VI. PATH INTEGRAL REPRESENTATION OF STOCHASTIC DYNAMICS

The mathematical formalism constructed to describe the stochastic dynamics of a Brownian particle has a fundamental connection to quantum mechanics, which manifests itself best within the path integral formulation. The Markov property of stochastic dynamics naturally lends itself to a path integral description, which can then be used to draw parallels with quantum mechanics, and in particular the use of Hilbert space and the definition of a Hamiltonian operator.

A. Exploiting the Markov property of Langevin dynamics

We start with the Langevin equation

$$\frac{\mathrm{d}\boldsymbol{r}}{\mathrm{d}t} = \boldsymbol{v}(\boldsymbol{r}) + \boldsymbol{u}(t) \quad , \tag{VI.1}$$

where the noise $\boldsymbol{u}$ has the Gaussian distribution

$$p[\boldsymbol{u}(t)] = \frac{1}{\mathsf{Z}} \exp\left[-\frac{1}{4D}\int_0^{\mathsf{T}} \mathrm{d}t\, \boldsymbol{u}(t)^2\right] \quad . \tag{VI.2}$$

Using explicit averaging over noise, we can define the probability of finding the Brownian particle at position $\boldsymbol{x}$ at time t given the initial position of $\boldsymbol{x}_0$ at time t_0, which we define as

$$\mathcal{P}(\boldsymbol{x}, t|\boldsymbol{x}_0, t_0) = \left\langle \delta^3\left(\boldsymbol{x} - \boldsymbol{r}(t)\right)\right\rangle\big|_{\boldsymbol{r}(0)=\boldsymbol{x}_0} \quad , \tag{VI.3}$$

so that the probability samples the relevant stochastic trajectories. Since the Langevin equation is local in time, and in particular the noise at any instant is uncorrelated to previous history, the probability distribution has the Markov property

$$\mathcal{P}(\boldsymbol{x}, t|\boldsymbol{x}_0, t_0) = \int \mathrm{d}^3\boldsymbol{x}_1\, \mathcal{P}(\boldsymbol{x}, t|\boldsymbol{x}_1, t_1)\, \mathcal{P}(\boldsymbol{x}_1, t_1|\boldsymbol{x}_0, t_0) \quad . \tag{VI.4}$$

Invoking the above trick $N-1$ times at regular time intervals of size $\Delta t = t_k - t_{k-1}$ (for all k) yields

$$\begin{aligned}\mathcal{P}(\boldsymbol{x}, t|\boldsymbol{x}_0, t_0) = \int \prod_{k=1}^{N-1} \mathrm{d}^3\boldsymbol{r}_k\, \mathcal{P}(\boldsymbol{r}_N = \boldsymbol{x}, t|\boldsymbol{r}_{N-1}, t_{N-1}) \cdots \mathcal{P}(\boldsymbol{r}_k, t_k|\boldsymbol{r}_{k-1}, t_{k-1}) \\ \times \mathcal{P}(\boldsymbol{r}_{k-1}, t_{k-1}|\boldsymbol{r}_{k-2}, t_{k-2}) \cdots \mathcal{P}(\boldsymbol{r}_2, t_2|\boldsymbol{r}_1, t_1)\, \mathcal{P}(\boldsymbol{r}_1, t_1|\boldsymbol{r}_0 = \boldsymbol{x}_0, t_0) \quad ,\end{aligned} \tag{VI.5}$$

which can be converted into a path integral in the limit $\Delta t \to 0$ ($N \to \infty$ keeping $t - t_0 = N\Delta t$ fixed).

We need to perform the noise averaging on propagators of the form $\mathcal{P}(\boldsymbol{y}, t' + \Delta t|\boldsymbol{y}', t')$. Using a Fourier representation of delta function, we can write the propagator as

$$\mathcal{P}(\boldsymbol{y}, t' + \Delta t|\boldsymbol{y}', t') = \left\langle \delta^3\left(\boldsymbol{y} - \boldsymbol{r}(t' + \Delta t)\right)\right\rangle\big|_{\boldsymbol{r}(t')=\boldsymbol{y}'} = \int \frac{\mathrm{d}^3\boldsymbol{k}}{(2\pi)^3}\, e^{i\boldsymbol{k}\cdot(\boldsymbol{y}-\boldsymbol{y}')+W} \quad , \tag{VI.6}$$

where

$$W = \ln\left\langle e^{-i\boldsymbol{k}\cdot\left[\boldsymbol{r}(t'+\Delta t)-\boldsymbol{r}(t')\right]}\right\rangle \quad , \tag{VI.7}$$

involves a portion of the stochastic trajectory

$$\Delta r_i \equiv r_i(t' + \Delta t) - r_i(t') = \int_{t'}^{t'+\Delta t} \mathrm{d}t_1 v_i(\boldsymbol{r}(t_1)) + \int_{t'}^{t'+\Delta t} \mathrm{d}t_1 u_i(t_1) \quad . \tag{VI.8}$$

The resulting expression for W will need to be evaluated in an expansion in Δt, keeping the leading order terms only. Cumulant expansion yields

$$W = \ln \left\langle e^{-ik_i \Delta r_i} \right\rangle \simeq -ik_i \left\langle \Delta r_i \right\rangle - \frac{1}{2} k_i k_j \left[\left\langle \Delta r_i \Delta r_j \right\rangle - \left\langle \Delta r_i \right\rangle \left\langle \Delta r_j \right\rangle \right] \quad , \tag{VI.9}$$

to the lowest order needed for our purposes. Averaging (VI.8) gives

$$\left\langle \Delta r_i \right\rangle \simeq v_i(\boldsymbol{r}(t'))\Delta t + O(\Delta t^{3/2}) \quad . \tag{VI.10}$$

For the higher order average, we need the expansion of (VI.8) up to $O(\Delta t^2)$, which reads as follows:

$$\Delta r_i = v_i(\boldsymbol{r}(t'))\Delta t + \partial_k v_i(\boldsymbol{r}(t')) \int_{t'}^{t'+\Delta t} \mathrm{d}t_1 \int_{t'}^{t_1} \mathrm{d}t_2 u_k(t_2) + \int_{t'}^{t'+\Delta t} \mathrm{d}t_1 u_i(t_1) \quad . \tag{VI.11}$$

Then straightforward algebra using averages of products of (VI.11) follows, which yields

$$\left\langle \Delta r_i \Delta r_j \right\rangle - \left\langle \Delta r_i \right\rangle \left\langle \Delta r_j \right\rangle = \mathcal{M}_{ij}(2D\Delta t) + O(\Delta t^{5/2}) \quad , \tag{VI.12}$$

where

$$\mathcal{M}_{ij} = \delta_{ij} + \Theta(0)\, \Delta t \left(\partial_j v_i + \partial_i v_j \right) \quad ,$$

This will then give

$$\mathcal{P}(\boldsymbol{y}, t' + \Delta t | \boldsymbol{y}', t') = \int \frac{\mathrm{d}^3 \boldsymbol{k}}{(2\pi)^3}\, e^{-\frac{1}{2}(2D\Delta t)\mathcal{M}_{ij} k_i k_j + i\boldsymbol{k}\cdot\left[\boldsymbol{y} - \boldsymbol{y}' - \boldsymbol{v}(\boldsymbol{y}')\Delta t\right]} \quad , \tag{VI.13}$$

which can be readily calculated to give

$$\mathcal{P}(\boldsymbol{y}, t' + \Delta t | \boldsymbol{y}', t') = \frac{1}{(4\pi D \Delta t)^{3/2}} \exp\left\{ -\frac{\Delta t}{4D} \left[\frac{(\boldsymbol{y} - \boldsymbol{y}')}{\Delta t} - \boldsymbol{v}(\boldsymbol{y}') \right]^2 - \frac{1}{2} \ln \det \mathcal{M} \right\} \quad . \tag{VI.14}$$

Noting that $\ln \det \mathcal{M} = \mathrm{tr} \ln \mathcal{M} \simeq \mathrm{tr} \Delta \mathcal{M} = 2\Theta(0)\Delta t\, [\boldsymbol{\nabla} \cdot \boldsymbol{v}(\boldsymbol{y}')]$, we obtain

$$\mathcal{P}(\boldsymbol{y}, t' + \Delta t | \boldsymbol{y}', t') = \frac{1}{(4\pi D \Delta t)^{3/2}} \exp\left\{ -\frac{\Delta t}{4D} \left[\frac{(\boldsymbol{y} - \boldsymbol{y}')}{\Delta t} - \boldsymbol{v}(\boldsymbol{y}') \right]^2 - \Theta(0)\, \Delta t\, [\boldsymbol{\nabla} \cdot \boldsymbol{v}(\boldsymbol{y}')] \right\} \quad . \tag{VI.15}$$

Taking the continuum limit in Eq. (VI.5) and inserting the relevant form of the infinitesimal propagator from above, we arrive at the following path integral representation for the probability distribution

$$\mathcal{P}(\boldsymbol{x}, t | \boldsymbol{x}_0, t_0) = \mathcal{N} \int_{\boldsymbol{r}(t_0) = \boldsymbol{x}_0}^{\boldsymbol{r}(t) = \boldsymbol{x}} \mathcal{D}\boldsymbol{r}(\tau)\, e^{-\mathcal{S}} \quad , \tag{VI.16}$$

where the action is defined as

$$\mathcal{S}[\boldsymbol{r}] = \int_{t_0}^{t} \mathrm{d}\tau \left[\frac{1}{4D} \Big(\dot{\boldsymbol{r}} - \boldsymbol{v}(\boldsymbol{r}) \Big)^2 + \Theta(0)\, \boldsymbol{\nabla} \cdot \boldsymbol{v}(\boldsymbol{r}) \right] \quad , \tag{VI.17}$$

and $\mathcal{N}$ is a normalization constant. We can now recover the specific results corresponding to the two cases of Ito and Stratonovich by using the value of the Heaviside step function at the origin $\Theta(0)$; Ito corresponds to $\Theta(0) = 0$ and Stratonovich corresponds to $\Theta(0) = 1/2$.

For the case when the drift velocity derives from a potential via $\boldsymbol{v}(\boldsymbol{r}) = -D\beta \boldsymbol{\nabla} U(\boldsymbol{r})$, Eqs. (VI.16) and

(VI.17) read

$$\mathcal{P}(\boldsymbol{x},t|\boldsymbol{x}_0,t_0) = \mathcal{N}\, e^{-\frac{1}{2}\beta[U(\boldsymbol{x})-U(\boldsymbol{x}_0)]} \int_{\boldsymbol{r}(t_0)=\boldsymbol{x}_0}^{\boldsymbol{r}(t)=\boldsymbol{x}} \mathcal{D}\boldsymbol{r}(\tau)\; e^{-\mathcal{S}_{\rm P}} \quad , \tag{VI.18}$$

where

$$\mathcal{S}_{\rm p}[\boldsymbol{r}] = \int_{t_0}^{t} {\rm d}\tau \left[\frac{\dot{\boldsymbol{r}}^2}{4D} + \frac{1}{4}\, D\,(\beta\boldsymbol{\nabla}U)^2 - \Theta(0)\, D\beta\boldsymbol{\nabla}^2 U \right] \quad . \tag{VI.19}$$

The above equations map to a Euclidean quantum mechanical path integral with the effective potential $\mathcal{W}(\boldsymbol{r}) = \frac{1}{4}\, D\,(\beta\boldsymbol{\nabla}U)^2 - \Theta(0)\, D\beta\boldsymbol{\nabla}^2 U$, whose generic form is clearly not directly related to that of $U(\boldsymbol{r})$.

B. Path integrals and constraints

There is a powerful method to arrive at the path integral representation of the stochastic dynamics using integral representation of constraints.

To see the essence of the method, let us first consider a coordinate transformation $\boldsymbol{x} \mapsto \boldsymbol{y}$, described via $y_i = f_i(\boldsymbol{x})$, in an n-dimensional Euclidean space. Assuming that the transformation can be inverted for sufficiently small $\boldsymbol{y}$, we can project any function $U(\boldsymbol{x})$ onto the $\boldsymbol{y} = 0$ sector by using the following transformation:

$$U(\boldsymbol{x})|_{\mathbf{f}(\boldsymbol{x})=0} = \int {\rm d}^n\boldsymbol{y}\, \delta^n(\boldsymbol{y})\, U\big(\boldsymbol{x}(\boldsymbol{y})\big) = \int {\rm d}^n\boldsymbol{x}\, \delta^n\big(\mathbf{f}(\boldsymbol{x})\big)\, J(\boldsymbol{x})\, U(\boldsymbol{x}) = \int {\rm d}^n\boldsymbol{x} \int \frac{{\rm d}^n\boldsymbol{\lambda}}{(2\pi)^n}\, e^{i\boldsymbol{\lambda}\cdot\mathbf{f}(\boldsymbol{x})}\, J(\boldsymbol{x})\, U(\boldsymbol{x}) \quad , \tag{VI.20}$$

where $J(\boldsymbol{x}) = |\det \partial_j f_i|$ is the Jacobian of the transformation and λ_i are Lagrange multipliers enforcing the constraints imposed by the delta functions.

We can now employ this method to enforce the Langevin equation [Eq. (VI.1)]. Let us consider a "partition function"

$$Z = \int \mathcal{D}\boldsymbol{r}(t)\; \delta\left\{\dot{\boldsymbol{r}} - \boldsymbol{v}(\boldsymbol{r}) - \boldsymbol{u}(t)\right\}\; \mathcal{J} \quad , \tag{VI.21}$$

where the functional delta function $\delta\{\cdots\}$ enforces the constraint at all times and $\mathcal{J}$ is the relevant Jacobian. Note that $Z = 1$ (or a constant, depending on the choice of normalization). We can rewrite the above expression by introducing a functional Lagrange multiplier as follows

$$Z = \int \mathcal{D}\boldsymbol{r}(t)\mathcal{D}\boldsymbol{\lambda}(t)\; \exp\left\{ i \int {\rm d}t\, \boldsymbol{\lambda}(t)\cdot[\dot{\boldsymbol{r}}(t) - \boldsymbol{v}(\boldsymbol{r}(t)) - \boldsymbol{u}(t)] \right\}\; \mathcal{J} \quad . \tag{VI.22}$$

The Jacobian is defined as $\mathcal{J} = \det\mathcal{K}$, in terms of the matrix

$$\mathcal{K}_{ij}(t,t') = \left[\delta_{ij}\frac{\rm d}{{\rm d}t} - \partial_j v_i \right] \delta(t-t') \quad , \tag{VI.23}$$

which is the functional derivative of the Langevin equation with respect to $\boldsymbol{r}(t')$. To simplify the calculation of the determinant, it is helpful to factorize the operator $\frac{\rm d}{{\rm d}t}$, which is independent of $\boldsymbol{r}$, and define $\mathcal{K} = \left(\frac{\rm d}{{\rm d}t}\right)\mathcal{M}$, where

$$\mathcal{M}_{ij}(t,t') = \delta_{ij}\,\delta(t-t') - \partial_j v_i\,\Theta(t-t') \quad , \tag{VI.24}$$

Then, we have

$$Z = \mathcal{N} \int \mathcal{D}\boldsymbol{r}(t)\mathcal{D}\boldsymbol{\lambda}(t)\ \exp\left\{ i \int \mathrm{d}t\, \boldsymbol{\lambda}(t) \cdot [\dot{\boldsymbol{r}}(t) - \boldsymbol{v}(\boldsymbol{r}(t)) - \boldsymbol{u}(t)] + \ln\det \mathcal{M} \right\} \quad , \tag{VI.25}$$

where $\mathcal{N}$ is a constant. Using the identity $\ln\det\mathcal{M} = \mathrm{tr}\ln\mathcal{M}$, we can write

$$\begin{aligned} \mathrm{tr}\ln\mathcal{M} \ &= \ -\Theta(0)\int \mathrm{d}t\, \partial_i v_i(t) - \frac{1}{2}\int \mathrm{d}t_1 \mathrm{d}t_2\, \Theta(t_1 - t_2)\Theta(t_2 - t_1)\, \partial_j v_i(t_1)\partial_i v_j(t_2) + \cdots \\ &- \ \frac{1}{n}\int \mathrm{d}t_1 \cdots \mathrm{d}t_n\, \Theta(t_1 - t_2)\cdots\Theta(t_n - t_1)\, \mathrm{tr}\left[\partial v(t_1)\cdots\partial v(t_n)\right] + \cdots \quad , \end{aligned} \tag{VI.26}$$

which manifestly shows that only the first term in the expansion contributes due to mutual exclusion of time intervals at higher orders. Therefore, we find

$$Z = \mathcal{N} \int \mathcal{D}\boldsymbol{r}(t)\mathcal{D}\boldsymbol{\lambda}(t)\ \exp\left\{ i \int \mathrm{d}t\, \boldsymbol{\lambda}(t) \cdot [\dot{\boldsymbol{r}}(t) - \boldsymbol{v}(\boldsymbol{r}(t)) - \boldsymbol{u}(t)] - \Theta(0)\int \mathrm{d}t\, \boldsymbol{\nabla}\cdot\boldsymbol{v}(\boldsymbol{r}(t)) \right\} \quad . \tag{VI.27}$$

We can next average over noise using the Gaussian distribution given in Eq. (VI.2), and obtain

$$Z = \mathcal{N} \int \mathcal{D}\boldsymbol{r}(t)\mathcal{D}\boldsymbol{\lambda}(t)\ \exp\left\{ -\int \mathrm{d}t \left[D\boldsymbol{\lambda}(t)^2 - i\boldsymbol{\lambda}(t)\cdot\Big(\dot{\boldsymbol{r}}(t) - \boldsymbol{v}(\boldsymbol{r}(t))\Big) + \Theta(0)\boldsymbol{\nabla}\cdot\boldsymbol{v}(\boldsymbol{r}(t)) \right] \right\} \quad , \tag{VI.28}$$

where $Z = \langle Z \rangle$ is implemented, as $Z = 1$ by construction. Finally, integrating over the Lagrange multiplier yields

$$Z = \mathcal{N} \int \mathcal{D}\boldsymbol{r}(t)\ e^{-\mathcal{S}} \quad , \tag{VI.29}$$

where the action reads

$$\mathcal{S}[\boldsymbol{r}] = \int \mathrm{d}t \left[\frac{1}{4D}\Big(\dot{\boldsymbol{r}} - \boldsymbol{v}(\boldsymbol{r})\Big)^2 + \Theta(0)\boldsymbol{\nabla}\cdot\boldsymbol{v}(\boldsymbol{r}) \right] \quad , \tag{VI.30}$$

as in Eq. (VI.17). Note that our more formal derivation in this section shows more explicitly why the choice of $\Theta(0)$ adequately captures the Ito/Stratonovich dilemma. We can repeat the above calculation for $\mathcal{P}(\boldsymbol{x}, t|\boldsymbol{x}_0, t_0)$ by inserting a $\delta^3\left(\boldsymbol{x} - \boldsymbol{r}(t)\right)$ at the start [Eq. (VI.21)]. The resulting calculation will be a straightforward generalization of the above, and will lead to Eqs. (VI.16) and (VI.17).

C. Quantum mechanical analogy: the Fokker-Planck Hamiltonian

The Markov property of stochastic dynamics lends itself to a very interesting quantum mechanical analogy. Starting from Eq. (VI.5), we can conveniently introduce the quantum mechanical notation of bras and kets for the propagators as

$$\mathcal{P}(\boldsymbol{x}, t|\boldsymbol{x}_0, t_0) \equiv \langle \boldsymbol{x}|\, P(t, t_0)\, |\boldsymbol{x}_0\rangle \quad , \tag{VI.31}$$

where

$$P(t, t_0) = e^{-(t - t_0)\mathcal{H}} \quad , \tag{VI.32}$$

is the corresponding evolution operator defined in terms of the Fokker-Planck Hamiltonian $\mathcal{H}$. Here, we have assumed time translation invariance, although a generalization to time-dependent forces is straightforward. Note that the corresponding quantum mechanical description involves an imaginary time, and it is called Euclidean quantum mechanics.

To derive an expression for the Fokker-Planck Hamiltonian, we go back to the transition probability for an infinitesimal time interval Δt given in Eq. (VI.13), namely

$$\langle \boldsymbol{y}| \, e^{-\Delta t \mathcal{H}} \, |\boldsymbol{y}'\rangle = \int \frac{\mathrm{d}^3\boldsymbol{k}}{(2\pi)^3} \, e^{-D\Delta t\left[\delta_{ij}+\Theta(0)\Delta t(\partial_j v_i+\partial_i v_j)\right]k_i k_j + i\boldsymbol{k}\cdot\left[\boldsymbol{y}-\boldsymbol{y}'-\boldsymbol{v}(\boldsymbol{y}')\Delta t\right]} \quad . \tag{VI.33}$$

Expanding both sides in Δt to the first order, we obtain

$$\begin{aligned} \langle \boldsymbol{y}| \, \mathcal{H} \, |\boldsymbol{y}'\rangle \; &= \; \int \frac{\mathrm{d}^3\boldsymbol{k}}{(2\pi)^3} \, e^{i\boldsymbol{k}\cdot(\boldsymbol{y}-\boldsymbol{y}')} \left[Dk^2 + i\boldsymbol{k}\cdot\boldsymbol{v}(\boldsymbol{y}')\right] \\ &= \; \left[-D\boldsymbol{\nabla}^2 + \boldsymbol{\nabla}\cdot\boldsymbol{v}(\boldsymbol{y})\right]\delta^3(\boldsymbol{y}-\boldsymbol{y}') \quad . \end{aligned} \tag{VI.34}$$

In terms of a momentum operator $\hat{\boldsymbol{p}} \equiv \frac{1}{i}\boldsymbol{\nabla}$ in quantum mechanical analogy ($\hbar = 1$), and a corresponding position operator $\hat{\boldsymbol{x}}$, the Hamiltonian reads

$$\mathcal{H} = D\hat{\boldsymbol{p}}^2 + i\hat{\boldsymbol{p}}\cdot\boldsymbol{v}(\hat{\boldsymbol{x}}) \quad . \tag{VI.35}$$

Using this Hamiltonian, we can write the quantum mechanical evolution equation as

$$\frac{\mathrm{d}P(t)}{\mathrm{d}t} = -\mathcal{H}\,P(t) \quad , \tag{VI.36}$$

which in position-space corresponds to the Fokker-Planck equation

$$\partial_t \mathcal{P}(\boldsymbol{x},t) = D\,\boldsymbol{\nabla}^2\mathcal{P}(\boldsymbol{x},t) - \boldsymbol{\nabla}\cdot\left[\boldsymbol{v}(\boldsymbol{x})\,\mathcal{P}(\boldsymbol{x},t)\right] \quad , \tag{VI.37}$$

Note that the Fokker-Planck Hamiltonian is *not* Hermitian. As a consequence its action on left (bra) and right (ket) will be different, and in particular, its left and right eigenvectors do not coincide. To explore this further, let us focus on the long-time stationary solution of the Fokker-Planck equation $\mathcal{P}_0(\boldsymbol{x})$, which may or may not correspond to thermal equilibrium. The solution corresponds to a ground state (vacuum) $|0\rangle$ which should be a right eigenvector of $\mathcal{H}$ with eigenvalue 0, i.e. $\mathcal{H}\,|0\rangle = 0$, and could be represented as $\mathcal{P}_0(\boldsymbol{x}) = \langle \boldsymbol{x}|0\rangle$. On the other hand, due to the conservation of probability, the Hamiltonian has an overall factor of $\boldsymbol{\nabla}$, which suggest that a left eigenvector with eigenvalue 0 can be constructed using a constant, i.e. $\langle 0|\,\mathcal{H} = 0$ with $\langle 0|\boldsymbol{x}\rangle = 1$. Combining these, we can show that the ground state exits as it is normalizable

$$\langle 0|0\rangle = \langle 0| \overbrace{\int \mathrm{d}^3\boldsymbol{x} \; |\boldsymbol{x}\rangle \, \langle \boldsymbol{x}|}^{I} |0\rangle = \int \mathrm{d}^3\boldsymbol{x} \, \mathcal{P}_0(\boldsymbol{x}) = 1 \quad . \tag{VI.38}$$

We note that the quantum mechanical formulation can be readily used to construct the backward Fokker-Planck equation, discussed in Sec. II.B.3.

1. Conservative systems

When the drift velocity can be described using a potential via $\boldsymbol{v}(\boldsymbol{x}) = -D\beta\boldsymbol{\nabla}U(\boldsymbol{x})$, it is possible to use a transformation to map the system to an alternative quantum mechanical representation for the stochastic dynamics in terms of a Hermitian Hamiltonian. The transformation is constructed as follows

$$\mathcal{P}(\boldsymbol{x},t|\boldsymbol{x}_0,t_0) \equiv e^{-\beta U(\boldsymbol{x})/2} \, \langle \boldsymbol{x}| \, Q(t,t_0) \, |\boldsymbol{x}_0\rangle \, e^{\beta U(\boldsymbol{x}_0)/2} \quad , \tag{VI.39}$$

with the aim of removing the asymmetry between the left and right eigenvectors. It yields

$$\partial_t \langle \boldsymbol{x}| Q(t,t_0) |\boldsymbol{x}_0\rangle = -D\left[-\boldsymbol{\nabla} + \frac{1}{2}\boldsymbol{\nabla}\beta U\right]\left[\boldsymbol{\nabla} + \frac{1}{2}\boldsymbol{\nabla}\beta U\right]\langle \boldsymbol{x}| Q(t,t_0) |\boldsymbol{x}_0\rangle \quad , \tag{VI.40}$$

which can written in operator form as

$$\partial_t Q(t,t_0) = -\widetilde{\mathcal{H}}\, Q(t,t_0) \quad , \tag{VI.41}$$

where the Hamiltonian reads

$$\widetilde{\mathcal{H}} = D\left[-i\hat{\boldsymbol{p}} + \frac{1}{2}\boldsymbol{\nabla}\beta U(\hat{\boldsymbol{x}})\right]\left[i\hat{\boldsymbol{p}} + \frac{1}{2}\boldsymbol{\nabla}\beta U(\hat{\boldsymbol{x}})\right] = D\left[\hat{\boldsymbol{p}}^2 + \frac{1}{4}\big(\boldsymbol{\nabla}\beta U(\hat{\boldsymbol{x}})\big)^2 - \frac{1}{2}\boldsymbol{\nabla}^2\beta U(\hat{\boldsymbol{x}})\right] \quad . \tag{VI.42}$$

We can define an operator

$$\hat{\mathbf{A}} = i\hat{\boldsymbol{p}} + \frac{1}{2}\boldsymbol{\nabla}\beta U(\hat{\boldsymbol{x}}) \quad , \tag{VI.43}$$

and use it to write the Hamiltonian as

$$\widetilde{\mathcal{H}} = D\,\hat{\mathbf{A}}^\dagger \cdot \hat{\mathbf{A}} \quad , \tag{VI.44}$$

which manifestly shows that it is positive and Hermitian. The ground state of the transformed Hamiltonian defined via $\widetilde{\mathcal{H}}\,|0\rangle = 0$ can be found by solving the following equation

$$\hat{\mathbf{A}}\,|0\rangle = 0 \quad , \tag{VI.45}$$

which in position space gives

$$\langle \boldsymbol{x}|\,\hat{\mathbf{A}}\,|0\rangle = \left[\boldsymbol{\nabla} + \frac{1}{2}\boldsymbol{\nabla}\beta U\right]\langle \boldsymbol{x}|0\rangle = 0 \qquad \Longrightarrow \qquad \langle \boldsymbol{x}|0\rangle = \frac{1}{\sqrt{\mathcal{Z}}}\, e^{-\beta U(\boldsymbol{x})/2} \quad , \tag{VI.46}$$

where $\mathcal{Z}$ is the partition function (see the normalization argument below). Similarly, we find $\langle 0|\boldsymbol{x}\rangle = \frac{1}{\sqrt{\mathcal{Z}}}\, e^{-\beta U(\boldsymbol{x})/2}$, and can therefore prove that the ground state is normalizable

$$\langle 0|0\rangle = \int \mathrm{d}^3\boldsymbol{x}\ \langle 0|\boldsymbol{x}\rangle\,\langle \boldsymbol{x}|0\rangle = \frac{1}{\mathcal{Z}}\int \mathrm{d}^3\boldsymbol{x}\, e^{-\beta U(\boldsymbol{x})} = 1 \quad . \tag{VI.47}$$

Moreover, in the long time limit, the operator $Q(t,t_0) = e^{-(t-t_0)\widetilde{\mathcal{H}}}$ projects onto the ground state, which helps us calculate the long time limit of the original system as

$$\mathcal{P}_0(\boldsymbol{x}) = \lim_{t\to\infty}\mathcal{P}(\boldsymbol{x},t|\boldsymbol{x}_0,t_0) = e^{-\beta U(\boldsymbol{x})/2}e^{\beta U(\boldsymbol{x}_0)/2}\,\langle \boldsymbol{x}|0\rangle\,\langle 0|\boldsymbol{x}_0\rangle = \frac{1}{\mathcal{Z}}\, e^{-\beta U(\boldsymbol{x})} \quad , \tag{VI.48}$$

which gives us equilibration.

2. Path integral formulation for orientation

The stochastic dynamics of orientation as formulated in Sec. II.C can also be represented via path integrals. For a free particle, a similar analysis to what was discussed in Sec. VI.A can be used to find the following path integral representation

$$\mathcal{P}(\hat{\boldsymbol{n}},t|\hat{\boldsymbol{n}}_0,t_0) = \int_{\hat{\boldsymbol{n}}(t_0)=\hat{\boldsymbol{n}}_0}^{\hat{\boldsymbol{n}}(t)=\hat{\boldsymbol{n}}} \mathcal{D}\hat{\boldsymbol{n}}(\tau)\, e^{-\int_{t_0}^{t}\mathrm{d}\tau\,\dot{\hat{\boldsymbol{n}}}^2/(4D_r)} \quad . \tag{VI.49}$$

In the quantum mechanical analogy, we can define a Hamiltonian through

$$\mathcal{P}(\hat{\boldsymbol{n}},t|\hat{\boldsymbol{n}}_0,t_0) \equiv \langle\hat{\boldsymbol{n}}|\, P(t,t_0)\,|\hat{\boldsymbol{n}}_0\rangle \quad , \tag{VI.50}$$

where the evolution operator $P(t,t_0)$ is defined as in Eq. (VI.32). This yields

$$\mathcal{H} = D_r\hat{\mathbf{L}}^2 = -D_r\boldsymbol{\mathcal{R}}^2 \quad , \tag{VI.51}$$

in terms of an angular momentum operator

$$\hat{\mathbf{L}} \equiv \hat{\boldsymbol{n}} \times \frac{1}{i}\frac{\partial}{\partial\hat{\boldsymbol{n}}} = \frac{1}{i}\boldsymbol{\mathcal{R}} \quad . \tag{VI.52}$$

Generalization to the case of driven systems (with nonzero angular velocity) is straightforward.

D. Path integral formulation on manifolds

In Sec. V.C, we have developed a formulation to study the stochastic dynamics of particles on Riemannian manifolds, and derived the corresponding covariant Fokker-Planck equation. Here, we develop an alternative path integral formulation. While we can construct the path integral formulation using the approach described in Sec. VI.A, we use the method we developed in Sec. VI.B instead. The starting point is to build up the probability distribution subject to the constraint that the dynamical Langevin equation [Eq. (V.52)] is satisfied by the stochastic trajectory. This yields

$$\mathcal{P}(\boldsymbol{x},t|\boldsymbol{x}_0,t_0) = \int_{\boldsymbol{r}(t_0)=\boldsymbol{x}_0}^{\boldsymbol{r}(t)=\boldsymbol{x}} \mathcal{D}r^k(\tau)\ \left\langle \delta\left\{\dot{r}^i(\tau) - v^i\left(\boldsymbol{r}(\tau)\right) - \sqrt{2D}\, e_a^i(\boldsymbol{r}(\tau))\,\xi_a(\tau)\right\}\ \mathcal{J}\right\rangle \quad , \tag{VI.53}$$

where the Jacobian is given by $\mathcal{J} = \det\mathcal{M}$ (up to a normalization constant) where

$$\mathcal{M}^i_j(\tau,\tau') = \delta^i_j\,\delta(\tau-\tau') - \left(\partial_j v^i + \sqrt{2D}\,\partial_j e^i_a\,\xi_a\right)\Theta(\tau-\tau') \quad . \tag{VI.54}$$

Following the steps detailed in Sec. VI.B, we obtain

$$\det\mathcal{M} = \exp\left\{-\Theta(0)\int \mathrm{d}\tau\left[\partial_i v^i + \sqrt{2D}\,\partial_i e^i_a\,\xi_a\right]\right\} \quad , \tag{VI.55}$$

which can be put back in Eq. (VI.53) to yield

$$\begin{aligned}\mathcal{P}(\boldsymbol{x},t|\boldsymbol{x}_0,t_0) = &\int_{\boldsymbol{r}(t_0)=\boldsymbol{x}_0}^{\boldsymbol{r}(t)=\boldsymbol{x}} \mathcal{D}r^k(\tau)\int\mathcal{D}\lambda_l(\tau)\\ &\times\left\langle \exp\left\{i\int\mathrm{d}\tau\ \lambda_i\left[\dot{r}^i - v^i - \sqrt{2D}\,e^i_a\,\xi_a\right] - \Theta(0)\int\mathrm{d}\tau\left[\partial_i v^i + \sqrt{2D}\,\partial_i e^i_a\,\xi_a\right]\right\}\right\rangle \quad ,\end{aligned} \tag{VI.56}$$

upon introducing the Lagrange multiplier field λ_i. We can now perform the averaging over the Gaussian white noise to obtain

$$\begin{aligned}\mathcal{P}(\boldsymbol{x},t|\boldsymbol{x}_0,t_0) = &\int_{\boldsymbol{r}(t_0)=\boldsymbol{x}_0}^{\boldsymbol{r}(t)=\boldsymbol{x}} \mathcal{D}r^k(\tau)\int\mathcal{D}\lambda_l(\tau)\\ &\times\exp\left\{-\int\mathrm{d}\tau\left[Dg^{ij}\lambda_i\lambda_j - i\lambda_i\Big(\dot{r}^i - v^i + 2D\Theta(0)\,e^i_a\partial_j e^j_a\Big) + \Theta(0)\partial_i v^i - \Theta(0)^2 D\partial_i\,e^i_a\partial_j e^j_a\right]\right\} \quad .\end{aligned} \tag{VI.57}$$

Finally, we can now perform the λ integration to find

$$\mathcal{P}(\boldsymbol{x},t|\boldsymbol{x}_0,t_0) = \int_{\boldsymbol{r}(t_0)=\boldsymbol{x}_0}^{\boldsymbol{r}(t)=\boldsymbol{x}} \prod_\tau \mathrm{d}^d\boldsymbol{r}(\tau)\sqrt{g(\boldsymbol{r}(\tau))}\ e^{-\mathcal{S}_g} \quad , \tag{VI.58}$$

where the action is given as

$$\mathcal{S}_g = \int \mathrm{d}\tau \left[\frac{1}{4D}\, g_{ij}\left(\dot{r}^i - v^i\right)\left(\dot{r}^j - v^j\right) + \Theta(0)\, g_{ij}\left(\dot{r}^i - v^i\right)\, e^j_a \nabla_k e^k_a + \Theta(0)\,\nabla_i v^i\right] \quad , \tag{VI.59}$$

where the covariant divergence is defined in Eq. (V.65). To obtain cancelations between the $(\partial e)(\partial e)$ terms we have assumed that e^i_a form a *vielbein*, i.e. $g_{ij}e^i_a e^j_b = \delta_{ab}$. We have also ignored a boundary term. Note that the process of integration over the Lagrange multiplier has generated the $\sqrt{g}$ factor, which makes the functional integration measure over r^k manifestly covariant. Equation (VI.59), which the generalization of Eq. (VI.30), is consistent with Eq. (V.69) provided $\Theta(0) = 1/2$.

VII. NONEQUILIBRIUM FLUCTUATIONS AND RESPONSE

A. Conservation laws in stochastic dynamics

Before embarking on a formal development of stochastic thermodynamics, let us first examine the global conservation laws that are embedded in the Fokker-Planck description of stochastic dynamics. Let us consider the Klein-Kramers equation that we derived in Sec. V.A, in the case where the friction coefficient ζ and the temperature T do not depend on space

$$\partial_t \mathcal{P}(\boldsymbol{x},\boldsymbol{p},t) = -\boldsymbol{\nabla}_{\boldsymbol{x}} \cdot \left[\frac{\boldsymbol{p}}{m}\,\mathcal{P}(\boldsymbol{x},\boldsymbol{p},t)\right] - \boldsymbol{\nabla}_{\boldsymbol{p}} \cdot \left[\left(\boldsymbol{F}(\boldsymbol{x}) - \zeta\,\frac{\boldsymbol{p}}{m}\right)\,\mathcal{P}(\boldsymbol{x},\boldsymbol{p},t)\right] + \zeta\, k_{\mathrm{B}} T \boldsymbol{\nabla}_{\boldsymbol{p}}^2 \mathcal{P}(\boldsymbol{x},\boldsymbol{p},t) \quad , \tag{VII.1}$$

and produce the first three global moments of momentum, namely equations for $\langle 1\rangle$, $\langle \boldsymbol{p}\rangle$, and $\left\langle \frac{\boldsymbol{p}^2}{2m}\right\rangle$, where the average is defined as

$$\langle \cdots \rangle \equiv \int \mathrm{d}^3\boldsymbol{x}\mathrm{d}^3\boldsymbol{p}\, \cdots\, \mathcal{P}(\boldsymbol{x},\boldsymbol{p},t) \quad . \tag{VII.2}$$

These global averages are not to be confused with the local average defined in Sec. V.A. The zeroth moment gives us a statement of number conservation, while the first moment yields

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \boldsymbol{p}\rangle = \langle \boldsymbol{F}\rangle - \zeta \left\langle \frac{\boldsymbol{p}}{m}\right\rangle \quad , \tag{VII.3}$$

which is a statement of conservation of momentum. In particular, for isolated systems where the overall momentum is expected to be conserved, Eq. (VII.3) gives us $\left\langle \frac{\boldsymbol{p}}{m}\right\rangle = \frac{1}{\zeta}\langle \boldsymbol{F}\rangle$, which is simple global statement of force balance. This shows, for example, that if the overall average force on the system is not zero, we need to be careful when considering averages of moments of $\boldsymbol{p}$, as its net average is nonzero. The second global moment, which we can write in terms of the velocity $\boldsymbol{v} = \boldsymbol{p}/m$ is found as

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\langle \frac{1}{2}m\boldsymbol{v}^2\right\rangle = \langle \boldsymbol{F}\cdot\boldsymbol{v}\rangle - \zeta\left\langle \boldsymbol{v}^2\right\rangle + 3\,\zeta\,\frac{k_{\mathrm{B}}T}{m} \quad . \tag{VII.4}$$

This is a statement of conservation of kinetic energy. For a generic force $\boldsymbol{F} = -\boldsymbol{\nabla}U + \boldsymbol{f}$, composed of a conservative component derived from potential energy U and a non-conservative component $\boldsymbol{f}$ (that is, perhaps, applied externally), Eq. (VII.4) can be recast into a statement of conservation of total internal energy as

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\langle \frac{1}{2}m\boldsymbol{v}^2 + U\right\rangle = \langle \boldsymbol{f}\cdot\boldsymbol{v}\rangle - \zeta\left\langle \boldsymbol{v}^2\right\rangle + 3\,\zeta\,\frac{k_{\mathrm{B}}T}{m} \quad . \tag{VII.5}$$

In particular, this global statement can be written in the notation of the first law of thermodynamics, as

$$\dot{W}_{\mathrm{ext}} = \dot{Q}_{\mathrm{out}} - \dot{Q}_{\mathrm{in}} + \dot{E}_{\mathrm{int}} \quad , \tag{VII.6}$$

where $\dot{Q}_{\mathrm{out}} = \zeta\left\langle \boldsymbol{v}^2\right\rangle$ is the work done by viscous drag force that is converted into heat and released to the medium, $\dot{Q}_{\mathrm{in}} = 3\zeta\, k_{\mathrm{B}}T/m$ is the work done by the stochastic Brownian force that is extracted from the thermal bath, $\dot{E}_{\mathrm{int}} = \frac{\mathrm{d}}{\mathrm{d}t}\left\langle \frac{1}{2}m\boldsymbol{v}^2 + U\right\rangle$ is the change in the internal energy of the system, and $\dot{W}_{\mathrm{ext}} = \langle \boldsymbol{f}\cdot\boldsymbol{v}\rangle$ is the work done by the external force.

B. Stochastic thermodynamics and fluctuation theorems

How can we generalize well-known concepts from thermodynamics to stochastic trajectories that are defined over finite periods of time and depend on initial conditions? The conservation laws derived in Sec. VII.A, which included a statement of the first law of thermodynamics, were constructed at the global scale. Moreover, they were derived from a phase-space description of the stochastic dynamics that had direct access to the kinetic energy via the momentum variable. We would like to develop stochastic thermodynamic concepts and tools using the position space description. This is the subject of a recently established field of stochastic thermodynamics, which has been presented in the literature using a variety different styles; here, we follow the pedagogical style of Seifert.

1. Small-systems: from trajectory to thermodynamics

We start by setting out the formal structure of the system under consideration, which is a particle undergoing stochastic dynamics under the influence of a force $\boldsymbol{F}$, which is composed of conservative and non-conservative components:

$$\boldsymbol{F}(\boldsymbol{r},\lambda) = -\boldsymbol{\nabla} U(\boldsymbol{r},\lambda) + \boldsymbol{f}(\boldsymbol{r},\lambda). \tag{VII.7}$$

We have assumed that the force could have a time-dependence through an external control parameter λ. The dynamics is described by the Langevin equation

$$\frac{\mathrm{d}\boldsymbol{r}}{\mathrm{d}\tau} = \mu \boldsymbol{F}(\boldsymbol{r},\lambda) + \boldsymbol{u}(\tau) \quad , \tag{VII.8}$$

where $\boldsymbol{u}$ is a Gaussian white noise with zero mean and variance $\langle u_i(\tau) u_j(\tau')\rangle = 2D\delta_{ij}\delta(\tau-\tau')$. We assume that Einstein relation holds, i.e. $D = \mu k_{\mathrm{B}} T$. The stochastic dynamics leads to the following Fokker-Planck equation

$$\partial_t \mathcal{P}(\boldsymbol{x},t) = -\boldsymbol{\nabla}\cdot\boldsymbol{J}(\boldsymbol{x},t), \tag{VII.9}$$

for the probability distribution $\mathcal{P}(\boldsymbol{x},t)$, where the (average) particle flux is defined as

$$\boldsymbol{J}(\boldsymbol{x},t) = -D\boldsymbol{\nabla}\mathcal{P}(\boldsymbol{x},t) + \mu \boldsymbol{F}(\boldsymbol{r},\lambda)\,\mathcal{P}(\boldsymbol{x},t). \tag{VII.10}$$

We will also use the path integral representation for the probability distribution

$$\mathcal{P}(\boldsymbol{x},t|\boldsymbol{x}_0,0) = \int_{\boldsymbol{r}(0)=\boldsymbol{x}_0}^{\boldsymbol{r}(t)=\boldsymbol{x}} \mathcal{D}\boldsymbol{r}(\tau)\; \mathsf{P}[\boldsymbol{r}(\tau)|\boldsymbol{x}_0] \quad , \tag{VII.11}$$

where the probability (weight) functional is defined as

$$\mathsf{P}[\boldsymbol{r}(\tau)|\boldsymbol{x}_0] = \mathcal{N}\, e^{-\mathcal{S}[\boldsymbol{r}(\tau)]} \quad , \tag{VII.12}$$

using the action

$$\mathcal{S}[\boldsymbol{r}(\tau)] = \int_0^t \mathrm{d}\tau \left[\frac{1}{4D}\Big(\dot{\boldsymbol{r}} - \mu\boldsymbol{F}(\boldsymbol{r})\Big)^2 + \Theta(0)\,\mu\boldsymbol{\nabla}\cdot\boldsymbol{F}(\boldsymbol{r})\right] \quad , \tag{VII.13}$$

and a normalization constant $\mathcal{N}$. Since the trajectories are defined over a finite time period $0<\tau<t$, and consequently, the probability functionals are conditional on initial position $\boldsymbol{x}_0$, the complete expectation

value of any physical quantity Ω will be defined as

$$\langle \Omega[\boldsymbol{r}] \rangle = \int \mathrm{d}^3\boldsymbol{x}\, \mathrm{d}^3\boldsymbol{x}_0 \int_{\boldsymbol{r}(0)=\boldsymbol{x}_0}^{\boldsymbol{r}(t)=\boldsymbol{x}} \mathcal{D}\boldsymbol{r}(\tau)\; \Omega[\boldsymbol{r}(\tau)]\, \mathsf{P}[\boldsymbol{r}(\tau)|\boldsymbol{x}_0]\, \mathcal{P}(\boldsymbol{x}_0) \quad , \tag{VII.14}$$

where an averaging over the initial position is performed in addition to the summation over all conditional paths.

2. The stochastic first law

A formal and mathematically consistent scheme has been put forward by Sekimoto to endow the dissipative Langevin dynamics in position space with stochastic thermodynamic interpretations. We aim to make a statement of the first law of the form

$$đ w = \mathrm{d}E + đ q \quad , \tag{VII.15}$$

using thermodynamic quantities representing work w, heat q, and internal energy E, which we define using a finite stochastic trajectory. We adopt the notation in which the work done on the system and the heat dissipated to the environment are taken as positive. Guided by what would be a natural choice at equilibrium, we set $E = U(\boldsymbol{r}, \lambda)$, and define heat as the work done by the total force $\boldsymbol{F}$ on the particle

$$đ q = \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{r} \quad , \tag{VII.16}$$

which is entirely dissipated and transfered into the environment. Using $\mathrm{d}U = \boldsymbol{\nabla} U \cdot \mathrm{d}\boldsymbol{r} + \partial_\lambda U\, \mathrm{d}\lambda$ and $đ q = \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{r} = -\boldsymbol{\nabla} U \cdot \mathrm{d}\boldsymbol{r} + \boldsymbol{f} \cdot \mathrm{d}\boldsymbol{r}$, we find that our statement of first law [Eq. (VII.15)] is formally equivalent to the following definition for work

$$đ w = \mathrm{d}U + đ q = \partial_\lambda U\, \mathrm{d}\lambda + \boldsymbol{f} \cdot \mathrm{d}\boldsymbol{r} \quad , \tag{VII.17}$$

which is consistent with our expectation: applying work to the particle can be achieved via the time-dependence in the potential and the external force.

We can now integrate the increments over the finite time period of interest, and obtain expressions for total work

$$w[\boldsymbol{r}(\tau)] = \int_0^t \mathrm{d}\tau \left[\partial_\lambda U\, \dot{\lambda} + \boldsymbol{f} \cdot \dot{\boldsymbol{r}} \right] \quad , \tag{VII.18}$$

and total heat

$$q[\boldsymbol{r}(\tau)] = \int_0^t \mathrm{d}\tau\, \boldsymbol{F} \cdot \dot{\boldsymbol{r}} \quad , \tag{VII.19}$$

which satisfy the integrated first law as

$$w[\boldsymbol{r}(\tau)] = q[\boldsymbol{r}(\tau)] + U(\boldsymbol{x}, \lambda(t)) - U(\boldsymbol{x}_0, \lambda(0)) \quad , \tag{VII.20}$$

at the level of an individual trajectory.

We now make an observation about the expression for the heat dissipated along a trajectory [Eq. (VII.19)]: it corresponds exactly to the cross term that one obtains by expanding the square in Eq. (VII.13). Since this cross term also happens to be the only term in Eq. (VII.13) that is odd under time

reversal transformation, we can write the following expression for stochastic heat

$$q[\boldsymbol{r}(\tau)] = -k_{\mathrm{B}}T\Big(\mathcal{S}[\boldsymbol{r}(\tau)] - \mathcal{S}[\boldsymbol{r}(t-\tau)]\Big) = -k_{\mathrm{B}}T\Big(\mathcal{S}[\boldsymbol{r}(\tau)] - \mathcal{S}[\tilde{\boldsymbol{r}}(\tau)]\Big) \quad , \tag{VII.21}$$

where we have defined the *time-reversed* trajectory $\tilde{\boldsymbol{r}}(\tau) \equiv \boldsymbol{r}(t-\tau)$ under the time-reversed protocol for the control parameter $\tilde{\lambda}(\tau) \equiv \lambda(t-\tau)$. Naturally, the initial and final positions will be reversed: $\tilde{\boldsymbol{r}}(0) = \boldsymbol{r}(t) = \boldsymbol{x}$ and $\tilde{\boldsymbol{r}}(t) = \boldsymbol{r}(0) = \boldsymbol{x}_0$. Equation (VII.21) can also be written in the following form

$$q[\boldsymbol{r}(\tau)] = k_{\mathrm{B}}T \ln\left(\frac{\mathsf{P}[\boldsymbol{r}(\tau)|\boldsymbol{x}_0]}{\mathsf{P}[\tilde{\boldsymbol{r}}(\tau)|\boldsymbol{x}]}\right) \quad , \tag{VII.22}$$

using the definition of the stochastic weight given in Eq. (VII.12). This result highlights the connection between time-reversal and dissipation, and provides a platform for a stochastic formulation of the second law.

3. Entropy production

The expression for the heat dissipated into the medium over a trajectory [Eq. (VII.19)] corresponds to the resulting increase in the entropy of the medium

$$\Delta s_{\mathrm{m}} \equiv q[\boldsymbol{r}(\tau)]/T = \frac{1}{T}\int_0^t \mathrm{d}\tau\, \boldsymbol{F}\cdot\dot{\boldsymbol{r}} \quad . \tag{VII.23}$$

This, however, does not represent the total change in entropy, as the system contribution also needs to be taken into consideration. The equilibrium definition of Gibbs entropy can be generalized to a nonequilibrium system as

$$S(t) = -k_{\mathrm{B}}\int \mathrm{d}^3\boldsymbol{x}\, \mathcal{P}(\boldsymbol{x},t)\ln\mathcal{P}(\boldsymbol{x},t) \equiv \langle s(t)\rangle \quad , \tag{VII.24}$$

which naturally leads to a definition of stochastic entropy of the system for a given finite trajectory

$$s(t) = -k_{\mathrm{B}}\ln\mathcal{P}(\boldsymbol{r}(t),t) \quad , \tag{VII.25}$$

or, alternatively,

$$s(t) = -k_{\mathrm{B}}\int \mathrm{d}^3\boldsymbol{x}\, \ln\mathcal{P}(\boldsymbol{x},t)\,\delta^3\left(\boldsymbol{x}-\boldsymbol{r}(t)\right) \quad . \tag{VII.26}$$

Note the peculiar structure of the definition as given in Eq. (VII.25): to calculate the entropy we first need to solve the Fokker-Planck equation for the average probability distribution $\mathcal{P}(\boldsymbol{x},t)$, and then evaluate it on the stochastic trajectory of interest.

The rate of entropy production can now be explicitly calculated from the above definition. We find

$$\dot{s}(t) = -k_{\mathrm{B}}\left.\frac{\partial_t\mathcal{P}(\boldsymbol{x},t)}{\mathcal{P}(\boldsymbol{x},t)}\right|_{\boldsymbol{r}(t)} - k_{\mathrm{B}}\left.\frac{\boldsymbol{\nabla}\mathcal{P}(\boldsymbol{x},t)}{\mathcal{P}(\boldsymbol{x},t)}\right|_{\boldsymbol{r}(t)}\cdot\dot{\boldsymbol{r}} \quad , \tag{VII.27}$$

which leads to the following expression for the total rate of entropy production

$$\dot{s}_{\mathrm{tot}}(t) = \dot{s}_{\mathrm{m}}(t) + \dot{s}(t) = -k_{\mathrm{B}}\left.\frac{\partial_t\mathcal{P}(\boldsymbol{x},t)}{\mathcal{P}(\boldsymbol{x},t)}\right|_{\boldsymbol{r}(t)} - k_{\mathrm{B}}\left.\frac{\boldsymbol{J}(\boldsymbol{x},t)}{D\mathcal{P}(\boldsymbol{x},t)}\right|_{\boldsymbol{r}(t)}\cdot\dot{\boldsymbol{r}} \quad , \tag{VII.28}$$

using the definition of the flux given in Eq. (VII.10).

To proceed from here, we need to calculate averages of the above terms over the trajectory. But this can be readily achieved by going back to the definition of Eq. (VII.24). We find

$$\dot{S}(t) = \langle \dot{s}(t) \rangle = -k_{\rm B} \int {\rm d}^3 \boldsymbol{x} \, \frac{\boldsymbol{\nabla} \mathcal{P} \cdot \boldsymbol{J}}{\mathcal{P}} \quad , \tag{VII.29}$$

by inserting the Fokker-Planck equation and integration by parts. Note that this calculation is formally equivalent to the original derivation of the Fokker-Planck equation discussed in Sec. II.B, and in particular, the time derivative is formally performed via an expansion in Δt.

The average change in the entropy of the medium is calculated as follows

$$\Delta S_{\rm m}(t) = S_{\rm m}(t + \Delta t) - S_{\rm m}(t) = \langle \Delta s_{\rm m}(t) \rangle = \frac{1}{T} \int_t^{t+\Delta t} {\rm d}\tau \, \langle \boldsymbol{F}(\boldsymbol{r}(\tau)) \cdot \dot{\boldsymbol{r}} \rangle \quad , \tag{VII.30}$$

which requires some attention. First, we insert the delta function and the explicit form of the Langevin equation, to obtain

$$\Delta S_{\rm m}(t) = \frac{1}{T} \int {\rm d}^3 \boldsymbol{x} \int_t^{t+\Delta t} {\rm d}\tau \, \boldsymbol{F}(\boldsymbol{x}) \cdot \Big\langle \delta^3 \left(\boldsymbol{x} - \boldsymbol{r}(\tau) \right) \Big(\mu \boldsymbol{F}(\boldsymbol{x}) + \boldsymbol{u}(\tau) \Big) \Big\rangle \quad , \tag{VII.31}$$

which can be written as

$$\Delta S_{\rm m}(t) = \frac{k_{\rm B}}{D} \int {\rm d}^3 \boldsymbol{x} \left[\Delta t \, \mathcal{P}(\boldsymbol{x}, t) \Big(\mu \boldsymbol{F}(\boldsymbol{x}) \Big)^2 + \mu \boldsymbol{F}(\boldsymbol{x}) \cdot \int_t^{t+\Delta t} {\rm d}\tau \, \big\langle \delta^3 \left(\boldsymbol{x} - \boldsymbol{r}(\tau) \right) \boldsymbol{u}(\tau) \big\rangle \right] \quad , \tag{VII.32}$$

to the leading in Δt. Now note

$$\begin{aligned}
\int_t^{t+\Delta t} {\rm d}\tau \, \big\langle \delta^3 \left(\boldsymbol{x} - \boldsymbol{r}(\tau) \right) u_j(\tau) \big\rangle &= \int_t^{t+\Delta t} {\rm d}\tau \, \big\langle \left[\delta^3 \left(\boldsymbol{x} - \boldsymbol{r}(t) \right) - \left(r_i(\tau) - r_i(t) \right) \partial_i \delta^3 \left(\boldsymbol{x} - \boldsymbol{r}(t) \right) \right] u_j(\tau) \big\rangle \\
&= \int_t^{t+\Delta t} {\rm d}\tau \left\langle \left[\delta^3 \left(\boldsymbol{x} - \boldsymbol{r}(t) \right) - \left(\int_t^{\tau} {\rm d}\tau' \, u_i(\tau') \right) \partial_i \delta^3 \left(\boldsymbol{x} - \boldsymbol{r}(t) \right) \right] u_j(\tau) \right\rangle \\
&= -\partial_i \int_t^{t+\Delta t} {\rm d}\tau \int_t^{\tau} {\rm d}\tau' \, \langle u_i(\tau') u_j(\tau) \rangle \, \big\langle \delta^3 \left(\boldsymbol{x} - \boldsymbol{r}(t) \right) \big\rangle \\
&= -2\Theta(0) D \Delta t \, \partial_j \mathcal{P}(\boldsymbol{x}, t)
\end{aligned}$$

to the leading order, which yields

$$\dot{S}_{\rm m}(t) = \frac{k_{\rm B}}{D} \int {\rm d}^3 \boldsymbol{x} \, \mu \boldsymbol{F}(\boldsymbol{x}) \cdot \left[\mu \boldsymbol{F}(\boldsymbol{x}) \, \mathcal{P}(\boldsymbol{x}, t) - 2\Theta(0) D \boldsymbol{\nabla} \mathcal{P} \right] \quad . \tag{VII.33}$$

Combining the above results, we obtain

$$\dot{S}_{\rm tot}(t) = \dot{S}_{\rm m}(t) + \dot{S}(t) = \frac{k_{\rm B}}{D} \int {\rm d}^3 \boldsymbol{x} \, \frac{\boldsymbol{J}(\boldsymbol{x}, t)^2}{\mathcal{P}(\boldsymbol{x}, t)} + k_{\rm B} \left[1 - 2\Theta(0) \right] \int {\rm d}^3 \boldsymbol{x} \, \mu \boldsymbol{F}(\boldsymbol{x}) \cdot \boldsymbol{\nabla} \mathcal{P} \quad . \tag{VII.34}$$

If we choose $\Theta(0) = 1/2$, this result leads to

$$\dot{S}_{\rm tot}(t) = \frac{k_{\rm B}}{D} \int {\rm d}^3 \boldsymbol{x} \, \frac{\boldsymbol{J}(\boldsymbol{x}, t)^2}{\mathcal{P}(\boldsymbol{x}, t)} \geq 0 \quad . \tag{VII.35}$$

which is a stochastic generalization of the second law of thermodynamics, and is analogous to the Boltzmann H-theorem. The equality will correspond to equilibrium, when the flux is identically zero. Note also that the system component of the entropy as calculated over a trajectory in itself does not have any restriction on its evolution; it can be produced or annihilated over the coarse of time, and it is only the total entropy that strictly increases over time.

The stochastic formalism developed here can be used to make much more powerful generalizations of the second law of thermodynamics, by exploiting the behaviour of the system under time reversal transformation. We can start from Eqs. (VII.22) and (VII.23) to relate the change of entropy of the medium to the conditional stochastic weights as

$$\Delta s_{\rm m}[\boldsymbol{r}(\tau)] = k_{\rm B} \ln \left(\frac{\mathsf{P}[\boldsymbol{r}(\tau)|\boldsymbol{x}_0]}{\mathsf{P}[\tilde{\boldsymbol{r}}(\tau)|\boldsymbol{x}]} \right) \quad . \tag{VII.36}$$

We next define a similar quantity in terms of unconditional weights as

$$R[\boldsymbol{r}(\tau), \lambda(\tau); \mathcal{P}_{\rm i}, \mathcal{P}_{\rm f}] = \ln \left(\frac{\mathsf{P}[\boldsymbol{r}(\tau)|\boldsymbol{x}_0]\, \mathcal{P}_{\rm i}(\boldsymbol{x}_0)}{\mathsf{P}[\tilde{\boldsymbol{r}}(\tau)|\boldsymbol{x}]\, \mathcal{P}_{\rm f}(\boldsymbol{x})} \right) = \frac{\Delta s_{\rm m}}{k_{\rm B}} + \ln \left(\frac{\mathcal{P}_{\rm i}(\boldsymbol{x}_0)}{\mathcal{P}_{\rm f}(\boldsymbol{x})} \right) \quad , \tag{VII.37}$$

by introducing the probability distributions $\mathcal{P}_{\rm i}(\boldsymbol{x}_0)$ and $\mathcal{P}_{\rm f}(\boldsymbol{x})$, for the initial and final states, respectively. We are now in a position to prove the generic fluctuation theorem $\left\langle e^{-R} \right\rangle = 1$ as follows

$$\begin{aligned} \left\langle e^{-R} \right\rangle &= \int \mathrm{d}^3\boldsymbol{x}\, \mathrm{d}^3\boldsymbol{x}_0 \int_{\boldsymbol{r}(0)=\boldsymbol{x}_0}^{\boldsymbol{r}(t)=\boldsymbol{x}} \mathcal{D}\boldsymbol{r}(\tau)\; e^{-R}\, \mathsf{P}[\boldsymbol{r}(\tau)|\boldsymbol{x}_0]\, \mathcal{P}_{\rm i}(\boldsymbol{x}_0) \quad , \\ &= \int \mathrm{d}^3\boldsymbol{x}_0\, \mathrm{d}^3\boldsymbol{x} \int_{\tilde{\boldsymbol{r}}(0)=\boldsymbol{x}}^{\tilde{\boldsymbol{r}}(t)=\boldsymbol{x}_0} \mathcal{D}\tilde{\boldsymbol{r}}(\tau)\; \mathsf{P}[\tilde{\boldsymbol{r}}(\tau)|\boldsymbol{x}]\, \mathcal{P}_{\rm f}(\boldsymbol{x}) = 1 \quad , \end{aligned}$$

where we have made use of the identity $\mathcal{D}\boldsymbol{r}(\tau) = \mathcal{D}\tilde{\boldsymbol{r}}(\tau)$. The result, which appears in the form of an equality, implies $\langle R \rangle \geq 0$, which represents a weaker form of the theorem. Since $\mathcal{P}_{\rm i}$ and $\mathcal{P}_{\rm f}$ are arbitrary at this stage, we have in fact produced an infinite number of fluctuation theorems, out of which there are a few notable specific cases, which we now discuss.

For the first special case, we set $\mathcal{P}_{\rm f}(\boldsymbol{x}) = \mathcal{P}(\boldsymbol{x}, t)$, i.e. the solution to the Fokker-Planck equation subject to the initial condition that the distribution at $t = 0$ is given by $\mathcal{P}_{\rm i}(\boldsymbol{x}_0)$. The definition of stochastic system entropy given in Eq. (VII.25) used in Eq. (VII.37) then leads to the following fluctuation theorem

$$\left\langle e^{-\Delta s_{\rm tot}} \right\rangle = 1 \quad , \tag{VII.38}$$

for the total entropy change, which implies the weaker form of $\Delta S_{\rm tot} = \langle \Delta s_{\rm tot} \rangle \geq 0$, which was the main result of our calculations in Sec. VII.B.3.

We next consider a case when the initial and final states of the system are taken to be at thermodynamic equilibrium described by the potential energy $U(\boldsymbol{r}, \lambda)$ [with $\boldsymbol{f} = 0$ in Eq. (VII.7)], i.e. $\mathcal{P}_{\rm i}(\boldsymbol{x}_0) = \exp\left\{ - \left[U(\boldsymbol{x}_0, \lambda(0)) - \mathcal{F}(\lambda(0)) \right] / k_{\rm B}T \right\}$ and $\mathcal{P}_{\rm f}(\boldsymbol{x}) = \exp\left\{ - \left[U(\boldsymbol{x}, \lambda(t)) - \mathcal{F}(\lambda(t)) \right] / k_{\rm B}T \right\}$, where $\mathcal{F}(\lambda)$ is the corresponding equilibrium Helmholtz free energy of the system. Inserting these distributions in Eq. (VII.37) and using the definition of work w given in Eq. (VII.20), we arrive at the following fluctuation theorem

$$\left\langle e^{-w/k_{\rm B}T} \right\rangle = e^{-\Delta \mathcal{F}/k_{\rm B}T} \quad , \tag{VII.39}$$

where $\Delta \mathcal{F} = \mathcal{F}(\lambda(t)) - \mathcal{F}(\lambda(0))$ denotes the change in the Helmholtz free energy between the initial and final states. Equation (VII.39) is the celebrated Jarzynski relation. Other fluctuation theorems such as Crooks relation etc can also be derived using appropriate choices for the initial and final distributions and similar calculations.

We finally note that for steady states with constant external driving force $\boldsymbol{f}$ and periodic boundary

condition, such as a driven nonequilibrium steady state on a ring, we can write an even stronger form of fluctuation theorem in the form

$$\frac{\mathcal{P}(-\Delta s_{\mathrm{tot}})}{\mathcal{P}(\Delta s_{\mathrm{tot}})} = e^{-\Delta s_{\mathrm{tot}}/k_{\mathrm{B}}} \quad , \tag{VII.40}$$

directly for the probability of measuring Δs_{tot}, by choosing $\mathcal{P}_{\mathrm{i}}(\boldsymbol{x}) = \mathcal{P}_{\mathrm{f}}(\boldsymbol{x}) = \mathcal{P}^{s}(\boldsymbol{x})$. Similar generalizations exist for other fluctuation relations and their respective thermodynamic variables. This so-called detailed fluctuation theorem constrains one half of the distribution, in the sense that the even moments can be determined from the odd moments and vice versa. The detailed fluctuation theorem trivially leads to the average form upon integration.