))$ for an arbitrary function f, we get

$$\begin{aligned} P(\mathcal{W}) &= \int d\mathbf{x}_n d\mathbf{x}_0 P_s(\mathbf{x}_0,\alpha(0))\int_{\mathbf{x}(0)=\mathbf{x}_n}^{\mathbf{x}(t)=\mathbf{x}_0}\mathcal{N}\exp\Big(-\mathcal{S}[\mathbf{x}] + \frac{\Delta U}{T} - \frac{1}{T}\int_0^t dt'\dot{\alpha}\partial_\alpha U\Big) \\ &\quad\times\delta\Big(\mathcal{W} + \int_0^t dt'\dot{\alpha}\partial_\alpha U\Big)\mathcal{D}\mathbf{x} \\ &= \int d\mathbf{x}_n d\mathbf{x}_0 P_s(\mathbf{x}_n,\alpha(t))\int_{\mathbf{x}(0)=\mathbf{x}_n}^{\mathbf{x}(t)=\mathbf{x}_0}\mathcal{N}\exp\Big(-\mathcal{S}[\mathbf{x}] + \frac{\Delta F+\mathcal{W}}{T}\Big)\delta\Big(\mathcal{W} + \int_0^t dt'\dot{\alpha}\partial_\alpha U\Big)\mathcal{D}\mathbf{x}, \end{aligned} \tag{107}$$

where we have used Eq. (105) and $P_s = e^{-(U-F)/T}$, yielding *Crook's theorem*:

$$\boxed{P(\mathcal{W})\exp(-\Delta F/T) = P(-\mathcal{W})\exp(\mathcal{W}/T).} \tag{108}$$

This result straightforwardly extends to the case $\mathbf{F} \neq \mathbf{0}$. Integrating Eq. (108) with respect to $\mathcal{W}$, and using the change of variable $\mathcal{W} \to -\mathcal{W}$ in the rhs, we obtain *Jarzynski's equality*:

$$\exp(-\Delta F/T) = \langle\exp(-\mathcal{W}/T)\rangle. \tag{109}$$

Finally, using Jensen's inequality leads to the *minimum work theorem*:

$$\langle\mathcal{W}\rangle \geq \Delta F. \tag{110}$$

Crook's theorem [Eq. (108)] is yet another consequence of the statistical time-reversal invariance of the equilibrium dynamics. Importantly, this theorem can be used to provide an indirect estimation of the free-energy difference ΔF from the distribution of work.

6 Self-propelled particles as active matter

In this Section, we discuss how to model the dynamics of active particles subject to an autonomous self-propelled motion. We derive the position statistics in simple cases, and discuss the differences with respect to the case of a passive Brownian particle [Sec. 1].

6.1 Modelling self-propulsion

We consider the dynamics of a self-propelled particle able to convert some energy resource into directed motion. To this end, we complement the overdamped Langevin equation [Eq. (9)] with the active force $\mathbf{F}_a$ which embodies the self-propulsion mechanism:

$$\gamma\dot{\mathbf{x}} = -\nabla U + \boldsymbol{\eta} + \mathbf{F}_a, \quad \langle \eta_\alpha(t)\eta_\beta(0)\rangle = 2\gamma T\delta_{\alpha\beta}\delta(t). \tag{111}$$

We first consider a model of *active Brownian particle* (ABP) in two dimensions, for which the active force $\mathbf{F}_a$ has a fixed amplitude and an orientation determined by the angle θ as

$$\mathbf{F}_a = \gamma v_0(\cos\theta, \sin\theta), \quad \dot{\theta} = \xi, \quad \langle \xi(t)\xi(0)\rangle = (2/\tau)\delta(t), \tag{112}$$

where v_0 is the velocity of self-propulsion, and τ is the persistence time. The angle θ follows a free diffusion, determined by the Gaussian noise ξ which has zero mean, and is uncorrelated with $\boldsymbol{\eta}$. The Gaussian statistics of θ follows the distribution $P(\theta,t) \sim \exp[-(\theta-\theta(0))^2/(2\mathrm{Var}_\theta(t))]$, where the variance $\mathrm{Var}_\theta(t) = \langle[\theta(t)-\theta(0)]^2\rangle$ can be computed by integrating Eq. (112) as

$$\mathrm{Var}_\theta(t) = \frac{2}{\tau}\int_0^t dt_1 \int_0^t dt_2 \langle \xi(t_1)\xi(t_2)\rangle = \frac{2t}{\tau}. \tag{113}$$

The correlations of the active force $\mathbf{F}_a$ are given by

$$\begin{aligned}\langle \mathbf{F}_a(t)\cdot\mathbf{F}_a(0)\rangle &= (\gamma v_0)^2\langle \cos(\theta(t))\cos(\theta(0)) + \sin(\theta(t))\sin(\theta(0))\rangle \\ &= (\gamma v_0)^2\langle \cos(\theta(t)-\theta(0))\rangle \\ &= (\gamma v_0)^2\int d\theta\cos(\theta(t)-\theta(0))P(\theta,t) = (\gamma v_0)^2\exp(-|t|/\tau).\end{aligned} \tag{114}$$

The persistence time τ coincides with the correlation time of the active force. It quantifies the typical time during which the direction of the active force stays constant. As the persistence time gets smaller, the correlation of the active force $\mathbf{F}_a$ gets closer to that of a white noise, analogous to the thermal noise $\boldsymbol{\eta}$ [Eq. (111)]. Yet, $\mathbf{F}_a$ has non-Gaussian statistics, since it is a nonlinear function of the Gaussian variable θ.

To consider a proper equilibrium limit of dynamics, we introduce an alternative model of an *active Ornstein-Uhlenbeck particle* (AOUP). We now enforce that the active force $\mathbf{F}_a$ has Gaussian statistics with correlations given by

$$\boxed{\langle F_{a\alpha}(t)F_{a\beta}(t)\rangle = \frac{\gamma T_a}{\tau}\delta_{\alpha\beta}\exp(-|t|/\tau) \underset{\tau\to 0}{\longrightarrow} 2\gamma T_a\delta_{\alpha\beta}\delta(t),} \tag{115}$$

where $T_a = \gamma\tau v_0^2$ is the active temperature. This is equivalent to enforcing that $\mathbf{F}_a$ obeys the following dynamics, given in terms of the zero-mean Gaussian noise $\boldsymbol{\eta}_a$ as

$$\tau\dot{\mathbf{F}}_a = -\mathbf{F}_a + \boldsymbol{\eta}_a, \quad \langle \eta_{a\alpha}(t)\eta_{a\beta}(0)\rangle = 2\gamma T_a\delta_{\alpha\beta}\delta(t). \tag{116}$$

Using that the thermal noise $\boldsymbol{\eta}$ and the active force $\mathbf{F}_a$ are uncorrelated, we get

$$\langle (F_{a\alpha}+\eta_\alpha)(t)(F_{a\beta}+\eta_\beta)(t)\rangle = \langle F_{a\alpha}(t)F_{a\beta}\rangle + \langle \eta_\alpha(t)\eta_\beta(t)\rangle \underset{\tau\to 0}{\longrightarrow} 2\gamma(T+T_a)\delta_{\alpha\beta}\delta(t). \tag{117}$$

At vanishing persistence, the dynamics in Eq. (111) then reduces to a passive Brownian particle at temperature $T + T_a$.

6.2 Position statistics

We consider the position statistics of an active particle [Eq. (111)]. In practice, we are only interested in the second moment of position, which is equivalent for ABP [Eq. (114)] and AOUP [Eq. (115)], given that both models have exponentially decaying correlations. First, in the absence of potential ($U = 0$), we evaluate the mean-squared displacement (MSD) [Eq. (17)] by integrating the dynamics in Eq. (111) as

$$\begin{aligned}
\left\langle \Delta\mathbf{x}^2(t)\right\rangle &= \left\langle \Delta\mathbf{x}^2(t)\right\rangle_p + \left\langle \Delta\mathbf{x}^2(t)\right\rangle_a, \\
\left\langle \Delta\mathbf{x}^2(t)\right\rangle_p &= \frac{1}{\gamma^2}\int_0^t dt_1 \int_0^t dt_2 \langle \boldsymbol{\eta}(t_1)\cdot\boldsymbol{\eta}(t_2)\rangle = 2dTt/\gamma, \\
\left\langle \Delta\mathbf{x}^2(t)\right\rangle_a &= \frac{1}{\gamma^2}\int_0^t dt_1 \int_0^t dt_2 \langle \mathbf{F}_a(t_1)\cdot\mathbf{F}_a(t_2)\rangle.
\end{aligned} \tag{118}$$

The MSD decomposes into some passive and active contributions, given that the thermal noise $\boldsymbol{\eta}$ and the active force $\mathbf{F}_a$ are uncorrelated. To perform the time integration in the expression of $\left\langle \Delta\mathbf{x}^2(t)\right\rangle_a$, we use the fact that the active force correlation is symmetric, and the integration domain is the same for t_1 and t_2, yielding

$$\left\langle \Delta\mathbf{x}^2(t)\right\rangle_a = \frac{2dT_a}{\gamma\tau}\int_0^t dt_1 \int_0^{t_1} dt_2 \exp(-(t_1-t_2)/\tau) = \frac{2dT_a}{\gamma}\Big[t+\tau\Big(1-\exp(-t/\tau)\Big)\Big]. \tag{119}$$

At small times ($t \ll \tau$), the active MSD has a ballistic regime depsite the absence of inertia: $\left\langle \Delta\mathbf{x}^2(t)\right\rangle_a \sim (dT_a\tau/\gamma)(t/\tau)^2$, which reflects the persistent motion of the particle. The crossover time $\bar{\tau}$ between the thermal diffusive and active ballistic regimes obeys: $\left\langle \Delta\mathbf{x}^2(\bar{\tau})\right\rangle_a = \left\langle \Delta\mathbf{x}^2(\bar{\tau})\right\rangle_p$. In practice, the active ballistic regime can be distinguished whenever $\bar{\tau} \ll \tau$, namely $T \ll T_a$, for which $\bar{\tau} \sim \tau T/T_a$. At large times ($t \gg \tau$), the MSD follows a diffusive behavior: $\left\langle \Delta\mathbf{x}^2(t)\right\rangle \sim 2d(T+T_a)t/\gamma$. In this regime, the free dynamics is equivalent to that of a passive particle at temperature $T + T_a$.

In the presence of a harmonic potential ($U = k\mathbf{x}^2/2$), we want to evaluate the position variance $\langle\mathbf{x}^2\rangle_s$ in steady state. To this end, we consider the AOUP dynamics [Eq. (116)], and we apply Itô's lemma [Eq. (56)] to the following observables:

$$\begin{aligned}
\frac{d}{dt}\frac{\langle\mathbf{x}^2\rangle}{2} &= \langle\mathbf{x}\cdot\dot{\mathbf{x}}\rangle + \frac{T}{2\gamma}\langle\nabla^2\mathbf{x}^2\rangle = \frac{1}{\gamma}\langle\mathbf{x}\cdot(-k\mathbf{x}+\mathbf{F}_a)\rangle + \frac{dT}{\gamma}, \\
\frac{d}{dt}\langle\mathbf{x}\cdot\mathbf{F}_a\rangle &= \langle\dot{\mathbf{x}}\cdot\mathbf{F}_a\rangle + \langle\mathbf{x}\cdot\dot{\mathbf{F}}_a\rangle = \frac{\langle\mathbf{F}_a^2\rangle}{\gamma} - \left(\frac{k}{\gamma}+\frac{1}{\tau}\right)\langle\mathbf{x}\cdot\mathbf{F}_a\rangle, \\
\frac{d}{dt}\frac{\langle\mathbf{F}_a^2\rangle}{2} &= \langle\mathbf{F}_a\cdot\dot{\mathbf{F}}_a\rangle + \frac{\gamma T_a}{2\tau^2}\left\langle\frac{d^2}{d\mathbf{F}_a^2}\mathbf{F}_a^2\right\rangle = -\frac{\langle\mathbf{F}_a^2\rangle}{\tau} + \frac{\gamma dT_a}{\tau^2},
\end{aligned} \tag{120}$$

where we have used that $\langle\boldsymbol{\eta}\cdot\mathbf{x}\rangle$, $\langle\boldsymbol{\eta}_a\cdot\mathbf{x}\rangle$, $\langle\boldsymbol{\eta}\cdot\mathbf{F}_a\rangle$, and $\langle\boldsymbol{\eta}_a\cdot\mathbf{F}_a\rangle$ all vanish within Itô convention. Note that there is not any contribution from noise correlations in the rhs of the second line in Eq. (120), because $\boldsymbol{\eta}$ and $\boldsymbol{\eta}_a$ are uncorrelated. In steady state, the rhs of Eq. (120) vanishes, from which we readily deduce

$$\boxed{\langle\mathbf{x}^2\rangle_s = \frac{T}{k} + \frac{T_a}{k}\frac{1}{1+\tau k/\gamma}} \tag{121}$$

At vanishing persistence ($\tau = 0$), we recover the equipartition theorem: $\langle\mathbf{x}^2\rangle_s = (T+T_a)/k$, with temperature $T + T_a$ as expected from the equilibrium limit discussed in Sec. 6.1. For arbitrary persistence, there is a clear deviation from equipartition theorem, as a signature of the nonequilibrium nature of the dynamics.

7 Effective potential and irreversibility in active matter

The aim of this Section is to demonstrate that we can derive analytically the stationary distribution and the breakdown of time-reversal symmetry of active particles. Such results allow us to pinpoint the deviation from equilibrium, and the emergence of effective attraction.

7.1 Effective potential

We want to derive the steady-state statistics of active particles [Eq. (111)] for an arbitrary potential U. To this end, we consider the model of AOUP [Eq. (115)] in the limit of negligible thermal noise ($T \ll T_a$). The dynamics then reads

$$\gamma\dot{\mathbf{x}} = -\nabla U + \mathbf{F}_a, \quad \tau\dot{\mathbf{F}}_a = -\mathbf{F}_a + \boldsymbol{\eta}_a, \quad \langle \eta_{a\alpha}(t)\eta_{a\beta}(0)\rangle = 2\gamma T_a \delta_{\alpha\beta}\delta(t). \tag{122}$$

We can express the dynamics in terms of the velocity $\mathbf{v} = \dot{\mathbf{x}}$ as

$$\begin{aligned}\gamma\tau\dot{\mathbf{v}} &= \tau(-(\dot{\mathbf{x}}\cdot\nabla)\nabla U + \dot{\mathbf{F}}_a)\\ &= -\tau(\mathbf{v}\cdot\nabla)\nabla U - \mathbf{F}_a + \boldsymbol{\eta}_a\\ &= -\gamma\mathbf{v} - \tau(\mathbf{v}\cdot\nabla)\nabla U - \nabla U + \boldsymbol{\eta}_a,\end{aligned} \tag{123}$$

where we have used Stratonovitch convention, for which the standard chain rule $\dot{U} = \dot{\mathbf{x}}\cdot\nabla U$ applies [see Sec. 2.4]. At vanishing persistence ($\tau = 0$), we recover the overdamped Langevin equation [Eq. (9)]; as expected, it corresponds to the equilibrium limit of a passive Brownian particle at temperature T_a, with steady-state distribution $P_s \sim \exp(-U/T_a)$ [see Sec. 6.1]. At finite persistence ($\tau \neq 0$), neglecting the term $\tau(\mathbf{v}\cdot\nabla)\nabla U$ in the rhs of Eq. (123) leads to the underdamped Langevin equation [Eq. (2)] with mass $m = \gamma\tau$ and temperature T_a, for which the steady-state reads $P_s \sim \exp(-(m\mathbf{v}^2/2 + U)/T_a)$. As for the regime of negligible persistence, one recover the standard Boltzmann distribution in terms of the potential U.

Let us now consider the case where we neglect the term $\gamma\tau\dot{\mathbf{v}}$ in the lhs of Eq. (123). This case is known as the *unified colored-noise approximation*:

$$\gamma\mathbb{M}_{\alpha\beta}\dot{x}_\beta = -\partial_\alpha U + \eta_{a\alpha}, \quad \mathbb{M}_{\alpha\beta} = \delta_{\alpha\beta} + (\tau/\gamma)\partial^2_{\alpha\beta}U, \tag{124}$$

where $\partial_\alpha = \partial/\partial x_\alpha$, and we use Einstein's convention for summation over repeated indices. The dynamics in Eq. (124) is a multiplicative overdamped Langevin equation. To obtain the corresponding steady-state distribution, let us turn this equation into an additive overdamped Langevin equation. We introduce the variable $\mathbf{r}$, and the corresponding potential V, which obeys the following dynamics:

$$\gamma\dot{\mathbf{r}} = -\partial_{\mathbf{r}}V + \boldsymbol{\eta}_a. \tag{125}$$

Comparing Eqs. (124) and (125), we obtain the following relations:

$$\dot{r}_\alpha = \mathbb{M}_{\alpha\beta}\dot{x}_\beta, \quad \partial_{\mathbf{r}}V = \nabla U, \tag{126}$$

yielding

$$dr_\alpha = \mathbb{M}_{\alpha\beta}dx_\beta, \quad V = \int \partial_\alpha U \frac{dr_\alpha}{dx_\beta}dx_\beta = \int \partial_\alpha U \mathbb{M}_{\alpha\beta}dx_\beta. \tag{127}$$

Substituting the expression of $\mathbb{M}$ from Eq. (124) into Eq. (127), we obtain an explicit relation between the potentials V and U:

$$V = \int \partial_\alpha U\left[\delta_{\alpha\beta} + \frac{\tau}{\gamma}\partial^2_{\alpha\beta}U\right]dx_\beta = U + \frac{\tau}{2\gamma}(\nabla U)^2 + \text{constant}. \tag{128}$$

The steady-state distribution $P_s(\mathbf{r}) \sim \exp(-V/T_a)$ of Eq. (125) can be readily converted in terms of the position $\mathbf{x}$ using the conservation of probability:

$$P_s(\mathbf{x}) = \left|\frac{d\mathbf{r}}{d\mathbf{x}}\right| P_s(\mathbf{r}) \sim |\det\mathbb{M}| \exp\left[-\frac{1}{T_a}\left(U + \frac{\tau}{2\gamma}(\nabla U)^2\right)\right]. \tag{129}$$

Finally, expanding $\det \mathbb{M}$ at small persistence τ, we deduce

$$\boxed{P_s(\mathbf{x}) \sim \exp(-\bar{U}/T_a), \quad \bar{U} = U + \tau(\nabla U)^2/(2\gamma) - (\tau T_a/\gamma)\nabla^2 U + o(\tau).} \tag{130}$$

Considering a bare potential U which is purely repulsive, the effective potential $\bar{U}$ can develop an attractive part. This result shows that effective attraction can arise from the combination of repulsion and persistence. In practice, it leads to the accumulation of active particles close to a wall: this is a purely nonequilibrium effect.

An alternative derivation of the effective potential $\bar{U}$ consists in looking for the steady state of the Fokker-Planck equation associated with the dynamics in Eq. (123):

$$\partial_t P = -\nabla \cdot (\mathbf{v}P) + \frac{1}{\gamma\tau}\partial_{\mathbf{v}} \cdot \left[(\gamma\mathbf{v} + \tau(\mathbf{v}\cdot\nabla)\nabla U + \nabla U)P + \frac{T_a}{\tau}\partial_{\mathbf{v}} P\right]. \tag{131}$$

Using the scaling $\bar{\mathbf{v}} = \sqrt{\tau}\mathbf{v} = o(\tau)$, the following distribution is a stationary solution of Eq. (131) to order $\tau^{3/2}$:

$$\begin{aligned} P_s(\mathbf{x}, \bar{\mathbf{v}}) \sim \Bigg[1 - \frac{\tau}{2T_a}\left(\frac{(\nabla U)^2}{\gamma} + (\bar{\mathbf{v}}\cdot\nabla)^2 U - \frac{3T_a}{\gamma}\nabla^2 U\right) \\ + \frac{\tau^{3/2}}{6T_a}\left((\bar{\mathbf{v}}\cdot\nabla)^2 - \frac{3T_a}{\gamma}\nabla^2\right)(\bar{\mathbf{v}}\cdot\nabla)U + o(\tau^{3/2})\Bigg] \exp\left(-\frac{\gamma}{2T_a}\bar{\mathbf{v}}^2 - \frac{U}{T_a}\right) \end{aligned} \tag{132}$$

Integrating this solution over the velocity $\bar{\mathbf{v}}$ yields the effective potential $\bar{U}$ in Eq. (130). Note that this expression of $\bar{U}$ remains valid for arbitrary potential U; in particular, it straightforwardly extends to the case of interacting active particles.

7.2 Breakdown of time-reversal symmetry

We want to evaluate the breakdown of time-reversal symmetry for the active dynamics in Eq. (123). The corresponding forward and reversed actions read

$$\begin{aligned} \mathcal{S}[\mathbf{v}, \mathbf{x}] &= \frac{1}{4\gamma T_a}\int_0^t dt' \Big[\gamma\tau\dot{\mathbf{v}} + \gamma\mathbf{v} + \tau(\mathbf{v}\cdot\nabla)\nabla U + \nabla U\Big]^2 + \text{even term under TR}, \\ \mathcal{S}[\mathbf{v}_R, \mathbf{x}_R] &= \frac{1}{4\gamma T_a}\int_0^t dt' \Big[\gamma\tau\dot{\mathbf{v}} - \gamma\mathbf{v} - \tau(\mathbf{v}\cdot\nabla)\nabla U + \nabla U\Big]^2 + \text{even term under TR}, \end{aligned} \tag{133}$$

where we have neglected to explicitly write some terms which are even under time reversal. We deduce the Kullback-Leibler divergence between forward and reversed path probabilities as

$$\begin{aligned} \ln\frac{\mathcal{P}[\mathbf{v}, \mathbf{x}]}{\mathcal{P}[\mathbf{v}_R, \mathbf{x}_R]} = \mathcal{S}[\mathbf{v}_R, \mathbf{x}_R] - \mathcal{S}[\mathbf{v}, \mathbf{x}] &= -\frac{1}{\gamma T_a}\int_0^t dt' (\tau\gamma\dot{\mathbf{v}} + \nabla U)\cdot(\gamma\mathbf{v} + \tau(\mathbf{v}\cdot\nabla)\nabla U) \\ &= -\frac{1}{T_a}\left(\Delta U + \frac{\tau}{2\gamma}\Delta(\nabla U)^2 + \frac{\tau\gamma}{2}\Delta\mathbf{v}^2\right) - \frac{\tau^2}{T_a}\int_0^t dt' \dot{\mathbf{v}}\cdot(\mathbf{v}\cdot\nabla)\nabla U. \end{aligned} \tag{134}$$

Considering the rate of divergence and eliminating some boundary terms, we then obtain

$$\boxed{\lim_{t\to\infty}\frac{1}{t}\ln\frac{\mathcal{P}[\mathbf{v}, \mathbf{x}]}{\mathcal{P}[\mathbf{v}_R, \mathbf{x}_R]} = -\frac{\tau^2}{T_a}\lim_{t\to\infty}\frac{1}{t}\int_0^t dt' \dot{\mathbf{v}}\cdot(\mathbf{v}\cdot\nabla)\nabla U = \frac{\tau^2}{2T_a}\langle(\mathbf{v}\cdot\nabla)^3 U\rangle_s,} \tag{135}$$

where we have performed an integration by parts, and we have used the correspondence between time and noise averages under ergodicity: $\lim_{t\to\infty}\frac{1}{t}\int_0^t dt' \cdot = \langle\cdot\rangle_s$. Substituting the steady-state distribution [Eq. (132)] to evaluate the average in Eq. (135), we deduce

$$\lim_{t\to\infty}\frac{1}{t}\ln\frac{\mathcal{P}[\mathbf{v}, \mathbf{x}]}{\mathcal{P}[\mathbf{v}_R, \mathbf{x}_R]} = \frac{T_a\tau^2}{2\gamma^3}\langle(\partial^3_{\alpha\beta\mu}U)(\partial^3_{\alpha\beta\mu}U)\rangle_s + o(\tau^2). \tag{136}$$

At vanishing persistence ($\tau = 0$), we recover that the rate of Kullback-Leibler divergence vanishes; as expected, the dynamics becomes statistically reversible in this equilibrium limit [see Sec. 6.1]. For a harmonic potential ($U = k\mathbf{x}^2/2$), we also obtain a vanishing Kullback-Leibler divergence; indeed, in such a case, the active dynamics [Eq. (123)] maps into an underdamped Langevin equation with mass $m = \gamma\tau$, damping $\gamma + 2\tau k$, and temperature T_a.

8 Collective dynamics of passive particles

The aim of this Section is to describe the time-evolution of the density field, which governs the collective of interacting passive Brownian particles, by coarse-graining the microscopic dynamics. It allows us to obtain and analyze a hydrodynamic theory, whose parameters explicitly depend on the particle-based potential.

8.1 Dynamics of the stochastic density

We consider the many-body dynamics of N passive Brownian particles:

$$\gamma\dot{\mathbf{x}}_i = -\nabla_i U + \boldsymbol{\eta}_i, \quad \langle \eta_{i\alpha}(t)\eta_{j\beta}(0)\rangle = 2\gamma T\delta_{ij}\delta_{\alpha\beta}\delta(t), \tag{137}$$

where $\nabla_i = \partial/\partial\mathbf{x}_i$. We are interested in the stochastic density field $\rho(\mathbf{x},t) = \sum_i \delta[\mathbf{x}-\mathbf{x}_i(t)]$ which counts the number of particles present at position $\mathbf{x}$ and time t. To derive the dynamics of $\rho(\mathbf{x},t)$, we use Itô's lemma [Eq. (56)] as

$$\begin{aligned}\dot\rho(\mathbf{x},t) &= \sum_i \dot{\mathbf{x}}_i(t)\cdot\nabla_i\delta[\mathbf{x}-\mathbf{x}_i(t)] + \frac{T}{\gamma}\sum_i \nabla_i^2\delta[\mathbf{x}-\mathbf{x}_i(t)]\\ &= -\nabla\cdot\sum_i \dot{\mathbf{x}}_i(t)\delta[\mathbf{x}-\mathbf{x}_i(t)] + \frac{T}{\gamma}\nabla^2\sum_i\delta[\mathbf{x}-\mathbf{x}_i(t)]\\ &= \frac{1}{\gamma}\nabla\cdot\sum_i(\nabla_i U - \boldsymbol{\eta}_i)\delta[\mathbf{x}-\mathbf{x}_i(t)] + \frac{T}{\gamma}\nabla^2\rho(\mathbf{x},t),\end{aligned} \tag{138}$$

where we have used $\nabla_i\delta[\mathbf{x}-\mathbf{x}_i(t)] = -\nabla\delta[\mathbf{x}-\mathbf{x}_i(t)]$. Considering a symmetric pairwise potential U of the form

$$U = \frac{1}{2}\sum_{i,j} V(\mathbf{x}_i-\mathbf{x}_j), \quad V(\mathbf{x}) = V(-\mathbf{x}), \tag{139}$$

we deduce

$$\sum_i \delta[\mathbf{x}-\mathbf{x}_i(t)]\nabla_i U = \sum_{i,j}\delta[\mathbf{x}-\mathbf{x}_i(t)]\nabla_i V(\mathbf{x}_i-\mathbf{x}_j) = \rho(\mathbf{x},t)\int d\mathbf{x}'\rho(\mathbf{x}',t)\nabla V(\mathbf{x}-\mathbf{x}'), \tag{140}$$

where we have used $\delta(\mathbf{x})f(\mathbf{x}) = \delta(\mathbf{x})f(\mathbf{0})$ for an arbitrary function f. Substituting Eq. (140) into Eq. (138), we then obtain *Dean's equation*:

$$\begin{aligned}\dot\rho(\mathbf{x},t) &= \nabla\cdot\left[\frac{\rho(\mathbf{x},t)}{\gamma}\int dx'\rho(\mathbf{x}',t)\nabla V(\mathbf{x}-\mathbf{x}') + \frac{T}{\gamma}\nabla\rho(\mathbf{x},t) + \boldsymbol{\Lambda}(\mathbf{x},t)\right],\\ \boldsymbol{\Lambda}(\mathbf{x},t) &= \frac{1}{\gamma}\sum_i\boldsymbol{\eta}_i\delta[\mathbf{x}-\mathbf{x}_i(t)].\end{aligned} \tag{141}$$

The total density $\bar\rho = \frac{1}{V}\int_V d\mathbf{x}\rho(\mathbf{x},t)$ is conserved in time, since $\int d\mathbf{x}\dot\rho = 0$, where V denotes the system size. The noise term $\boldsymbol{\Lambda}$ is a linear combination of the white Gaussian noises $\boldsymbol{\eta}_i$; thus, it has Gaussian statistics with zero mean and correlations given by

$$\begin{aligned}\langle\Lambda_\alpha(\mathbf{x},t)\Lambda_\beta(\mathbf{x}',t')\rangle &= \frac{1}{\gamma^2}\sum_{i,j}\delta[\mathbf{x}-\mathbf{x}_i(t)]\delta[\mathbf{x}'-\mathbf{x}_j(t')]\langle\eta_{i\alpha}(t)\eta_{j\beta}(t')\rangle\\ &= \frac{2T}{\gamma}\delta_{\alpha\beta}\delta(t-t')\sum_i\delta[\mathbf{x}-\mathbf{x}_i(t)]\delta[\mathbf{x}'-\mathbf{x}_i(t)]\\ &= \frac{2T}{\gamma}\delta_{\alpha\beta}\rho(\mathbf{x},t)\delta(t-t')\delta(\mathbf{x}-\mathbf{x}'),\end{aligned} \tag{142}$$

where we have used $\delta(\mathbf{x})f(\mathbf{x}) = \delta(\mathbf{x})f(\mathbf{0})$ for an arbitrary function f. It follows that the stochastic dynamics of the density field [Eq. (141)] is actually written in a closed form: both the drift terms and the noise correlations are expressed in terms of ρ.

To deduce the steady-state distribution associated with the density dynamics [Eq. (141)], we introduce the *free-energy functional* $\mathcal{F}[\rho]$ as

$$\boxed{\mathcal{F}[\rho] = T\int d\mathbf{x}\rho(\mathbf{x})(\ln\rho(\mathbf{x})-1) + \frac{1}{2}\iint d\mathbf{x}d\mathbf{x}'\rho(\mathbf{x})\rho(\mathbf{x}')V(\mathbf{x}-\mathbf{x}').} \tag{143}$$

This free-energy functional should not be confused with the free energy $F = -T\ln\big(\int e^{-U/T}\prod_i d\mathbf{r}_i\big)$ which characterizes the steady-state properties [Eq. (97)]. The functional in Eq. (143) is the sum of entropic and energetic contributions; the latter coincides with the potential in Eq. (139), and the former leads to a diffusion of density, as detailed below. We evaluate the functional derivative of $\mathcal{F}[\rho]$ as

$$\frac{\delta\mathcal{F}}{\delta\rho(\mathbf{x})} = T\ln\rho(\mathbf{x}) + \int d\mathbf{x}'\rho(\mathbf{x}')V(\mathbf{x}-\mathbf{x}'), \tag{144}$$

yielding

$$\rho(\mathbf{x})\nabla\frac{\delta\mathcal{F}}{\delta\rho(\mathbf{x})} = T\nabla\rho(\mathbf{x}) + \rho(\mathbf{x})\int d\mathbf{x}'\rho(\mathbf{x}')\nabla V(\mathbf{x}-\mathbf{x}'). \tag{145}$$

It follows that the density dynamics [Eq. (141)] can be written as

$$\boxed{\begin{aligned}&\dot\rho = -M(\rho,\nabla)\frac{\delta\mathcal{F}}{\delta\rho} + \Gamma, \quad M(\rho,\nabla) = -\frac{1}{\gamma}\nabla\cdot(\rho\nabla),\\ &\langle\Gamma(\mathbf{x},t)\Gamma(\mathbf{x}',t')\rangle = 2T\delta(t-t')M(\rho(\mathbf{x},t),\nabla)\delta(\mathbf{x}-\mathbf{x}'),\end{aligned}} \tag{146}$$

where we have used $\gamma M(\rho(\mathbf{x}),\nabla)\delta(\mathbf{x}-\mathbf{x}') = -\nabla\cdot[\rho(\mathbf{x})\nabla\delta(\mathbf{x}-\mathbf{x}')] = \nabla\cdot\nabla'[\rho(\mathbf{x})\delta(\mathbf{x}-\mathbf{x}')]$ in terms of $\nabla' = \partial/\partial\mathbf{x}'$. Equation (146) shows that the density field obeys a Langevin equation analogous to its particle-based counterpart [Eq. (137)]. In particular, the noise correlations obey the fluctuation-dissipation theorem [Eq. (16)] in terms of the temperature T and the mobility M, as expected from equilibrium. We readily deduce that the Fokker-Planck equation for the functional distribution $P([\rho],t)$ reads

$$\partial_t P = \int d\mathbf{x}\frac{\delta}{\delta\rho}\left[M(\rho,\nabla)\left(\frac{\delta\mathcal{F}}{\delta\rho}P + T\frac{\delta P}{\delta\rho}\right)\right]. \tag{147}$$

The stationary solution is given by the Boltzmann distribution $P_s([\rho]) \sim \exp(-\mathcal{F}[\rho]/T)$. It differs from its particle-based counterpart $P_s(\{\mathbf{x}_i\}) \sim \exp(-U(\{\mathbf{x}_i\})/T)$ only by the entropic contribution in $\mathcal{F}$ [Eq. (143)]: this difference reflects the the indistinguishability of particles at the density level, which stems from the coarse-graining of the dynamics.

8.2 Dynamics of the averaged density

We want to derive the dynamics of the averaged density $\langle\rho(\mathbf{x},t)\rangle$ from Dean's equation. Taking the average of Eq. (141), we obtain

$$\langle\dot\rho(\mathbf{x},t)\rangle = \frac{1}{\gamma}\nabla\cdot\left[T\nabla\langle\rho(\mathbf{x},t)\rangle + \int d\mathbf{x}'\langle\rho(\mathbf{x},t)\rho(\mathbf{x}',t)\rangle\nabla V(\mathbf{x}-\mathbf{x}')\right], \tag{148}$$

where we have used $\langle\Lambda_\alpha(\mathbf{x},t)\rangle = 0$. The dynamics of the averaged density depends on the two-point correlations. Introducing the notations $\rho_i = \rho(\mathbf{x}_i,t)$ and $V_{ij} = V(\mathbf{x}_i-\mathbf{x}_j)$, we use Itô's lemma [Eq. (56)] to obtain the dynamics of the two-point correlation as

$$\begin{aligned}\frac{d}{dt}\langle\rho_1\rho_2\rangle &= \langle\dot\rho_1\rho_2\rangle + \langle\rho_1\dot\rho_2\rangle\\ &= \frac{T}{\gamma}(\nabla_2^2+\nabla_1^2)\langle\rho_1\rho_2\rangle + \frac{1}{\gamma}\int d\mathbf{x}_3\Big[\nabla_1\cdot(\langle\rho_1\rho_2\rho_3\rangle\nabla_1 V_{12}) + \nabla_2\cdot(\langle\rho_1\rho_2\rho_3\rangle\nabla_2 V_{12})\Big].\end{aligned} \tag{149}$$

Note that there is not any contribution from the noise correlations, since $\mathbf{\Lambda}$ is uncorrelated in space [Eq. (141)]. It appears that the dynamics of the n-point correlation systematically depends on the $(n+1)$-point correlation: there is an infinite set of equations, known as the *Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy.*

To close the hierarchy, we turn our attention to the probability $p_n(\mathbf{x}_1,\dots,\mathbf{x}_n,t)$ to simultaneously observe n particles at distinct positions $\{\mathbf{x}_1,\dots\,\mathbf{x}_n\}$ for a given time t, defined as

$$p_n(\mathbf{x}_1,\dots,\mathbf{x}_n,t)=\sum_{i_1}{}'\cdots\sum_{i_n}{}'\langle\delta[\mathbf{x}_1-\mathbf{x}_{i_1}(t)]\cdots\delta[\mathbf{x}_n-\mathbf{x}_{i_n}(t)]\rangle. \tag{150}$$

The sums $\sum'$ exclude identical indices ($i_1=\cdots=i_n$) to preclude cases where particles have the same position. For each n, the probability p_n can be related to some density correlations:

$$\begin{aligned}\langle\rho(\mathbf{x},t)\rangle&=p_1(\mathbf{x},t),\\ \langle\rho(\mathbf{x},t)\rho(\mathbf{x}',t)\rangle&=\sum_{i,j\neq i}\langle\delta[\mathbf{x}-\mathbf{x}_i(t)]\delta[\mathbf{x}'-\mathbf{x}_j(t)]\rangle+\sum_i\langle\delta[\mathbf{x}-\mathbf{x}_i(t)]\delta[\mathbf{x}'-\mathbf{x}_i(t)]\rangle\\ &=p_2(\mathbf{x},\mathbf{x}',t)+\delta(\mathbf{x}-\mathbf{x}')p_1(\mathbf{x},t),\\ \langle\rho(\mathbf{x},t)\rho(\mathbf{x}',t)\rho(\mathbf{x}'',t)\rangle&=p_3(\mathbf{x},\mathbf{x}',\mathbf{x}'',t)+\delta(\mathbf{x}'-\mathbf{x}'')p_2(\mathbf{x},\mathbf{x}',t)+\delta(\mathbf{x}-\mathbf{x}')p_2(\mathbf{x},\mathbf{x}'',t)\\ &\quad+\delta(\mathbf{x}-\mathbf{x}'')p_2(\mathbf{x},\mathbf{x}',t)+\delta(\mathbf{x}-\mathbf{x}')\delta(\mathbf{x}-\mathbf{x}'')p_1(\mathbf{x},t),\end{aligned} \tag{151}$$

we have used $\delta(\mathbf{x})f(\mathbf{x})=\delta(\mathbf{x})f(\mathbf{0})$ for an arbitrary function f. Substituting the relations Eq. (151) into Eqs. (148) and (149), we deduce

$$\begin{aligned}\dot{p}_1(\mathbf{x},t)&=\frac{1}{\gamma}\nabla\cdot\Big[\nabla p_1(\mathbf{x},t)+\int d\mathbf{x}'p_2(\mathbf{x},\mathbf{x}',t)\nabla V(\mathbf{x}-\mathbf{x}')\Big],\\ \dot{p}_2(\mathbf{x}_1,\mathbf{x}_2,t)&=\frac{T}{\gamma}(\nabla_1^2+\nabla_2^2)p_2(\mathbf{x}_1,\mathbf{x}_2,t)+\frac{1}{\gamma}\Big[\nabla_1\cdot(p_2(\mathbf{x}_1,\mathbf{x}_2,t)\nabla_1V_{12})+\nabla_2\cdot(p_2(\mathbf{x}_1,\mathbf{x}_2,t)\nabla_2V_{12})\Big]\\ &\quad+\text{term depending on }p_3,\end{aligned} \tag{152}$$

where we have used $V(\mathbf{0})=0$.

Our aim is to discard the term depending on p_3 in the dynamics of p_2. To this end, given that the density p_n scales like $\bar{\rho}^n$, we consider the regime of small density $\bar{\rho}$ in what follows. As a result, the stationary solution p_{2s} obeys

$$0=T(\nabla_1^2+\nabla_2^2)p_{2s}(\mathbf{x}_1,\mathbf{x}_2)+\nabla_1\cdot(p_{2s}(\mathbf{x}_1,\mathbf{x}_2)\nabla_1V_{12})+\nabla_2\cdot(p_{2s}(\mathbf{x}_1,\mathbf{x}_2)\nabla_2V_{12}), \tag{153}$$

whose solution reads $p_{2s}\sim\exp(-V_{12}/T)$. Inspired by this solution, we assume that the term depending on p_2 in the dynamics of p_1 can be approximated using a heuristic ansatz:

$$p_2(\mathbf{x},\mathbf{x}',t)=p_1(\mathbf{x},t)p_1(\mathbf{x}',t)\exp(-V(\mathbf{x}-\mathbf{x}')/T), \tag{154}$$

yielding

$$\begin{aligned}\int d\mathbf{x}_1p_2(\mathbf{x},\mathbf{x}_1,t)\nabla V(\mathbf{x}-\mathbf{x}_1)&=p_1(\mathbf{x},t)\int d\mathbf{x}_1p_1(\mathbf{x}_1,t)\exp(-V(\mathbf{x}-\mathbf{x}_1)/T)\nabla V(\mathbf{x}-\mathbf{x}_1)\\ &=Tp_1(\mathbf{x},t)\int d\mathbf{x}_1p_1(\mathbf{x}_1,t)\nabla_1\exp(-V(\mathbf{x}-\mathbf{x}_1)/T)\\ &=Tp_1(\mathbf{x},t)\int d\mathbf{x}_1\Big[1-\exp(-V(\mathbf{x}_1)/T)\Big]\nabla p_1(\mathbf{x}_1+\mathbf{x},t),\end{aligned} \tag{155}$$

where we have integrated by parts with the convention $V(\infty)=0$, changed variable $\mathbf{x}_1\to\mathbf{x}_1-\mathbf{x}$, and used $\nabla_1p_1(\mathbf{x}_1+\mathbf{x})=\nabla p_1(\mathbf{x}_1+\mathbf{x})$. Assuming that the potential V has a short-ranged repulsive component ($V(\mathbf{x}_1)\to\infty$ for $|\mathbf{x}_1|<\sigma$), the integral in the rhs of Eq. (155) is essentially concentrated at $\mathbf{x}_1=\mathbf{0}$, from which we deduce

$$\int d\mathbf{x}_1\Big[1-\exp(-V(\mathbf{x}_1)/T)\Big]p_1(\mathbf{x}_1+\mathbf{x},t)=p(\mathbf{x},t)\int d\mathbf{x}_1\Big[1-\exp(-V(\mathbf{x}_1)/T)\Big]. \tag{156}$$

Substituting Eqs. (155) and (156) into the dynamics for p_1 [Eq. (152)], we obtain

$$\boxed{\dot{p}_1=-M(p_1,\nabla)\frac{\delta\bar{\mathcal{F}}}{\delta p_1},\quad\bar{\mathcal{F}}=\int d\mathbf{x}\Big[Tp_1(\ln p_1-1)+\frac{a}{2}p_1^2\Big],\quad a=T\int d\mathbf{x}'\Big[1-\exp\big(-V(\mathbf{x}')/T\big)\Big].} \tag{157}$$

The dynamics for the average density is given in a closed form. The free energy functional $\bar{\mathcal{F}}$ has the same entropic contribution as in $\mathcal{F}$ [Eq. (143)], yet the energetic contribution is now a local function of p_1 given in terms of the *Virial coefficient* a. For a purely repulsive potential ($V(\mathbf{x}) > 0$), we obtain $a > 0$, so that the free-energy density admits a single minimum: p_1 is uniform across the whole system. For a potential with some attraction ($V(\mathbf{x}) < 0$ for $\bar{\sigma} < |\mathbf{x}_1|$), we obtain $a < 0$ at a sufficiently small temperature T, so that the free-energy density admits two minima: p_1 can now accommodate a coexistence between regions of high and low density.

9 Landau-Ginzburg theory

In this Section, we analyze the dynamical instability arising in a hydrodynamic theory of phase separation. We postulate the form of such a theory using a top-down approach, without coarse-graining any particle-based dynamics, and describe the properties of the phase-separated profile.

9.1 Dynamical instability and phase diagram

We want to study the phase-separation dynamics in terms of a scalar field $\phi(\mathbf{x},t)$, which represents the local value of some non-dimensional density; for instance, the proportion of particles A in a mixtures of particles with types A and B. Instead of deriving the theory by a systematic coarse-graining, we now postulate the dynamics as

$$\boxed{\begin{aligned}&\dot\phi = -M(\phi,\nabla)\frac{\delta\mathcal{F}}{\delta\phi}+\Gamma, \quad \langle\Gamma(\mathbf{x},t)\Gamma(\mathbf{x}',t')\rangle = 2T\delta(t-t')M(\phi(\mathbf{x},t),\nabla)\delta(\mathbf{x}-\mathbf{x}'),\\ &\mathcal{F}=\int d\mathbf{x}\left[\frac{a}{2}\phi^2+\frac{b}{4}\phi^4+\frac{\kappa}{2}(\nabla\phi)^2\right], \quad M(\phi,\nabla)=-\nabla^2.\end{aligned}} \tag{158}$$

The *Landau-Ginzburg free energy* $\mathcal{F}$ is given by an expansion to lowest order in powers of ϕ and its gradients. The local term $(a/2)\phi^2+(b/4)\phi^4$ can have either one or two minima depending on the sign of a, where $b>0$. The coefficient $\kappa>0$ controls the energy cost associated with stabilizing a non-homogeneous profile of ϕ. We evaluate the functional derivative as

$$\frac{\delta}{\delta\phi(\mathbf{x},t)}\frac{\kappa}{2}\int d\mathbf{x}_1(\nabla_1\phi(\mathbf{x}_1,t))^2 = \kappa\int d\mathbf{x}_1\nabla_1\phi(\mathbf{x}_1,t)\cdot\nabla_1\delta(\mathbf{x}-\mathbf{x}_1) = -\kappa\nabla^2\phi(\mathbf{x},t), \tag{159}$$

where we have integrated by parts. The field dynamics is then given by

$$\dot\phi = \nabla^2[(a+b\phi^2-\kappa\nabla^2)\phi]+\Gamma. \tag{160}$$

We want to study the stability of the homogeneous state $\bar\phi = \frac{1}{V}\int_V d\mathbf{x}\phi(\mathbf{x},t)$. To this end, we decompose $\delta\phi(\mathbf{x},t)=\phi(\mathbf{x},t)-\bar\phi$ in the Fourier domain as

$$\delta\phi(\mathbf{x},t) = \int\frac{d\mathbf{q}}{(2\pi)^d}e^{-i\mathbf{q}\cdot\mathbf{x}}\phi_q(t), \quad \phi_q(t)=\int d\mathbf{x}e^{i\mathbf{q}\cdot\mathbf{x}}\delta\phi(\mathbf{x},t). \tag{161}$$

Linearizing the field dynamics [Eq. (160)] around $\bar\phi$ in the Fourier domain, the time evolution of each mode ϕ_q decouples as

$$\dot\phi_q = \lambda(\mathbf{q})\phi_q+\Gamma_q, \quad \lambda(\mathbf{q}) = -\mathbf{q}^2(a+3b\bar\phi^2+\kappa\mathbf{q}^2), \tag{162}$$

where we have used

$$\int d\mathbf{x}e^{i\mathbf{q}\cdot\mathbf{x}}\nabla^n\delta\phi(\mathbf{x},t) = (-i\mathbf{q})^n\int d\mathbf{x}e^{i\mathbf{q}\cdot\mathbf{x}}\delta\phi(\mathbf{x},t) = (-i\mathbf{q})^n\phi_q(t). \tag{163}$$

The noise correlations are given by

$$\begin{aligned}\langle\Gamma_q(t)\Gamma_{q'}(t')\rangle &= \iint d\mathbf{x}d\mathbf{x}'e^{i(\mathbf{q}\cdot\mathbf{x}+\mathbf{q}'\mathbf{x}')}\langle\Gamma(\mathbf{x},t)\Gamma(\mathbf{x}',t')\rangle\\ &= -2T\mathbf{q}\cdot\mathbf{q}'\delta(t-t')\int d\mathbf{x}e^{i(\mathbf{q}+\mathbf{q}')\cdot\mathbf{x}} = 2T\mathbf{q}^2(2\pi)^d\delta(t-t')\delta(\mathbf{q}+\mathbf{q}').\end{aligned} \tag{164}$$

We deduce the dynamics of the structure factor $S_q(t)=\langle|\phi_q(t)|^2\rangle$ using Itô's lemma [Eq. (56)] as

$$\dot S_q = \langle\dot\phi_q\phi_{-q}\rangle+\langle\phi_q\dot\phi_{-q}\rangle = 2\lambda(\mathbf{q})S_q, \tag{165}$$

where we have used $\lambda(-\mathbf{q})=\lambda(\mathbf{q})$, yielding $S_q(t)=S_q(0)e^{2\lambda(\mathbf{q})t}$. At large wavenumber $\mathbf{q}$, the rate of growth $\lambda(\mathbf{q})$ is negative, so that the effect of the perturbation $\delta\phi$ always decays. At small wavenumber $\mathbf{q}$, $\lambda(\mathbf{q})$ becomes negative for $a+3b\bar\phi^2<0$: in this regime, the perturbation $\delta\phi$ does not relax, so that the homogeneous state is linearly unstable. Therefore, we deduce that the phase boundary $a+3b\bar\phi^2=0$ distinguishes parameter regimes of stable and unstable homogeneous states. Note that the phase diagram here depends not only on the free-energy parameters $\{a,b\}$, but also on the total density $\bar\phi$.

9.2 Phase coexistence and domain walls

We want to describe the system configuration when the homogeneous state $\bar{\phi}$ is unstable ($a+3b\bar{\phi}^2 < 0$). In this regime, the free energy $\mathcal{F}$ [Eq. (158)] is minimized by demixing the homogeneous state into a coexistence between domains at different densities. The free-energy density $(a/2)\phi^2+(b/4)\phi^4$ is minimal at the densities $\phi = \pm\sqrt{a/b}$, and the gradient term $(\kappa/2)(\nabla\phi)^2$ wants to minimize the number of interfaces. Therefore, after a transient relaxation, the system reaches a steady state with a single interface between two domains at densities $\phi = \pm\sqrt{a/b}$. In the noise-less limit ($T = 0$), the shape of the corresponding density profile obeys

$$(\ell\nabla)^2\phi = \phi\big[(\phi/\phi_b)^2 - 1\big], \quad \ell = \sqrt{-\kappa/a}, \quad \phi_b = \sqrt{-a/b}. \tag{166}$$

In one dimension, we can obtain an exact solution of the profile connecting two domains. Multiplying Eq. (166) by $d\phi/dx$ and integrating with respect to x leads to

$$\ell^2(d\phi/dx)^2 = (\phi_b^2/2)\big[(\phi/\phi_b)^2 - 1\big]^2, \tag{167}$$

where we have used $\phi(\infty) = \phi_b$ and $(d\phi/dx)(\infty) = 0$. After separation of variables and integration, we deduce the solution for *domain walls*:

$$\boxed{\phi(x) = \phi_b \tanh\big[x/(\sqrt{2}\ell)\big].} \tag{168}$$

The interfacial length ℓ increases with κ [Eq. (166)], which controls the cost of stabilizing gradients of ϕ in the free energy [Eq. (158)].

Let us consider the effect of a polar field $\mathbf{p}$ with dynamics

$$\begin{aligned} &\dot{\mathbf{p}} = -M_p\frac{\delta\mathcal{F}}{\delta\mathbf{p}} + \mathbf{\Omega}, \quad \langle\Omega_\alpha(\mathbf{x},t)\Omega_\beta(\mathbf{x}',t')\rangle = 2M_pT\delta(t-t')\delta(\mathbf{x}-\mathbf{x}'), \\ &\mathcal{F} = \int d\mathbf{x}\left[\frac{a}{2}\phi^2 + \frac{b}{4}\phi^4 + \frac{\kappa}{2}(\nabla\phi)^2 + \frac{a_p}{2}\mathbf{p}^2 + \chi\mathbf{p}\cdot\nabla\phi\right], \end{aligned} \tag{169}$$

where the dynamics of ϕ [Eq. (158)] is now given in terms of the free energy in Eq. (169). The mobility M_p does not depend on gradients, so that $\mathbf{p}$ is not conserved: $\int d\mathbf{x}\dot{\mathbf{p}} \neq \mathbf{0}$. The coupling term $\chi\mathbf{p}\cdot\nabla\phi$ favors anchoring of $\mathbf{p}$ perpendicular to the interfaces formed by ϕ. Since the dynamics of $(\phi,\mathbf{p})$ obey the relation between noise strength and mobility given by the fluctuation-dissipation theorem [Eq. (16)], it follows that the steady state is given by the Boltzmann distribution $P_s([\phi,\mathbf{p}]) \sim e^{-\mathcal{F}[\phi,\mathbf{p}]/T}$. The stationary distribution can be written in terms of ϕ only as

$$P_s([\phi]) = \int \mathcal{D}\mathbf{p}P_s([\phi,\mathbf{p}]) \sim e^{-\bar{\mathcal{F}}[\phi]/T}, \quad \bar{\mathcal{F}} = \int d\mathbf{x}\left[\frac{a}{2}\phi^2 + \frac{b}{4}\phi^4 + \frac{1}{2}\left(\kappa - \frac{\chi^2}{2a_p}\right)(\nabla\phi)^2\right], \tag{170}$$

where we have used the Gaussian integral $\int d\mathbf{x}e^{-\mathbf{b}\cdot\mathbf{x}-a\mathbf{x}^2/2} \sim e^{\mathbf{b}^2/(2a)}$. Comparing with the free energy $\mathcal{F}$ [Eq. (158)], it appears that the effect of the coupling between ϕ and $\mathbf{p}$ amounts to a renormalization of the coefficient of the gradient term. While stability requires $\kappa > \chi^2/(2a_p)$, one can arbitrarily reduce the cost of forming interfaces by choosing $\kappa \approx \chi^2/(2a_p)$. Such a choice leads to long-lived domain walls, corresponding to a *metastable emulsion* with coexistence between multiple droplets. The effect of surfactants, for instance amphiphilic molecules anchoring at interfaces between domains of water and oil, is captured by the coupling constant χ: by strengthening anchoring, one can thus stabilize emulsions.

10 Collective dynamics of active particles

In this Section, we examine collective effects in active particles. We coarse-grain the particle-based dynamics, and analyze the corresponding hydrodynamic instability in two cases: repulsive particles leading to a phase separation, and aligning particles yielding a polar order.

10.1 Motility-induced phase separation

We consider the dynamics of an assembly of active Brownian particles (ABPs) [see Sec. 6.1] in two dimensions as

$$\begin{aligned}&\gamma\dot{\mathbf{x}}_i = -\nabla_i U + \gamma v_0(\cos\theta_i, \sin\theta_i) + \boldsymbol{\eta}_i, \quad \dot{\theta}_i = \xi_i,\\ &\langle \eta_{i\alpha}(t)\eta_{j\beta}(0)\rangle = 2\gamma T\delta_{ij}\delta_{\alpha\beta}\delta(t), \quad \langle \xi_i(t)\xi_j(0)\rangle = (2/\tau)\delta_{ij}\delta(t).\end{aligned} \tag{171}$$

For a repulsive pairwise potential $U = (1/2)\sum_{i,j} V(\mathbf{x}_i - \mathbf{x}_j)$, numerical simulations reveal some effective attraction between particles. To capture such an effect, we simplify the dynamics by considering *quorum-sensing interactions* of the form

$$\dot{\mathbf{x}}_i = v(\rho(\mathbf{x}_i, t))\hat{\mathbf{e}}(\theta_i), \quad \dot{\theta}_i = \xi_i, \quad \langle \xi_i(t)\xi_j(0)\rangle = (2/\tau)\delta_{ij}\delta(t). \tag{172}$$

where $\hat{\mathbf{e}}(\theta) = (\cos\theta, \sin\theta)$, and we have neglected the effect of thermal fluctuations ($T \ll \gamma\tau v_0^2$). The self-propulsion speed $v(\rho)$ is a decreasing function of the local density $\rho(\mathbf{x}, t) = \sum_i \delta[\mathbf{x} - \mathbf{x}_i(t)]$: it reproduces the slowing-down of the dynamics due to collisions between particles in dense regions.

To study the collective dynamics, we introduce the joint density ψ of position $\mathbf{x}$ and orientation θ as

$$\psi(\mathbf{x}, \theta, t) = \sum_i \psi_i(\mathbf{x}, \theta, t), \quad \psi_i(\mathbf{x}, \theta, t) = \delta[\mathbf{x} - \mathbf{x}_i(t)]\delta[\theta - \theta_i(t)]. \tag{173}$$

Using Itô's lemma [Eq. (56)], we obtain

$$\begin{aligned}&\dot{\psi} = \sum_i \left[\dot{\mathbf{x}}_i \cdot \nabla_i + \dot{\theta}_i \frac{\partial}{\partial\theta_i} + \frac{1}{\tau}\frac{\partial^2}{\partial\theta_i^2}\right]\psi_i = -\nabla\cdot(v(\rho)\hat{\mathbf{e}}(\theta)\psi) + \frac{1}{\tau}\frac{\partial^2}{\partial\theta^2}\psi - \frac{\partial\Upsilon}{\partial\theta},\\ &\Upsilon(\mathbf{x}, \theta, t) = \sum_i \xi_i(t)\psi_i(\mathbf{x}, \theta, t),\end{aligned} \tag{174}$$

where we have used $\nabla_i\psi_i = -\nabla\psi_i$ and $\partial\psi_i/\partial\theta_i = -\partial\psi_i/\partial\theta$. The noise field Υ has Gaussian statistics with correlations given by

$$\begin{aligned}\langle \Upsilon(\mathbf{x}, \theta, t)\Upsilon(\mathbf{x}', \theta', t')\rangle &= \sum_{i,j} \psi_i(\mathbf{x}, \theta, t)\psi_j(\mathbf{x}', \theta', t')\langle \xi_i(t)\xi_j(t')\rangle\\ &= \frac{2}{\tau}\psi(\mathbf{x}, \theta, t)\delta(t - t')\delta(\theta - \theta')\delta(\mathbf{x} - \mathbf{x}').\end{aligned} \tag{175}$$

Therefore, the dynamics for the joint density ψ is actually written in in a closed form. We readily deduce the dynamics of the local density ρ by integrating Eq. (174) with respect to θ, in terms of the *local polarization* $\mathbf{p}$ as

$$\dot{\rho} = -\nabla\cdot(v(\rho)\mathbf{p}), \quad \mathbf{p}(\mathbf{x}, t) = \int d\theta\hat{\mathbf{e}}\psi = \sum_i \hat{\mathbf{e}}(\theta_i)\delta[\mathbf{x} - \mathbf{x}_i(t)]. \tag{176}$$

The dynamics of $\mathbf{p}$ follows by multiplying Eq. (174) by $\hat{\mathbf{e}}(\theta)$ and integrating with respect to θ, leading to

$$\dot{p}_\alpha = -\int d\theta\partial_\beta(v(\rho)\hat{e}_\alpha\hat{e}_\beta\psi) - p_\alpha/\tau + \Xi_\alpha, \quad \Xi_\alpha(\mathbf{x}, t) = \sum_i \hat{e}_\alpha(\theta_i(t))\xi_i(t)\delta[\mathbf{x} - \mathbf{x}_i(t)], \tag{177}$$

where we have used $\int d\theta e_\alpha(\theta)\partial^2\psi/\partial\theta^2 = -\int d\theta e_\alpha(\theta)\psi$ after integration by part. The first term in the rhs of Eq. (177) can be written as

$$\begin{aligned}\int d\theta\hat{e}_\alpha\hat{e}_\beta\psi &= \int d\theta\psi \begin{bmatrix}\cos^2\theta & \cos\theta\sin\theta\\ \cos\theta\sin\theta & \sin^2\theta\end{bmatrix}\\ &= \frac{1}{2}\int d\theta\psi \begin{bmatrix}1 + \cos(2\theta) & \sin(2\theta)\\ \sin(2\theta) & 1 - \sin(2\theta)\end{bmatrix} = \frac{\rho\delta_{\alpha\beta} + Q_{\alpha\beta}}{2},\end{aligned} \tag{178}$$

where we have introduced the *local nematic tensor* defined as

$$Q_{\alpha\beta}(\mathbf{x},t)=\sum_i(\hat{e}_\alpha(\theta_i)\hat{e}_\beta(\theta_i)-\delta_{\alpha\beta})\delta[\mathbf{x}-\mathbf{x}_i(t)]. \tag{179}$$

The correlations of the noise term in the rhs of Eq. (177) follow as

$$\begin{aligned}\langle\Xi_\alpha(\mathbf{x},t)\Xi_\beta(\mathbf{x}',t')\rangle&=\sum_{i,j}\hat{e}_\alpha(\theta_i(t))\hat{e}_\beta(\theta_j(t'))\langle\xi_i(t)\xi_j(t')\rangle\delta[\mathbf{x}-\mathbf{x}_i(t)]\delta[\mathbf{x}'-\mathbf{x}_j(t')]\\&=\frac{1}{\tau}(\rho\delta_{\alpha\beta}+Q_{\alpha\beta})(\mathbf{x},t)\delta(t-t')\delta(\mathbf{x}-\mathbf{x}').\end{aligned} \tag{180}$$

It appears that there is an infinite hierarchy of equations for the moments of the density ψ. To close the hierarchy, we neglect the contribution of the nematic tensor in the polarization dynamics [Eq. (177)] and in the noise correlations [Eq. (180)], and we assume that the polarization relaxes fast ($\dot{\mathbf{p}}=\mathbf{0}$). These assumptions provide a route to relate $\mathbf{p}$ to ρ, and substituting this relation in the density dynamics [Eq. (176)], we obtain

$$\boxed{\dot{\rho}=\frac{1}{2\tau}\nabla\cdot\Big[v(\rho)\nabla(\rho v(\rho))\Big]+\Gamma,\quad\langle\Gamma(\mathbf{x},t)\Gamma(\mathbf{x}',t')\rangle=-\frac{\rho(\mathbf{x},t)v(\rho(\mathbf{x},t))^2}{\tau}\delta(t-t')\nabla^2\delta(\mathbf{x}-\mathbf{x}')}. \tag{181}$$

We consider a perturbation of the homogeneous state $\bar{\rho}=\frac{1}{V}\int_V d\mathbf{x}\rho$ as $\delta\rho(\mathbf{x},t)=\rho(\mathbf{x},t)-\bar{\rho}$, whose linearized dynamics in the Fourier domain [Eq. (161)] reads

$$\dot{\rho}_q=\lambda(\mathbf{q})\rho_q+\Gamma_q,\quad\lambda(\mathbf{q})=-\mathbf{q}^2\left[v(\bar{\rho})+\bar{\rho}\frac{dv}{d\rho}(\bar{\rho})\right],\quad\langle\Gamma_q(t)\Gamma_{q'}(t')\rangle=\frac{\bar{\rho}v(\bar{\rho})^2}{\tau}\mathbf{q}^2(2\pi)^d\delta(t-t')\delta(\mathbf{q}+\mathbf{q}'). \tag{182}$$

Following the same steps as in Sec. 9.1, we deduce that the structure factor $S_q=\langle|\delta\rho_q|^2\rangle$ reads $S_q(t)=S_q(0)e^{2\lambda(\mathbf{q})t}$. The rate of growth $\lambda(\mathbf{q})$ becomes positive for $\bar{\rho}(dv/d\rho)(\bar{\rho})<-v(\bar{\rho})$, namely when the self-propulsion speed decays sufficiently fast with density: this provides an explicit criterion for linear instability of the homogeneous state. Note that, in contrast with the Landau-Ginzburg theory in Sec. 9.1, $\lambda(\mathbf{q})$ is now positive for an arbitrary large $\mathbf{q}$. Indeed, the dynamics in Eq. (181) misses higher order gradients to stabilize large wavenumbers. At large times, the dynamical instability leads to a coexistence between dense and dilute domains, known as *motility-induced phase separation*.

10.2 Flocking of aligning particles

We now consider the dynamics of an assembly of ABPs in two dimensions without any repulsion, yet with aligning interactions where each particle aligns with neighbors within a radius σ, yielding

$$\dot{\mathbf{x}}_i=v_0\hat{\mathbf{e}}(\theta_i),\quad\dot{\theta}_i=\frac{\varepsilon}{\pi\sigma^2}\sum_j\sin(\theta_i-\theta_j)H(\sigma-|\mathbf{x}_i-\mathbf{x}_j|)+\xi_i,\quad\langle\xi_i(t)\xi_j(0)\rangle=(2/\tau)\delta_{ij}\delta(t), \tag{183}$$

where H is the Heaviside function defined such that $H(z)=1$ for $z>0$, and $H(z)=0$ for $z<0$. To study collective effects, we obtain the dynamics of the joint density [Eq. (173)] using Itô's lemma [Eq. (56)] as

$$\dot{\psi}(\mathbf{x},\theta,t)=-\nabla\cdot(v_0\hat{\mathbf{e}}(\theta)\psi)+\frac{1}{\tau}\frac{\partial^2\psi}{\partial\theta^2}+\varepsilon\frac{\partial}{\partial\theta}\left[\psi(\mathbf{r},\theta,t)\int\sin(\theta'-\theta)\psi(\mathbf{r},\theta',t)d\theta'\right]+\Upsilon, \tag{184}$$

where we have approximated $H(\sigma-|\mathbf{x}|)$ by $\pi\sigma^2\delta(\mathbf{x})$ at the coarse-grained level, for simplicity. The noise term Υ has the same statistics as in Eq. (175). Any dynamical instability is best detected in terms of the angular modes ψ_n, defined as

$$\psi_n(\mathbf{x},t)=\int e^{-in\theta}\psi(\mathbf{x},\theta,t)d\theta,\quad\psi(\mathbf{x},\theta,t)=\frac{1}{2\pi}\sum_n e^{in\theta}\psi_n(\mathbf{x},t). \tag{185}$$

Multiplying Eq. (184) by $e^{-in\theta}$ and integrating over θ, we obtain

$$\begin{aligned}\dot{\psi}_n &= -\frac{v_0}{2}\Big[\partial_x(\psi_{n+1}+\psi_{n-1}) - i\partial_y(\psi_{n+1}-\psi_{n-1})\Big] - \frac{n^2}{\tau}\psi_n - \frac{n\varepsilon}{2}(\psi_{n+1}\psi_{-1} - \psi_{n-1}\psi_1) + in\Upsilon_n,\\ \Upsilon_n(\mathbf{x},t) &= \sum_j e^{-in\theta_j(t)}\xi_j(t)\delta[\mathbf{x}-\mathbf{x}_j(t)],\end{aligned} \tag{186}$$

where we have used

$$\begin{aligned}&\int e^{-in\theta}\frac{\partial}{\partial\theta}\Big[\psi(\mathbf{x},\theta,t)\int \sin(\theta'-\theta)\psi(\mathbf{x},\theta',t)d\theta'\Big]d\theta\\ &\quad= \frac{n}{2}\int e^{in\theta}\psi(\mathbf{x},\theta,t)\int\Big[e^{i(\theta'-\theta)} - e^{-i(\theta'-\theta)}\Big]\psi(\mathbf{x},\theta',t)d\theta' d\theta = \frac{n}{2}(\psi_1\psi_{n-1} - \psi_{-1}\psi_{n+1}).\end{aligned} \tag{187}$$

The dynamics of the moment ψ_n in Eq. (186) depends on the higher moment ψ_{n+1}: as for the case of repulsive active particles [Sec. 10.1], we obtain an infinite hierarchy of equations for the angular moments of the joint density ψ.

We are interested in obtaining a closed dynamics for the local density $\rho = \psi_0$ and polarization $\mathbf{p} = \mathrm{Re}(\psi_1)\hat{\mathbf{x}} + \mathrm{Im}(\psi_1)\hat{\mathbf{y}}$. Assuming that we can neglect depending on ψ_3 in the dynamics of ψ_2, the stationary solution for ψ_2 reads

$$\psi_2 = \frac{\tau}{4}\Big[-\frac{v_0}{2}(\partial_x + i\partial_y)\psi_1 + \varepsilon\psi_1^2\Big]. \tag{188}$$

Substituting this ansatz into the dynamics of ψ_1, we deduce

$$\boxed{\begin{aligned}\dot{\rho} &= -v_0\nabla\cdot\mathbf{p},\\ \dot{\mathbf{p}} &= \Big(\frac{\varepsilon\rho}{2} - \frac{1}{\tau}\Big)\mathbf{p} - \frac{\varepsilon^2\tau}{8}\mathbf{p}|\mathbf{p}|^2 - \frac{v_0}{2}\nabla\rho + \frac{v_0^2\tau}{16}\nabla^2\mathbf{p}\\ &\quad + \frac{\varepsilon v_0\tau}{32}\Big[5\nabla\mathbf{p}^2 - 10\mathbf{p}(\nabla\cdot\mathbf{p}) - 6(\mathbf{p}\cdot\nabla)\mathbf{p}\Big] + \boldsymbol{\Xi}\\ \langle\Xi_\alpha(\mathbf{x},t)\Xi_\beta(\mathbf{x}',t')\rangle &= \frac{\rho(\mathbf{x},t)}{\tau}\delta_{\alpha\beta}\delta(t-t')\delta(\mathbf{x}-\mathbf{x}').\end{aligned}} \tag{189}$$

We consider a perturbation of the homogeneous apolar state $(\bar{\rho}, \mathbf{p}=\mathbf{0})$ as $\delta\rho(\mathbf{x},t) = \rho(\mathbf{x},t) - \bar{\rho}$ and $\delta\mathbf{p}(\mathbf{x},t) = \mathbf{p}(\mathbf{x},t)$, whose linearized dynamics in Fourier domain reads

$$\frac{d}{dt}\begin{bmatrix}\rho_q\\ \mathbf{p}_q\end{bmatrix} = \mathbb{L}(\mathbf{q})\begin{bmatrix}\rho_q\\ \mathbf{p}_q\end{bmatrix} + \begin{bmatrix}0\\ \boldsymbol{\Xi}_q\end{bmatrix}, \quad \mathbb{L}(\mathbf{q}) = \begin{bmatrix}-i\mathbf{q}\cdot v_0 & 0\\ \frac{\varepsilon\bar{\rho}}{2} - \frac{1}{\tau} - \frac{(v_0\mathbf{q})^2\tau}{16} & -i\mathbf{q}\cdot v_0\end{bmatrix}. \tag{190}$$

The largest eigenvalue $\lambda(\mathbf{q})$ of $\mathbb{L}(\mathbf{q})$, which determines the evolution of the structure factor $S_q = \langle|\rho_q|^2\rangle$ as $S_q(t) = S_q(0)e^{2\lambda(\mathbf{q})t}$, reads

$$\lambda(\mathbf{q}) = \frac{1}{2}\Big(\frac{\varepsilon\bar{\rho}}{2} - \frac{1}{\tau} - \frac{(v_0\mathbf{q})^2\tau}{16}\Big) + \frac{1}{2}\sqrt{\Big(\frac{\varepsilon\bar{\rho}}{2} - \frac{1}{\tau} - \frac{(v_0\mathbf{q})^2\tau}{16}\Big)^2 - 2(v_0\mathbf{q})^2}. \tag{191}$$

Given that $\mathrm{Re}(\lambda(\mathbf{q})) < \mathrm{Re}(\lambda(\mathbf{q}=\mathbf{0}))$, it suffices to analyze the sign of $\lambda(\mathbf{q}=\mathbf{0}) = \varepsilon\bar{\rho}/2 - 1/\tau$ to determine the stability of the homogeneous apolar state: such a state is unstable whenever the global density $\bar{\rho}$ exceeds the critical value $\rho_c = 2/(\tau\varepsilon)$, leading to the *flocking transition*. In this regime, the system exhibits a coexistence between a dense polar band, made of active particles all moving in the same direction, and a dilute apolar background. At even higher density, a polar homogeneous state stabilizes with polarization amplitude $|\mathbf{p}| = 2\sqrt{\rho_c(\bar{\rho}-\rho_c)}$, as given by the fixed point of Eq. (189), and direction chosen through spontaneous symmetry breaking.