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PAPER: Quantum statistical physics, condensed matter, integrable systems

Boltzmann to Lindblad: classical and quantum approaches to out-of-equilibrium statistical mechanics

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Abstract. Open quantum systems play a central role in current nanoscale technologies, such as molecular electronics, quantum heat engines, quantum computation and information processing. A major theoretical challenge is to construct

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dynamical models that are simultaneously consistent with classical thermodynamics and with the requirement of complete positivity of quantum evolution. In this work we develop a framework that addresses this issue by systematically extending classical stochastic dynamics to the quantum domain. We begin by formulating a generalized Langevin equation in which both friction and noise act symmetrically on the two Hamiltonian equations. From this, we derive a generalized Klein–Kramers equation expressed in terms of Poisson brackets, and we show that it admits the Boltzmann distribution as its stationary solution while fulfilling the first and second laws of thermodynamics along individual trajectories. Applying canonical quantization to this classical framework yields two distinct quantum master equations, depending on whether the friction operators are taken to be Hermitian or non-Hermitian. By analyzing the dynamics of a harmonic oscillator, we determine the conditions under which these equations reduce to a Lindblad-type generator. Our results demonstrate that complete positivity is ensured only when friction and noise are included in both Hamiltonian equations, fully justifying the classical construction. Moreover, we find that the friction coefficients must adhere to the same positivity condition in both the Hermitian and non-Hermitian formulations, revealing a form of universality that transcends the specific operator representation. The formalism developed here presents a thermodynamically consistent and completely positive quantum extension of classical stochastic mechanics. It offers a versatile tool for deriving quantum versions of thermodynamic laws and is directly applicable to a broad class of non-equilibrium nanoscale systems of current theoretical and technological interest.

Keywords: Brownian motion, quantum dissipative systems, quantum thermalization, stochastic thermodynamics

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1. Introduction

The study of open quantum systems has emerged from the recognition that quantum systems are rarely isolated, as their coupling to external environments inevitably induces noise, dissipation and decoherence. An early attempt to include these effects within quantum mechanics led to the development of the Caldirola–Kanai equation [1, 2], derived by incorporating nonconservative forces into Schrödinger’s framework through a nonlinear time transformation originally proposed by Levi-Civita. Although initially controversial because of this unusual transformation of time, this approach was later shown to be consistent with the physics of open systems and laid the foundation for quantum dissipation theory [3, 4], which was subsequently developed in numerous works [5–7].

A major advance came with the formulation of the quantum master equation, describing the evolution of an open system’s density matrix [8–11]. The Redfield equation, valid for weak system–environment coupling [8], found early applications in nuclear magnetic resonance but does not ensure the positivity of the density matrix [12]. This limitation motivated the design of more rigorous approaches, such as path-integral formulations, quantum thermodynamics and quantum Brownian motion [13–20]. In the 1970s, these efforts culminated in the Gorini–Kossakowski–Sudarshan–Lindblad equation [21–25], providing a fully Markovian and mathematically consistent framework for quantum dynamical semigroups, refining the Redfield approximation [8] and advancing the theoretical foundations of quantum thermodynamics [26–34]. This framework clarified the mechanisms of decoherence and environmental coupling [35–37] and inspired subsequent studies on quantum equipartition [38–42] and fluctuation theorems [43, 44].

Today, open quantum systems theory constitutes a cornerstone of modern physics. It underpins applications in nuclear magnetic resonance [45, 46], optical pumping [47], masers [48, 49], lasers [50, 51], quantum computation [52–55], quantum information [56, 57] and molecular electronics [58, 59]. The same framework informs quantum biology [60–63], notably in photosynthetic energy transfer [64–66], and plays a central role in quantum thermodynamic devices [67], quantum batteries [68], heat engines [69] and in understanding the thermodynamic arrow of time [70–72]. Furthermore, it provides the theoretical foundation for quantum metrology and sensing [73–75], optomechanics [76, 77], non-equilibrium phenomena in nanoscale and condensed matter systems [78–81] and the engineering of active quantum matter [82]. In several realistic physical situations, the interaction between a system and its environment generates memory effects, making non-Markovian descriptions of open quantum dynamics both necessary and physically meaningful [83–86].

In the present work, which extends the analysis of [87], we first construct a generalized classical Langevin equation [88], wherein both friction and noise appear symmetrically in the Hamiltonian formalism. By using the Fokker–Planck methodology [89, 90], we derive a generalized Klein–Kramers equation [91, 92], expressed in terms of Poisson brackets. Next, we show that the asymptotic solution of this equation corresponds to the classical canonical distribution. Moreover, by introducing the definitions of heat [93, 94] and entropy [95–97], along a single trajectory, we demonstrate that this approach is fully consistent with the first and second laws of thermodynamics. It is worth noting that such a formalism, based on the theory of stochastic processes [98–102], is now systematically applied within statistical mechanics [103–113], such as holonomic underdamped and overdamped systems [114–117]. Second, we introduce the quantum analog of the classical theory. We build on our previous studies [118–121], by means of which we show that noise in quantum mechanics always enters multiplicatively, and demonstrate that canonical quantization—that is replacing Poisson brackets with commutators [122, 123]—constitutes a rigorous procedure for the classical-to-quantum transition [87]. This approach has also been discussed and/or applied in various studies [124–129]. Accordingly, we apply canonical quantization to the Klein–Kramers equation, which is based on the symmetric inclusion of friction and noise in the Hamiltonian equations. This procedure necessitates the introduction of certain friction operators, which can be defined in two distinct ways depending on whether Hermiticity is imposed or not. By following both approaches in parallel, we thus obtain two different master equations to describe the non-equilibrium statistical mechanics of a quantum system. For both master equations, we analyze their behavior for a simple system, such as the harmonic oscillator (HO). This analysis, based on [125, 126], demonstrates that the resulting equations are of the Lindblad type, that is, they are completely positive, only if both Hamiltonian equations include friction and noise terms. This fully justifies the initial choice made in reconstructing classical statistical mechanics, where friction and noise are introduced in both Hamiltonian equations. Furthermore, we demonstrate that in the quantum case the two always-positive friction coefficients must also fulfill an additional inequality to ensure complete positivity. Remarkably, this inequality is identical for both the Hermitian and non-Hermitian operator approaches, suggesting that it could be a more general feature rather than a consequence of the specific choice of friction operators. In the following, we show how quantum thermodynamics can be developed starting from the master equation, leading to a novel formulation of the first and second laws. The first law is based on a generalized definition of heat at the quantum level, whereas the second law asserts the positivity of entropy production, highlighting its deep connection with the monotonicity of the quantum relative entropy [21, 22]. It should be noted that multiple approaches have been developed to investigate the positivity of entropy production in the quantum context [26–32].

Finally, we implement our formalism to describe the non-equilibrium dynamics of the HO. To elucidate our results, we compare five different models. The first comprises the full equation, with friction and noise included in both Hamiltonian–Langevin equations, using Hermitian friction operators. The second is the full equation with friction and noise

in both Langevin–Hamilton equations, but with non-Hermitian friction operators. The third and fourth models include friction and noise only in the first Hamiltonian equation, as done classically, with Hermitian and non-Hermitian friction operators, respectively. Finally, the fifth model corresponds to the Caldeira–Leggett approach [13–15], in which friction and noise act only on the first equation and the mathematical form of the friction operator is further approximated. The numerical results display that the first two models are fully consistent with thermodynamics and preserve the positivity of the density matrix at all times. This finding is fully in line with the theoretical framework developed in the first part of this work. The third and fourth models, discussed respectively in [87] and [127–129], are thermodynamically consistent but may yield negative eigenvalues of the density matrix in certain situations. This occurs for specific initial conditions, such as pure states defined by the energy eigenbasis. Consequently, these two models constitute reasonable approximations only for initial mixed states that ensure positivity is preserved throughout the evolution. Finally, it is straightforward to verify that the Caldeira–Leggett model violates thermodynamic consistency and can also generate negative eigenvalues during the dynamics.

2. Generalized classical stochastic thermodynamics

We develop a generalized classical stochastic thermodynamics model by considering a system comprising N particles with masses m_i , described by coordinates \vec{r}_i and linear momenta \vec{p}_i ($i = 1, \dots, N$). The total kinetic energy of the system K_0 is written as $K_0 = \sum_{i=1}^N \frac{1}{2m_i} \vec{p}_i \cdot \vec{p}_i$, and the potential energy describing the system is given by $V_0 = V_0(\vec{r}_1, \dots, \vec{r}_N)$. For this system, we introduce a set of stochastic generalized Hamilton equations in the following form:

$$\dot{\vec{p}}_i = -\frac{\partial V_0}{\partial \vec{r}_i} - \beta_p \vec{p}_i + \sqrt{D_p m_i} \vec{n}_{p,i}(t) + \vec{f}_i(t), \quad (1)$$

$$\dot{\vec{r}}_i = \frac{1}{m_i} \vec{p}_i - \beta_q m_i \frac{\partial V_0}{\partial \vec{r}_i} + \sqrt{D_q m_i} \vec{n}_{q,i}(t), \quad (2)$$

where $\beta_p = 0$ and $\beta_q = 0$ are two friction coefficients and $D_p = 0$ and $D_q = 0$ are two diffusion constants. When $\beta_q = 0$ and $D_q = 0$, we retrieve the classical Langevin model, where each particle is subjected to a force $\vec{F}_i = -\frac{\partial V_0}{\partial \vec{r}_i} - \beta_p \vec{p}_i + \sqrt{D_p m_i} \vec{n}_{p,i}(t) + \vec{f}_i(t)$, which includes: (i) a conservative force field describing the system structure, (ii) an external force field representing the work performed on the system (in addition to time, forces \vec{f}_i can also depend on the positions of the particles $\vec{r}_1, \dots, \vec{r}_N$), (iii) a friction force (coefficient β_p) mimicking the energy transfer from the particles to the thermal bath and (iv) a noise term (diffusion coefficient D_p) mimicking the energy transfer from the bath to the system. The friction and noise forces (iii) and (iv) represent the so-called Langevin thermal bath [88]. The system of the Hamilton equations with $\beta_q = 0$ and $D_q = 0$ is consistent with both equilibrium and out-of-equilibrium thermodynamics and statistical mechanics [114, 115]. Here, we want to prove that the

additional terms with coefficients $\beta_q \neq 0$ and $D_q \neq 0$ leave these important properties unaltered. This finding is particularly relevant in quantum mechanics. We assume the following hypotheses for the noises: $\vec{n}_{p,i}(t) \in \mathbb{R}^3$ and $\vec{n}_{q,i}(t) \in \mathbb{R}^3$ are Gaussian stochastic processes with expectation value $\mathbb{E}\{\vec{n}_{p,i}(t)\} = 0$, $\mathbb{E}\{\vec{n}_{q,i}(t)\} = 0$ and correlation $\mathbb{E}\{\vec{n}_{p,i}(t_1) \otimes \vec{n}_{p,j}(t_2)\} = 2\delta_{ij}I_3\delta(t_1 - t_2)$, $\mathbb{E}\{\vec{n}_{q,i}(t_1) \otimes \vec{n}_{q,j}(t_2)\} = 2\delta_{ij}I_3\delta(t_1 - t_2)$ and $\mathbb{E}\{\vec{n}_{q,i}(t_1) \otimes \vec{n}_{p,j}(t_2)\} = 0$. Here, δ_{ij} is the Kronecker delta, $\delta(\cdot)$ is the Dirac delta function, \otimes is the tensor product of vectors and I_3 is a 3×3 identity matrix [98–100]. If we introduce the Hamiltonian function of the system as $\mathcal{H}_0 = K_0 + V_0$, we can rewrite the Hamilton equation in the following more symmetrical form:

$$\dot{\vec{p}}_i = -\frac{\partial \mathcal{H}_0}{\partial \vec{r}_i} - m_i\beta_p \frac{\partial \mathcal{H}_0}{\partial \vec{p}_i} + \sqrt{D_p m_i} \vec{n}_{p,i}(t) + \vec{f}_i(t), \tag{3}$$

$$\dot{\vec{r}}_i = \frac{\partial \mathcal{H}_0}{\partial \vec{p}_i} - m_i\beta_q \frac{\partial \mathcal{H}_0}{\partial \vec{r}_i} + \sqrt{D_q m_i} \vec{n}_{q,i}(t). \tag{4}$$

The symmetry of this Hamiltonian form justifies the choice to have a form of friction in equation (2) proportional to $\frac{\partial V_0}{\partial \vec{r}_i} = \frac{\partial \mathcal{H}_0}{\partial \vec{r}_i}$. Further examples of generalized Hamilton–Langevin formulations are available in the existing literature [109–113]. From a mathematical point of view, our peculiar writing of the Hamilton equations represents a stochastic differential problem with additive noise [101, 102]. We can then apply the Fokker–Planck methodology, which is briefly recalled here for an arbitrary interpretation of the stochastic calculus [98–100]. Although this distinction is strictly speaking not relevant here because the classical Hamilton equations have additive noise, we underline that the corresponding quantum equations have multiplicative noise, as thoroughly discussed in [87, 124]. We thus consider the stochastic differential system

$$\frac{dx_i}{dt} = h_i(\vec{x}, t) + \sum_{j=1}^m g_{ij}(\vec{x}, t) n_j(t), \tag{5}$$

with n equations and m noise terms ($\forall i = 1, \dots, n, \forall j = 1, \dots, m$). It assumes a precise meaning only after declaring the adopted interpretation of the stochastic calculus. To achieve this, we must specify the parameter α , with $0 \leq \alpha \leq 1$, that defines the position of the point at which we calculate any integrated function in the small intervals of the adopted Riemann sum. Gaussian noises $n_j(t)$ ($\forall j = 1, \dots, m$) satisfy the properties $\mathbb{E}\{n_j(t)\} = 0$, and $\mathbb{E}\{n_i(t_1)n_j(t_2)\} = 2\delta_{ij}\delta(t_1 - t_2)$. This stochastic differential equation corresponds to the following Fokker–Planck equation for the probability density $W(\vec{x}, t)$ [99, 100]:

$$\begin{aligned} \frac{\partial W(\vec{x}, t)}{\partial t} = & -\sum_{i=1}^n \frac{\partial}{\partial x_i} [h_i W(\vec{x}, t)] - \sum_{i=1}^n \frac{\partial}{\partial x_i} \left\{ 2\alpha \left[\sum_{k=1}^n \sum_{j=1}^m g_{kj} \frac{\partial g_{ij}}{\partial x_k} \right] W(\vec{x}, t) \right\} \\ & + \sum_{i=1}^n \sum_{j=1}^m \frac{\partial^2}{\partial x_i \partial x_j} \left\{ \left[\sum_{k=1}^m g_{ik} g_{jk} \right] W(\vec{x}, t) \right\}, \end{aligned} \tag{6}$$

where the first term represents the drift, the second is the noise-induced drift (which depends on α , and is zero when $\frac{\partial g_{ij}}{\partial x_k} = 0$) and the third is the diffusion (characterizing the effect of the noise). This expression includes the Itô ($\alpha = 0$) [130], the Fisk–Stratonovich ($\alpha = 1/2$) [131, 132] and the Hänggi–Klimontovich ($\alpha = 1$) [133, 134] interpretations as particular cases (see [135]).

Eventually, we can write the Fokker–Planck [89, 90] (or Klein–Kramers [91, 92]) equation associated with equation (1) in the following form:

$$\begin{aligned} \frac{\partial W}{\partial t} = & - \sum_{i=1}^N \frac{\vec{p}_i}{m_i} \cdot \frac{\partial W}{\partial \vec{r}_i} + \sum_{i=1}^N \frac{\partial V}{\partial \vec{r}_i} \cdot \frac{\partial W}{\partial \vec{p}_i} - \sum_{i=1}^N \vec{f}_i \cdot \frac{\partial W}{\partial \vec{p}_i} \\ & + 3N\beta_p W + \beta_p \sum_{i=1}^N \vec{p}_i \cdot \frac{\partial W}{\partial \vec{p}_i} + D_p \sum_{i=1}^N m_i \frac{\partial^2 W}{\partial \vec{p}_i^2} \\ & + \beta_q \sum_{i=1}^N m_i \frac{\partial^2 V_0}{\partial \vec{r}_i^2} W + \beta_q \sum_{i=1}^N m_i \frac{\partial V_0}{\partial \vec{r}_i} \cdot \frac{\partial W}{\partial \vec{r}_i} + D_q \sum_{i=1}^N m_i \frac{\partial^2 W}{\partial \vec{r}_i^2}, \end{aligned} \quad (7)$$

where $W = W(\vec{r}_1, \dots, \vec{r}_N, \vec{p}_1, \dots, \vec{p}_N, t)$. The derivative $\frac{\partial^2 W}{\partial \vec{p}_i^2}$ (or $\frac{\partial^2 W}{\partial \vec{r}_i^2}$) represents the Laplacian operator with respect to the three components of \vec{p}_i (or \vec{r}_i).

A more interesting form for the following developments can be found by introducing the Poisson brackets as follows [136]:

$$\begin{aligned} \frac{\partial W}{\partial t} = & \{ \mathcal{H}, W \} - \sum_{i=1}^N \vec{f}_i \cdot \frac{\partial W}{\partial \vec{p}_i} \\ & + \beta_p \sum_{i=1}^N m_i \left(\left\{ r_{xi}, \frac{\partial \mathcal{H}_0}{\partial p_{xi}} W \right\} + \left\{ r_{yi}, \frac{\partial \mathcal{H}_0}{\partial p_{yi}} W \right\} + \left\{ r_{zi}, \frac{\partial \mathcal{H}_0}{\partial p_{zi}} W \right\} \right) \\ & + D_p \sum_{i=1}^N m_i (\{ r_{xi}, \{ x_i, W \} \} + \{ r_{yi}, \{ y_i, W \} \} + \{ r_{zi}, \{ z_i, W \} \}) \\ & - \beta_q \sum_{i=1}^N m_i \left(\left\{ p_{xi}, \frac{\partial \mathcal{H}_0}{\partial r_{xi}} W \right\} + \left\{ p_{yi}, \frac{\partial \mathcal{H}_0}{\partial r_{yi}} W \right\} + \left\{ p_{zi}, \frac{\partial \mathcal{H}_0}{\partial r_{zi}} W \right\} \right) \\ & + D_q \sum_{i=1}^N m_i (\{ p_{xi}, \{ p_{xi}, W \} \} + \{ p_{yi}, \{ p_{yi}, W \} \} + \{ p_{zi}, \{ p_{zi}, W \} \}), \end{aligned} \quad (8)$$

where $\vec{r}_i = (r_{xi}, r_{yi}, r_{zi})$, $\vec{p}_i = (p_{xi}, p_{yi}, p_{zi})$, and $\mathcal{H}_0 = K_0 + V_0$. This form is particularly suitable for the application of canonical quantization.

The asymptotic behavior of equation (8) for large times ($t \gg 1/\beta_p$, $t \gg 1/\beta_q$) is characterized by the canonical or Gibbs distribution [137]. Indeed, if the forces \vec{f}_i are

absent, and the integral defining the classical partition function

$$Z_{\text{cl}} = \int_{\mathbb{R}^{3N}} \int_{\mathbb{R}^{3N}} e^{-\frac{1}{k_B T} \mathcal{H}_0(\vec{q}, \vec{p})} d\vec{q} d\vec{p}, \quad (9)$$

is convergent (with $\vec{q} = (\vec{r}_1, \dots, \vec{r}_N) \in \mathbb{R}^{3N}$ and $\vec{p} = (\vec{p}_1, \dots, \vec{p}_N) \in \mathbb{R}^{3N}$), then the asymptotic solution of equation (8) is given by the Gibbs distribution in the phase space

$$W_{\text{eq}}(\vec{q}, \vec{p}) = \frac{1}{Z_{\text{cl}}} e^{-\frac{1}{k_B T} \mathcal{H}_0(\vec{q}, \vec{p})}, \quad (10)$$

as can be easily proved by substitution. This asymptotic solution allows the identification of the diffusion constants through the expressions $D_p = k_B T \beta_p$ and $D_q = k_B T \beta_q$, referred to as the classical Einstein fluctuation–dissipation relations [99, 100]. This means that our formalism is consistent with equilibrium thermodynamics, but it must also be verified that it behaves correctly during relaxation. To this end, in the following, we show how the two laws of thermodynamics can be rederived out of equilibrium.

We define the internal energy \mathcal{E} of the system as the average value, with respect to the probability density defined by equation (7) or (8), of the sum of kinetic energy and potential energy $\mathcal{E} = \mathbb{E}\{K_0 + V_0\}$, and we calculate the rate $\frac{d\mathcal{E}}{dt}$. After straightforward calculations, we obtain

$$\begin{aligned} \frac{d\mathcal{E}}{dt} &= \sum_{i=1}^N \vec{f}_i \cdot \frac{\mathbb{E}\{\vec{p}_i\}}{m_i} + \beta_p \left(k_B T \sum_{i=1}^N m_i \mathbb{E} \left\{ \frac{\partial^2 \mathcal{H}_0}{\partial \vec{p}_i^2} \right\} - \sum_{i=1}^N m_i \mathbb{E} \left\{ \frac{\partial \mathcal{H}_0}{\partial \vec{p}_i} \cdot \frac{\partial \mathcal{H}_0}{\partial \vec{p}_i} \right\} \right) \\ &\quad + \beta_q \left(k_B T \sum_{i=1}^N m_i \mathbb{E} \left\{ \frac{\partial^2 \mathcal{H}_0}{\partial \vec{r}_i^2} \right\} - \sum_{i=1}^N m_i \mathbb{E} \left\{ \frac{\partial \mathcal{H}_0}{\partial \vec{r}_i} \cdot \frac{\partial \mathcal{H}_0}{\partial \vec{r}_i} \right\} \right) \\ &= \sum_{i=1}^N \vec{f}_i \cdot \frac{\mathbb{E}\{\vec{p}_i\}}{m_i} + 2\beta_p \left(\frac{3}{2} N k_B T - \mathbb{E}\{K_0\} \right) \\ &\quad + \beta_q \left(k_B T \sum_{i=1}^N m_i \mathbb{E} \left\{ \frac{\partial^2 V_0}{\partial \vec{r}_i^2} \right\} - \sum_{i=1}^N m_i \mathbb{E} \left\{ \frac{\partial V_0}{\partial \vec{r}_i} \cdot \frac{\partial V_0}{\partial \vec{r}_i} \right\} \right) \\ &= \frac{d\mathbb{E}\{L\}}{dt} + \frac{d\mathbb{E}\{Q\}}{dt}. \end{aligned} \quad (11)$$

This expression represents the first law of thermodynamics, from which we can identify the rate of average work $\frac{d\mathbb{E}\{L\}}{dt}$ performed on the system with the average power $\sum_{i=1}^N \vec{f}_i \cdot \mathbb{E}\{\vec{p}_i\}/m_i$, and the remaining two terms, proportional to β_p and β_q , respectively, with the rate of average heat $\frac{d\mathbb{E}\{Q\}}{dt}$ entering the system.

We then prove that the heat flux is zero when the following generalized equipartition of energy is satisfied. At equilibrium, we can write

$$\begin{aligned}
 \mathbb{E} \left\{ \frac{\partial^2 \mathcal{H}_0}{\partial \vec{s}_i^2} \right\} &= \frac{1}{Z_{\text{cl}}} \int_{\mathbb{R}^{3N}} \int_{\mathbb{R}^{3N}} \frac{\partial^2 \mathcal{H}_0}{\partial \vec{s}_i^2} e^{-\frac{1}{k_B T} \mathcal{H}_0(\vec{q}, \vec{p})} d\vec{q} d\vec{p} \\
 &= \frac{1}{k_B T} \frac{1}{Z_{\text{cl}}} \int_{\mathbb{R}^{3N}} \int_{\mathbb{R}^{3N}} \frac{\partial \mathcal{H}_0}{\partial \vec{s}_i} \cdot \frac{\partial \mathcal{H}_0}{\partial \vec{s}_i} e^{-\frac{1}{k_B T} \mathcal{H}_0(\vec{q}, \vec{p})} d\vec{q} d\vec{p} \\
 &= \frac{1}{k_B T} \mathbb{E} \left\{ \frac{\partial \mathcal{H}_0}{\partial \vec{s}_i} \cdot \frac{\partial \mathcal{H}_0}{\partial \vec{s}_i} \right\}, \tag{12}
 \end{aligned}$$

where $s = p$ or r , and a multidimensional integration by parts is used. It is shown that both terms in the definition of heat flow tend toward zero when thermodynamic equilibrium is reached. Indeed, for $s = p$, the classical equipartition theorem is obtained in the form $\mathbb{E}\{K_0\} = \frac{3}{2} N k_B T$, and when $s = r$, we get a new dual expression $\sum_{i=1}^N m_i \mathbb{E} \left\{ \frac{\partial V_0}{\partial \vec{q}_i} \cdot \frac{\partial V_0}{\partial \vec{q}_i} \right\} = k_B T \sum_{i=1}^N m_i \mathbb{E} \left\{ \frac{\partial^2 V_0}{\partial \vec{q}_i^2} \right\}$. It can also be remarked that the heat rate here defined is consistent with the development of stochastic energetics [93, 94].

To substantiate the previous explicit expressions for the heat rate, we reobtain the second law of thermodynamics by introducing the Gibbs entropy of the system as follows:

$$\mathcal{S} = -k_B \mathbb{E} \{ \log W \} = -k_B \int_{\mathbb{R}^{3N}} \int_{\mathbb{R}^{3N}} W \log W d\vec{q} d\vec{p}. \tag{13}$$

This expression means that the microscopic (nonaveraged) entropy along a given system trajectory is defined as $-k_B \log W$, consistent with [95–97]. The evolution equation for W can be rewritten as follows:

$$\frac{\partial W}{\partial t} = \{ \mathcal{H}_0, W \} - \sum_{i=1}^N \vec{f}_i \cdot \frac{\partial W}{\partial \vec{p}_i} - \sum_{i=1}^N \frac{\partial \vec{J}_{pi}}{\partial \vec{p}_i} - \sum_{i=1}^N \frac{\partial \vec{J}_{ri}}{\partial \vec{r}_i}, \tag{14}$$

where we introduce

$$\vec{J}_{pi} = -\beta_p W \vec{p}_i - k_B T \beta_p m_i \frac{\partial W}{\partial \vec{p}_i} = -\beta_p m_i W \frac{\partial \mathcal{H}_0}{\partial \vec{p}_i} - k_B T \beta_p m_i \frac{\partial W}{\partial \vec{p}_i}, \tag{15}$$

$$\vec{J}_{ri} = -\beta_q m_i W \frac{\partial V_0}{\partial \vec{r}_i} - k_B T \beta_q m_i \frac{\partial W}{\partial \vec{r}_i} = -\beta_q m_i W \frac{\partial \mathcal{H}_0}{\partial \vec{r}_i} - k_B T \beta_q m_i \frac{\partial W}{\partial \vec{r}_i}, \tag{16}$$

which are the fluxes in momentum space and in configurational space, respectively. We note that the derivatives $\frac{\partial \vec{J}_{pi}}{\partial \vec{p}_i}$ and $\frac{\partial \vec{J}_{ri}}{\partial \vec{r}_i}$ represent the divergence with respect to the components of \vec{p}_i and \vec{r}_i , respectively, giving the Fokker–Planck equation the form of a continuity equation. The total entropy rate can be written in the form

$$\frac{d\mathcal{S}}{dt} = -k_B \int_{\mathbb{R}^{3N}} \int_{\mathbb{R}^{3N}} \frac{\partial W}{\partial t} \log W d\vec{q} d\vec{p}, \tag{17}$$

in which equation (14) can be substituted for $\partial W / \partial t$. It can then be verified that the Liouville term and the term with external forces (depending solely on position and time) have zero entropic contribution. Therefore

$$\begin{aligned} \frac{d\mathcal{S}}{dt} &= k_B \int_{\mathbb{R}^{3N}} \int_{\mathbb{R}^{3N}} \left(\sum_{i=1}^N \frac{\partial \vec{J}_{pi}}{\partial \vec{p}_i} + \sum_{i=1}^N \frac{\partial \vec{J}_{ri}}{\partial \vec{r}_i} \right) \log W d\vec{q}d\vec{p} \\ &= -k_B \int_{\mathbb{R}^{3N}} \int_{\mathbb{R}^{3N}} \frac{1}{W} \left(\sum_{i=1}^N \vec{J}_{pi} \cdot \frac{\partial W}{\partial \vec{p}_i} + \vec{J}_{ri} \cdot \sum_{i=1}^N \frac{\partial W}{\partial \vec{r}_i} \right) d\vec{q}d\vec{p}. \end{aligned} \quad (18)$$

We can now express the derivatives $\frac{\partial W}{\partial \vec{p}_i}$ and $\frac{\partial W}{\partial \vec{r}_i}$ as a function of the fluxes \vec{J}_{pi} and \vec{J}_{ri} , using equations (15) and (16). This procedure leads to an entropy balance in the form

$$\begin{aligned} \frac{d\mathcal{S}}{dt} &= \frac{1}{T} \frac{d\mathbb{E}\{Q\}}{dt} + \frac{1}{\beta_p T} \int_{\mathbb{R}^{3N}} \int_{\mathbb{R}^{3N}} \frac{1}{W} \sum_{i=1}^N \frac{\vec{J}_{pi} \cdot \vec{J}_{pi}}{m_i} d\vec{q}d\vec{p} \\ &\quad + \frac{1}{\beta_q T} \int_{\mathbb{R}^{3N}} \int_{\mathbb{R}^{3N}} \frac{1}{W} \sum_{i=1}^N \frac{\vec{J}_{ri} \cdot \vec{J}_{ri}}{m_i} d\vec{q}d\vec{p}, \end{aligned} \quad (19)$$

where

$$\begin{aligned} \frac{d\mathbb{E}\{Q\}}{dt} &= \beta_p \left(k_B T \sum_{i=1}^N m_i \mathbb{E} \left\{ \frac{\partial^2 \mathcal{H}_0}{\partial \vec{p}_i^2} \right\} - \sum_{i=1}^N m_i \mathbb{E} \left\{ \frac{\partial \mathcal{H}_0}{\partial \vec{p}_i} \cdot \frac{\partial \mathcal{H}_0}{\partial \vec{p}_i} \right\} \right) \\ &\quad + \beta_q \left(k_B T \sum_{i=1}^N m_i \mathbb{E} \left\{ \frac{\partial^2 \mathcal{H}_0}{\partial \vec{r}_i^2} \right\} - \sum_{i=1}^N m_i \mathbb{E} \left\{ \frac{\partial \mathcal{H}_0}{\partial \vec{r}_i} \cdot \frac{\partial \mathcal{H}_0}{\partial \vec{r}_i} \right\} \right), \end{aligned} \quad (20)$$

consistent with the analysis conducted above to rederive the first law of thermodynamics. In equation (19), we identify the first term with the entropy flow (heat-driven disorder) and the sum of the second and third terms with the entropy production (irreversibility). It may be noted that entropy production is always non-negative since it is constituted by positive-definite quadratic expressions [103–108, 115]. Therefore, the second law of thermodynamics is reobtained in the classical form

$$\frac{d\mathcal{S}}{dt} \geq \frac{1}{T} \frac{d\mathbb{E}\{Q\}}{dt}, \quad (21)$$

where the equality is satisfied only for quasistatic transformations, evolving not far from the thermodynamic equilibrium [115]. It is interesting to note that this thermodynamic structure is preserved even when we treat a holonomic system with arbitrary mechanical constraints [114, 115]. Moreover, this scheme can be further generalized to introduce the overdamped approximation [114–116] and multiple reservoirs [117].

3. Density matrix evolution in quantum mechanics

First, the concept of density matrix in quantum mechanics is briefly recalled. A mixed state for an arbitrary system is described by M wave-functions Ψ_1, \dots, Ψ_M , associated

with the corresponding probabilities p_1, \dots, p_M , with $\sum_{j=1}^M p_j = 1$. The density operator is thereby defined as $\varrho(\vec{q}, \vec{q}', t) = \sum_{j=1}^M p_j \Psi_j(\vec{q}, t) \Psi_j^*(\vec{q}', t)$. The expectation value of an observable f is then calculated as $\mathbb{E}\{f\} = \sum_{j=1}^M p_j \langle \Psi_j | f | \Psi_j \rangle = \int (f \varrho) |_{\vec{q}'=\vec{q}} d\vec{q}$, where f represents the quantum operator acting only on the variables \vec{q} . By adopting the orthonormal basis $\{\varphi_n(\vec{q}) : \mathbb{R}^{3N} \rightarrow \mathbb{C}\}$, we have that $\Psi_j = a_{kj} \varphi_k$, with $a_{kj} = \langle \varphi_k | \Psi_j \rangle$ (Einstein's summation convention is assumed). Hence, the expectation value of f can be written as $\mathbb{E}\{f\} = \int \sum_{j=1}^M p_j a_{kj} f \varphi_k a_{hj}^* \varphi_h^* d\vec{q} = \varrho_{kh} f_{hk} = \text{Tr}(\varrho f)$, where we identify the density matrix representation $\varrho_{kh} = \sum_{j=1}^M p_j a_{kj} a_{hj}^*$, and the operator representation $f_{hk} = \int \varphi_h^* f \varphi_k d\vec{q} = \langle \varphi_h | f | \varphi_k \rangle$.

The density matrix ϱ_{kh} satisfies certain properties that will also have to be fulfilled during the time evolution [122, 123]: (i) its trace is unitary, $\text{Tr} \varrho = \varrho_{kk} = \sum_{j=1}^M p_j a_{kj} a_{kj}^* = \sum_{j=1}^M p_j \langle \Psi_j | \Psi_j \rangle = 1$; (ii) the diagonal elements are non-negative, $\varrho_{kk} = \sum_{j=1}^M p_j a_{kj} a_{kj}^* = \sum_{j=1}^M p_j |\langle \varphi_k | \Psi_j \rangle|^2 \geq 0$ (without the sum over k); (iii) the density matrix $\varrho_{kh} = \sum_{j=1}^M p_j a_{kj} a_{hj}^*$ is Hermitian, $\varrho_{hk}^* = \sum_{j=1}^M p_j a_{hj}^* a_{kj} = \varrho_{kh}$, or $\varrho^{T*} = \varrho$ (T means ‘transposed’); (iv) the density matrix is positive-definite, $v^{T*} \varrho v = v_k^* \varrho_{kh} v_h = \sum_{j=1}^M p_j v_k^* a_{kj} v_h a_{hj}^* = \sum_{j=1}^M p_j (v_k a_{kj}^*)^* (v_h a_{hj}^*) = \sum_{j=1}^M p_j |v_k a_{kj}^*|^2 > 0$.

Here, for the sake of clarity and simplicity, all properties are presented assuming a finite ensemble of M pure states. We emphasize, however, that the formalism is fully general and can be extended to more general statistical mixtures. In particular, the derivations remain valid for countably infinite ensembles, where the sum over the states extends to infinity, provided the probabilities converge so that the density matrix remains trace class. Furthermore, the findings also hold for continuous ensembles, wherein the discrete sum is replaced by an integral over a continuous set of states. In both cases, the key properties of the density matrix—Hermiticity, positivity and unit trace—are preserved, ensuring that all conclusions drawn for finite ensembles carry over straightforwardly to these more general settings.

For a conservative system defined by the Hamiltonian \mathcal{H}_0 , the time evolution of the density matrix is described by the Liouville–von Neumann equation [122, 123]

$$\frac{d\varrho}{dt} = \frac{1}{i\hbar} [\mathcal{H}_0, \varrho], \quad (22)$$

where $[\mathcal{A}, \mathcal{B}] = \mathcal{A}\mathcal{B} - \mathcal{B}\mathcal{A}$ is the commutator of operators \mathcal{A} and \mathcal{B} . In the following sections, we will discuss the modifications made to this conservative equation in order to consider the interactions with a thermal bath. This procedure can be performed using Hermitian friction operators (as discussed in section 4) or non-Hermitian friction operators (see section 5). In both cases, a master equation for open quantum systems is obtained.

4. First approach: Hermitian friction operators

By introducing noise and dissipation terms into this equation, we exploit the analogy with the classical approach. In particular, we apply the canonical quantization, which

replaces Poisson brackets $\{\mathcal{A}, \mathcal{B}\}$ with commutators $\frac{1}{i\hbar} [\mathcal{A}, \mathcal{B}]$ [122, 123]. Following this principle, we develop the quantum counterpart of equation (8).

The terms on the third and fifth lines, containing double Poisson brackets, can be easily converted to the quantum case by using a double commutator. The quantization of these terms is rigorous in that they correspond to the average with respect to a stochastic quantum Hamiltonian, as exhaustively described in [87, 124]. This development involves a multidimensional geometric Brownian motion (see appendix A in [87]), which is a generalization of the simpler case discussed in [119].

Regarding the second line, the terms $m_i \frac{\partial \mathcal{H}_0}{\partial p_{xi}} W$, $m_i \frac{\partial \mathcal{H}_0}{\partial p_{yi}} W$ and $m_i \frac{\partial \mathcal{H}_0}{\partial p_{zi}} W$ must be transformed into Hermitian operators. Similarly, in the fourth line, the terms $m_i \frac{\partial \mathcal{H}_0}{\partial r_{xi}} W$, $m_i \frac{\partial \mathcal{H}_0}{\partial r_{yi}} W$ and $m_i \frac{\partial \mathcal{H}_0}{\partial r_{zi}} W$ must also be transformed into Hermitian operators.

Since the product of two Hermitian operators is not necessarily Hermitian, but their symmetrization is always Hermitian, we substitute the terms in the second line with the quantum symmetrizations $\frac{1}{2}(\Theta_{xi}^p \varrho + \varrho \Theta_{xi}^p)$, $\frac{1}{2}(\Theta_{yi}^p \varrho + \varrho \Theta_{yi}^p)$ and $\frac{1}{2}(\Theta_{zi}^p \varrho + \varrho \Theta_{zi}^p)$, where Θ_{xi}^p , Θ_{yi}^p and Θ_{zi}^p are Hermitian operators to be determined ($\forall i = 1..N$), taking the role of classical momenta p_{xi}, p_{yi} and p_{zi} . Similarly, we substitute the terms in the fourth line with the quantum symmetrizations $\frac{1}{2}(\Theta_{xi}^q \varrho + \varrho \Theta_{xi}^q)$, $\frac{1}{2}(\Theta_{yi}^q \varrho + \varrho \Theta_{yi}^q)$ and $\frac{1}{2}(\Theta_{zi}^q \varrho + \varrho \Theta_{zi}^q)$, where Θ_{xi}^q , Θ_{yi}^q and Θ_{zi}^q are Hermitian operators to be determined ($\forall i = 1..N$), taking the role of classical terms $m_i \frac{\partial V_0}{\partial r_{xi}}$, $m_i \frac{\partial V_0}{\partial r_{yi}}$ and $m_i \frac{\partial V_0}{\partial r_{zi}}$.

By considering all these terms added to equation (22), we obtain the complete equation

$$\begin{aligned} \frac{d\varrho}{dt} = & \frac{1}{i\hbar} [\mathcal{H}_0, \varrho] - \frac{1}{i\hbar} \sum_{k=1}^N \sum_{s=x,y,z} f_{sk} [r_{sk}, \varrho] - \frac{k_B T \beta_p}{\hbar^2} \sum_{k=1}^N m_k \left(\sum_{s=x,y,z} [r_{sk}, [r_{sk}, \varrho]] \right) \\ & + \frac{\beta_p}{2i\hbar} \sum_{k=1}^N \left(\sum_{s=x,y,z} [r_{sk}, \Theta_{sk}^p \varrho + \varrho \Theta_{sk}^p] \right) - \frac{k_B T \beta_q}{\hbar^2} \sum_{k=1}^N m_k \left(\sum_{s=x,y,z} [p_{sk}, [p_{sk}, \varrho]] \right) \\ & - \frac{\beta_q}{2i\hbar} \sum_{k=1}^N \left(\sum_{s=x,y,z} [p_{sk}, \Theta_{sk}^q \varrho + \varrho \Theta_{sk}^q] \right), \end{aligned} \tag{23}$$

which represents the master equation for the evolution of the density matrix.

Now we must find the mathematical form of the friction Hermitian operators $\Theta_{sk}^{p,q}$, $s = x, y, z$, $k = 1, \dots, N$, in such a way that the asymptotic behavior of the equation, without external forces f_{sk} , is described by the canonical quantum distribution

$$\lim_{t \rightarrow \infty} \varrho = \varrho_{\text{eq}} = \frac{1}{Z_{\text{qu}}} e^{-\frac{\mathcal{H}_0}{k_B T}}, \tag{24}$$

where Z_{qu} is the quantum partition function

$$Z_{\text{qu}} = \text{Tr} \left(e^{-\frac{\mathcal{H}_0}{k_B T}} \right). \tag{25}$$

We impose this asymptotic quantum canonical distribution on equation (23) (with $f_{sk} = 0$), obtaining the relations

$$\frac{2im_k k_B T}{\hbar} \left[r_{sk}, e^{-\frac{\mathcal{H}_0}{k_B T}} \right] = \Theta_{sk}^p e^{-\frac{\mathcal{H}_0}{k_B T}} + e^{-\frac{\mathcal{H}_0}{k_B T}} \Theta_{sk}^p, \quad (26)$$

$$-\frac{2im_k k_B T}{\hbar} \left[p_{sk}, e^{-\frac{\mathcal{H}_0}{k_B T}} \right] = \Theta_{sk}^q e^{-\frac{\mathcal{H}_0}{k_B T}} + e^{-\frac{\mathcal{H}_0}{k_B T}} \Theta_{sk}^q, \quad (27)$$

for $s = x, y, z$ and $k = 1, \dots, N$. From a mathematical point of view, these equations in $\Theta_{sk}^{p,q}$ are matrix equations of the form $AX + XA = C$, which are sometimes called the Sylvester or Lyapunov equations [138, 139]. We proved in [87] that this equation has a unique solution

$$X = - \int_0^{+\infty} e^{A\xi} C e^{A\xi} d\xi, \quad (28)$$

provided that A has all eigenvalues with a negative real part. Hence, we can write the explicit solutions of equations (26) and (27) as

$$\Theta_{sk}^p = \frac{2im_k k_B T}{\hbar} \int_0^{+\infty} e^{-\xi e^{-\frac{\mathcal{H}_0}{k_B T}}} \left[r_{sk}, e^{-\frac{\mathcal{H}_0}{k_B T}} \right] e^{-\xi e^{-\frac{\mathcal{H}_0}{k_B T}}} d\xi, \quad (29)$$

$$\Theta_{sk}^q = -\frac{2im_k k_B T}{\hbar} \int_0^{+\infty} e^{-\xi e^{-\frac{\mathcal{H}_0}{k_B T}}} \left[p_{sk}, e^{-\frac{\mathcal{H}_0}{k_B T}} \right] e^{-\xi e^{-\frac{\mathcal{H}_0}{k_B T}}} d\xi. \quad (30)$$

These expressions are rather complicated, but they lead to simpler results when projected onto the energy basis of the Hamiltonian operator. By assuming that the spectrum of the system is discrete and nondegenerate, we can write $\mathcal{H}_0 \varphi_n(\vec{q}) = E_n \varphi_n(\vec{q})$, with $\langle \varphi_n | \varphi_m \rangle = \delta_{nm}$. Based on this, the operator $e^{-\frac{\mathcal{H}_0}{k_B T}}$ is diagonal with elements $e^{-\frac{E_n}{k_B T}}$. To simplify the notation, we introduce the quantity $e_n = e^{-\frac{E_n}{k_B T}} > 0$. Therefore, the matrix $[r_{sk}, e^{-\frac{\mathcal{H}_0}{k_B T}}]$ comprises the elements $[r_{sk}, e^{-\frac{\mathcal{H}_0}{k_B T}}]_{pq} = r_{sk,pq}(e_q - e_p)$ and the matrix $[p_{sk}, e^{-\frac{\mathcal{H}_0}{k_B T}}]$ consists of the elements $[p_{sk}, e^{-\frac{\mathcal{H}_0}{k_B T}}]_{pq} = p_{sk,pq}(e_q - e_p)$.

Hence, the structure of the friction operators in equations (29) and (30) takes a manifestly Hermitian form

$$\Theta_{sk,\ell j}^p = \frac{2im_k k_B T}{\hbar} r_{sk,\ell j} \frac{e_j - e_\ell}{e_j + e_\ell}, \quad (31)$$

$$\Theta_{sk,\ell j}^q = -\frac{2im_k k_B T}{\hbar} p_{sk,\ell j} \frac{e_j - e_\ell}{e_j + e_\ell}. \quad (32)$$

To further simplify these results, we use a simple relation between the coefficients $r_{sk,\ell j} = \langle \varphi_\ell | r_{sk} \varphi_j \rangle$ and $p_{sk,\ell j} = -i\hbar \langle \varphi_\ell | \frac{\partial}{\partial r_{sk}} \varphi_j \rangle$. We start by observing that $[r_{sk}, p_{sk}] = i\hbar$, and therefore $[r_{sk}, p_{sk}^2] = [r_{sk}, p_{sk}] p_{sk} + p_{sk} [r_{sk}, p_{sk}] = 2i\hbar p_{sk}$. Then, we can write $[r_{sk}, \mathcal{H}_0] = [r_{sk}, K_0 + V_0] = \frac{1}{2m_k} [r_{sk}, p_{sk}^2] = \frac{i\hbar}{m_k} p_{sk}$. Projecting the latter relationship onto the energy basis of the system, we obtain $r_{sk,\ell j} = \frac{i\hbar}{m_k} \frac{p_{sk,\ell j}}{E_j - E_\ell}$. On the other hand, we can also

Boltzmann to Lindblad: classical and quantum approaches to out-of-equilibrium statistical mechanics consider the relation $[p_{sk}, \mathcal{H}_0] = [p_{sk}, K_0 + V_0] = -i\hbar \frac{\partial V_0}{\partial r_{sk}}$. The projection of this equality onto the energy basis leads to $p_{sk,\ell j} = -\frac{i\hbar}{E_j - E_\ell} \left(\frac{\partial V_0}{\partial r_{sk}} \right)_{\ell j}$. Finally, substituting these results and using the property $\frac{e_j - e_\ell}{e_j + e_\ell} = \tanh\left(\frac{E_\ell - E_j}{2k_B T}\right)$ into equations (31) and (32), we obtain

$$\Theta_{sk,\ell j}^p = p_{sk,\ell j} \frac{\tanh\left(\frac{E_\ell - E_j}{2k_B T}\right)}{\frac{E_\ell - E_j}{2k_B T}}, \tag{33}$$

$$\Theta_{sk,\ell j}^q = m_k \left(\frac{\partial V_0}{\partial r_{sk}} \right)_{\ell j} \frac{\tanh\left(\frac{E_\ell - E_j}{2k_B T}\right)}{\frac{E_\ell - E_j}{2k_B T}}. \tag{34}$$

These expressions show that the friction operators Θ_{sk}^p cannot be exactly identified with p_{sk} , and the friction operators Θ_{sk}^q are not exactly identified with $m_k \frac{\partial V_0}{\partial r_{sk}}$. However, these operators are formally similar to moments and masses multiplied by potential gradients, whereas they also depend on the energy levels of the system and the temperature itself. A generalization to degenerate energy spectra is provided in appendix D of [87].

Another general form of the friction operators was obtained in [87]. In that work we only provided proof for Θ_{sk}^p , but the result can easily be generalized for Θ_{sk}^q , as follows:

$$\Theta_{sk}^p = \frac{2}{\pi} \int_{-\infty}^{+\infty} e^{+i\frac{\mathcal{H}_0}{k_B T}\eta} p_{sk} e^{-i\frac{\mathcal{H}_0}{k_B T}\eta} \log \left[\coth \left(\frac{\pi}{2} |\eta| \right) \right] d\eta, \tag{35}$$

$$\Theta_{sk}^q = \frac{2}{\pi} \int_{-\infty}^{+\infty} e^{+i\frac{\mathcal{H}_0}{k_B T}\eta} m_k \frac{\partial V_0}{\partial r_{sk}} e^{-i\frac{\mathcal{H}_0}{k_B T}\eta} \log \left[\coth \left(\frac{\pi}{2} |\eta| \right) \right] d\eta. \tag{36}$$

Of course, the interpretation of these results is similar to the previous one. Moreover, these expressions allow friction operators to be written as power series with coefficients $\frac{1}{(k_B T)^{2n}}$, as

$$\begin{aligned} \Theta_{sk}^p &= 4 \sum_{n=0}^{+\infty} \frac{1}{(k_B T)^{2n}} [\mathcal{H}_0, p_{sk}]_{2n} \frac{2^{2n+2} - 1}{(2n+2)!} B_{2n+2} \\ &= p_{sk} - \frac{1}{12(k_B T)^2} [\mathcal{H}_0, [\mathcal{H}_0, p_{sk}]] + \frac{1}{120(k_B T)^4} [\mathcal{H}_0, [\mathcal{H}_0, [\mathcal{H}_0, [\mathcal{H}_0, p_{sk}]]]] \dots, \end{aligned} \tag{37}$$

$$\begin{aligned} \frac{\Theta_{sk}^q}{m_k} &= 4 \sum_{n=0}^{+\infty} \frac{1}{(k_B T)^{2n}} \left[\mathcal{H}_0, \frac{\partial V_0}{\partial r_{sk}} \right]_{2n} \frac{2^{2n+2} - 1}{(2n+2)!} B_{2n+2} \\ &= \frac{\partial V_0}{\partial r_{sk}} - \frac{1}{12(k_B T)^2} \left[\mathcal{H}_0, \left[\mathcal{H}_0, \frac{\partial V_0}{\partial r_{sk}} \right] \right] \\ &\quad + \frac{1}{120(k_B T)^4} \left[\mathcal{H}_0, \left[\mathcal{H}_0, \left[\mathcal{H}_0, \left[\mathcal{H}_0, \frac{\partial V_0}{\partial r_{sk}} \right] \right] \right] \right] \dots, \end{aligned} \tag{38}$$

where B_k are the Bernoulli numbers $B_2 = 1/6$, $B_4 = -1/30$, $B_6 = 1/42$, ..., and we define the symbol $[\mathcal{H}_0, \mathcal{A}]_n$ through the recursive relation $[\mathcal{H}_0, \mathcal{A}]_0 = \mathcal{A}$, and $[\mathcal{H}_0, \mathcal{A}]_{n+1} = [\mathcal{H}_0, [\mathcal{H}_0, \mathcal{A}]_n]$ (see [87] for details).

4.1. Application to the quantum HO

This approach can be applied to the one-dimensional HO that, besides representing a paradigmatic example of an exactly solvable model in quantum mechanics, has numerous applications ranging from quantum optics to quantum information. The HO is, as usual, defined by the quadratic potential energy $V(x) = \frac{1}{2}m\omega^2q^2$, where $\omega = \sqrt{k/m}$ is the classical angular frequency and k is the elastic constant. The Hamiltonian of the system is $\mathcal{H}_0 = \frac{1}{2m}p^2 + \frac{1}{2}m\omega^2q^2$, whose energy levels are given by $\mathcal{H}_0\varphi_n = E_n\varphi_n$ with $E_n = \hbar\omega(n + \frac{1}{2})$, $n \geq 0$; the HO eigenfunctions can be obtained as $\varphi_n(q) = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}q^2} H_n\left(\sqrt{\frac{m\omega}{\hbar}}q\right)$, where $H_n(z)$ are the Hermite polynomials. By calculating the matrices associated with the operators q and p as $q_{nm} = \langle \varphi_n(q) | x \varphi_m(q) \rangle$ and $p_{nm} = -i\hbar \langle \varphi_n(q) | \frac{d}{dq} \varphi_m(q) \rangle$, the following results are obtained:

$$q_{nm} = \sqrt{\frac{\hbar}{2m\omega}} (\delta_{n+1,m}\sqrt{n+1} + \delta_{n,m+1}\sqrt{n}), \tag{39}$$

and

$$p_{nm} = -i\sqrt{\frac{m\omega\hbar}{2}} (\delta_{n+1,m}\sqrt{n+1} - \delta_{n,m+1}\sqrt{n}), \tag{40}$$

for $n \geq 0$ and $m \geq 0$. Therefore, the corresponding HO friction operators, defined in equations (33) and (34), are given by

$$\Theta^p = p \frac{\tanh\left(\frac{\hbar\omega}{2k_B T}\right)}{\frac{\hbar\omega}{2k_B T}}, \quad \Theta^q = m^2\omega^2q \frac{\tanh\left(\frac{\hbar\omega}{2k_B T}\right)}{\frac{\hbar\omega}{2k_B T}}. \tag{41}$$

We observe that Θ^p is proportional to p , whereas Θ^q is proportional to q . These premises allow us to write the evolution of the density matrix in the form

$$\begin{aligned} \frac{d\rho}{dt} = & \frac{1}{i\hbar} [\mathcal{H}_0, \rho] - \frac{k_B T \beta_p m}{\hbar^2} [q, [q, \rho]] + \frac{\beta_p}{2i\hbar} \frac{\tanh\left(\frac{\hbar\omega}{2k_B T}\right)}{\frac{\hbar\omega}{2k_B T}} [q, p\rho + \rho p] \\ & - \frac{k_B T \beta_q m}{\hbar^2} [p, [p, \rho]] - \frac{m^2\omega^2\beta_q}{2i\hbar} \frac{\tanh\left(\frac{\hbar\omega}{2k_B T}\right)}{\frac{\hbar\omega}{2k_B T}} [p, q\rho + \rho q]. \end{aligned} \tag{42}$$

There are two important particular cases of this equation: (i) when $\beta_q = 0$, we obtain the equation discussed in [87], corresponding to the quantization of the standard Langevin equation; and (ii) if $\beta_q = 0$ and $\hbar\omega \ll k_B T$, the Caldeira–Legget equation is obtained, with the ratio $\tanh\left(\frac{\hbar\omega}{2k_B T}\right) / \frac{\hbar\omega}{2k_B T} \simeq 1$ [13–15].

Starting from the general form stated in equation (42), we now search for the conditions under which this equation is in the Lindblad form.

The most general Lindblad master equation [21–25], which is Markovian, trace-preserving and completely positive for any initial condition, can be written in the form

$$\frac{d\rho}{dt} = \frac{1}{i\hbar} [\mathcal{H}_0, \rho] + \sum_i \gamma_i \left[\mathcal{L}_i \rho \mathcal{L}_i^\dagger - \frac{1}{2} \left(\mathcal{L}_i^\dagger \mathcal{L}_i \rho + \rho \mathcal{L}_i^\dagger \mathcal{L}_i \right) \right], \quad (43)$$

where $\gamma_i \geq 0$ are non-negative real coefficients, and \mathcal{L}_i are arbitrary operators (the symbol \dagger means ‘adjoint operator’). In [125, 126], by starting from Heisenberg’s uncertainty principle, or by using only two Lindblad operators $\mathcal{L}_i = a_i p + b_i q$, $i = 1, 2$, the authors prove that the equation is of the general mathematical form

$$\begin{aligned} \frac{d\rho}{dt} = \frac{1}{i\hbar} [\mathcal{H}_0, \rho] - \frac{\mathcal{D}_{pp}}{\hbar^2} [q, [q, \rho]] + \frac{\lambda + \mu}{2i\hbar} [q, p\rho + \rho p] + \frac{\mathcal{D}_{pq}}{\hbar^2} [q, [p, \rho]] \\ - \frac{\mathcal{D}_{qq}}{\hbar^2} [p, [p, \rho]] - \frac{\lambda - \mu}{2i\hbar} [p, q\rho + \rho q] + \frac{\mathcal{D}_{qp}}{\hbar^2} [p, [q, \rho]], \end{aligned} \quad (44)$$

where \mathcal{H}_0 represents the HO and $\mathcal{D}_{qp} = \mathcal{D}_{pq}$, is in the Lindblad form if and only if the following conditions are met:

$$\mathcal{D}_{pp} > 0, \quad (45)$$

$$\mathcal{D}_{qq} > 0, \quad (46)$$

$$\mathcal{D}_{pp}\mathcal{D}_{qq} - \mathcal{D}_{pq}^2 \geq \frac{\lambda^2 \hbar^2}{4}. \quad (47)$$

By comparing equation (42) with equation (44), we see that in our formalism $\mathcal{D}_{qp} = 0$ and

$$\mathcal{D}_{pp} = k_B T \beta_p m, \quad \mathcal{D}_{qq} = k_B T \beta_q m, \quad (48)$$

$$\lambda + \mu = \beta_p \frac{\tanh \xi}{\xi}, \quad \lambda - \mu = m^2 \omega^2 \beta_q \frac{\tanh \xi}{\xi}, \quad (49)$$

where we have defined $\xi = \frac{\hbar \omega}{2k_B T}$ to compact the notation. First, since both \mathcal{D}_{pp} and \mathcal{D}_{qq} must be strictly positive (see equations (45) and (46)), we obtain from equation (48) that both β_p and β_q must be strictly positive. This definitely demonstrates that in the classical Hamilton–Langevin equation, equations (1) and (2), the friction and noise terms must be included in both equations so that canonical quantization yields the correct results (completely positive evolution).

We also study the consequences of the constraint in equation (47). By defining $x = \beta_p / (m^2 \omega^2 \beta_q)$, this relation can be rewritten as follows:

$$4x \geq (x + 1)^2 \tanh^2 \xi \Rightarrow x^2 \tanh^2 \xi + 2x (\tanh^2 \xi - 2) + \tanh^2 \xi \leq 0. \quad (50)$$

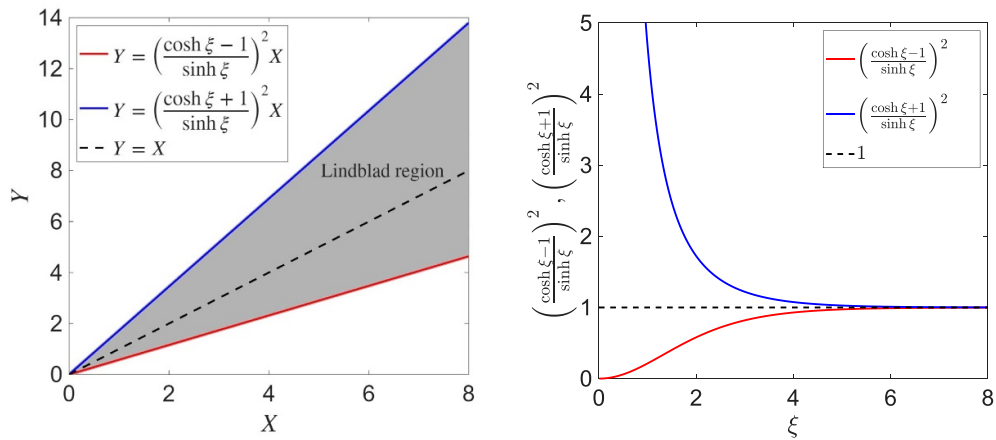


Figure 1. Left: plot of the straight lines $Y = \left(\frac{\cosh \xi - 1}{\sinh \xi}\right)^2 X$ and $Y = \left(\frac{\cosh \xi + 1}{\sinh \xi}\right)^2 X$ for $\xi = 2$, delimiting the Lindblad region ($Y = \beta_p, X = m^2 \omega^2 \beta_q$). The bisector of the first quadrant is also shown for completeness. Right: behavior of the functions $\left(\frac{\cosh \xi - 1}{\sinh \xi}\right)^2$ and $\left(\frac{\cosh \xi + 1}{\sinh \xi}\right)^2$ versus ξ . For large values of ξ , both converge to 1.

It corresponds to a second-degree inequality with discriminant $\Delta = 16(1 - \tanh^2 \xi)$; therefore, the two solutions of the associated second-degree equation can be found as

$$x_{1,2} = \left(\frac{\cosh \xi \pm 1}{\sinh \xi}\right)^2, \quad (51)$$

where we used the property $1 - \tanh^2 \xi = 1/(\cosh^2 \xi)$. The values of x that satisfy the inequality in equation (50) are in the interval $x_1 < x < x_2$, which is written more explicitly as

$$\left(\frac{\cosh \xi - 1}{\sinh \xi}\right)^2 \leq \frac{\beta_p}{m^2 \omega^2 \beta_q} \leq \left(\frac{\cosh \xi + 1}{\sinh \xi}\right)^2, \quad (52)$$

or, equivalently, as

$$-1 \leq \frac{1}{m\omega} \sqrt{\frac{\beta_p}{\beta_q}} \sinh\left(\frac{\hbar\omega}{2k_B T}\right) - \cosh\left(\frac{\hbar\omega}{2k_B T}\right) \leq +1. \quad (53)$$

This relationship must always be satisfied by the parameters $\beta_p > 0$ and $\beta_q > 0$, so that the evolution is completely positive. From the geometrical point of view, on the plane ($Y = \beta_p, X = m^2 \omega^2 \beta_q$), the region of points that satisfy the inequality corresponds to the angle in the first quadrant between the straight lines $Y = \left(\frac{\cosh \xi - 1}{\sinh \xi}\right)^2 X$ and $Y = \left(\frac{\cosh \xi + 1}{\sinh \xi}\right)^2 X$. The first straight line is always below the bisector of the first quadrant and the second is always above it (see figure 1). Therefore, a straightforward choice is to take $Y = X$ or $\beta_p = m^2 \omega^2 \beta_q$, corresponding to $\mu = 0$ (see equation (49)). Another

possibility is to take $\frac{\beta_p}{m^2\omega^2\beta_q} = \coth^2 \xi$, corresponding to the average value of the endpoints of the interval in equation (53).

We underline that although in the classical case the parameters β_p and β_q are fully arbitrary, in the quantum counterpart they are subjected to the discussed constraint to preserve complete positivity.

4.2. Relation with the quantum optical master equation

In this section, we investigate the connection between the results obtained for the dissipative quantum oscillator within the proposed framework and those based on the quantum optical master equation (QOME) [140–142]. The QOME, its derivation, approximations and validity have been widely investigated due to its large spectrum of applications, ranging from quantum optics to quantum information and computation.

In the regime of the so-called rotating wave approximation and neglecting Lamb and Stark shifts [140–142], the QOME for a damped HO (for instance, describing the damping of an electromagnetic field mode inside a cavity) reads

$$\begin{aligned} \frac{d\rho}{dt} = & -i\omega [a^\dagger a, \rho] + \frac{\gamma_0}{2} (\bar{n} + 1) \{2a\rho a^\dagger - a^\dagger a\rho - \rho a^\dagger a\} \\ & + \frac{\gamma_0}{2} \bar{n} \{2a^\dagger \rho a - a a^\dagger \rho - \rho a a^\dagger\}, \end{aligned} \quad (54)$$

where the evolution of the density operator is described in terms of the creation and annihilation operators a^\dagger and a , respectively. Although the first term represents the Hamiltonian evolution, the second and third Lindblad terms describe spontaneous emission, thermally induced emission and absorption processes. They are described by the rate γ_0 (damping of the cavity mode) and by the average number of quanta in the thermal bath of a mode with frequency ω , defined as

$$\bar{n} = \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}. \quad (55)$$

The relation between these operators and the canonical operators q , p is given by

$$a^\dagger = \sqrt{\frac{m\omega}{2\hbar}}q - i\sqrt{\frac{1}{2m\hbar\omega}}p, \quad a = \sqrt{\frac{m\omega}{2\hbar}}q + i\sqrt{\frac{1}{2m\hbar\omega}}p, \quad (56)$$

satisfying the commutation relations

$$[a, a^\dagger] = 1, \quad [a, a] = [a^\dagger, a^\dagger] = 0. \quad (57)$$

By substituting equation (56) into the QOME in equation (54), and comparing the results with equation (42), we can find the conditions among the coefficients β_p , β_q and the couple (γ_0, \bar{n}) such that the two equations coincide. After some algebra, we find that the following relation must be verified:

$$\beta_p = m^2 \omega^2 \beta_q = \frac{\gamma_0}{2} \frac{\hbar \omega}{2k_B T} (2\bar{n} + 1) = \frac{\gamma_0}{2} \frac{\frac{\hbar \omega}{2k_B T}}{\tanh\left(\frac{\hbar \omega}{2k_B T}\right)}. \quad (58)$$

We notice that this result is in perfect agreement with what we found in the previous subsection about the conditions for the Lindblad structure of equation (42). In particular, equation (42) coincides with the QOME in equation (54) for the choice $\mu = 0$ in equation (49). Importantly, it means that the QOME in equation (54) is always represented by a point lying on the bisector represented in figure 1. Thus, the results obtained for the damped HO in the quantum framework described in the previous section are fully coherent with the outcomes used in the literature based on the QOME. We also note that the cavity model introduced in [86] exhibits a clear analogy with our approach based on symmetric friction and noise in the Langevin equations and is indeed consistent with the optical master equation.

5. Second approach: non-Hermitian friction operators

We describe an alternative procedure to perform the canonical quantization of equation (8). This approach has been recently proposed in the literature in the case with $\beta_q = 0$ [127–129], and is generalized here for arbitrary values of β_p and β_q to solve the complete-positivity issue.

As before, the terms on the third and fifth lines of equation (8) containing double Poisson brackets are easily converted to the quantum case using a double commutator. Instead, the classical terms $m_i \frac{\partial \mathcal{H}_0}{\partial p_{xi}} W$, $m_i \frac{\partial \mathcal{H}_0}{\partial p_{yi}} W$ and $m_i \frac{\partial \mathcal{H}_0}{\partial p_{zi}} W$ can be converted into Hermitian operators by introducing the quantities $\frac{1}{2}(\Xi_{xi}^\dagger \varrho + \varrho \Xi_{xi}^p)$, $\frac{1}{2}(\Xi_{yi}^\dagger \varrho + \varrho \Xi_{yi}^p)$ and $\frac{1}{2}(\Xi_{zi}^\dagger \varrho + \varrho \Xi_{zi}^p)$, where Ξ_{xi}^p , Ξ_{yi}^p and Ξ_{zi}^p are non-Hermitian operators to be determined $\forall i = 1, \dots, N$ (the symbol \dagger means ‘adjoint operator’). Similarly, the classical terms $m_i \frac{\partial \mathcal{H}_0}{\partial r_{xi}} W$, $m_i \frac{\partial \mathcal{H}_0}{\partial r_{yi}} W$ and $m_i \frac{\partial \mathcal{H}_0}{\partial r_{zi}} W$ are converted into Hermitian operators by introducing the quantities $\frac{1}{2}(\Xi_{xi}^q \varrho + \varrho \Xi_{xi}^q)$, $\frac{1}{2}(\Xi_{yi}^q \varrho + \varrho \Xi_{yi}^q)$ and $\frac{1}{2}(\Xi_{zi}^q \varrho + \varrho \Xi_{zi}^q)$, where Ξ_{xi}^q , Ξ_{yi}^q and Ξ_{zi}^q are non-Hermitian operators to be determined ($\forall i = 1, \dots, N$). This choice leads to some simplifications in the calculations; however, it must be kept in mind that non-Hermitian friction operators cannot be directly associated with real physical observables.

With these premises, the complete equation, analogous to equation (23) above, is eventually obtained

$$\begin{aligned} \frac{d\varrho}{dt} = & \frac{1}{i\hbar} [\mathcal{H}_0, \varrho] - \frac{1}{i\hbar} \sum_{k=1}^N \sum_{s=x,y,z} f_{sk} [r_{sk}, \varrho] - \frac{k_B T \beta_p}{\hbar^2} \sum_{k=1}^N m_k \left(\sum_{s=x,y,z} [r_{sk}, [r_{sk}, \varrho]] \right) \\ & + \frac{\beta_p}{2i\hbar} \sum_{k=1}^N \left(\sum_{s=x,y,z} [r_{sk}, \Xi_{sk}^\dagger \varrho + \varrho \Xi_{sk}^p] \right) - \frac{k_B T \beta_q}{\hbar^2} \sum_{k=1}^N m_k \left(\sum_{s=x,y,z} [p_{sk}, [p_{sk}, \varrho]] \right) \\ & - \frac{\beta_q}{2i\hbar} \sum_{k=1}^N \left(\sum_{s=x,y,z} [p_{sk}, \Xi_{sk}^q \varrho + \varrho \Xi_{sk}^q] \right), \end{aligned} \quad (59)$$

which represents a new version of the quantum master equation. The friction operators $\Xi_{sk}^{p,q}$ must be obtained by imposing the asymptotic canonical quantum distribution stated in equation (24). Therefore, the following relations must be satisfied:

$$\frac{2im_k k_B T}{\hbar} \left[r_{sk}, e^{-\frac{\mathcal{H}_0}{k_B T}} \right] = \Xi_{sk}^{p\dagger} e^{-\frac{\mathcal{H}_0}{k_B T}} + e^{-\frac{\mathcal{H}_0}{k_B T}} \Xi_{sk}^p, \quad (60)$$

$$-\frac{2im_k k_B T}{\hbar} \left[p_{sk}, e^{-\frac{\mathcal{H}_0}{k_B T}} \right] = \Xi_{sk}^{q\dagger} e^{-\frac{\mathcal{H}_0}{k_B T}} + e^{-\frac{\mathcal{H}_0}{k_B T}} \Xi_{sk}^q, \quad (61)$$

for $s = x, y, z$, and $k = 1, \dots, N$. The solutions can be easily obtained in the form

$$\begin{aligned} \Xi_{sk}^p &= \frac{im_k k_B T}{\hbar} \left(e^{+\frac{\mathcal{H}_0}{k_B T}} r_{sk} e^{-\frac{\mathcal{H}_0}{k_B T}} - r_{sk} \right), & \Xi_{sk}^{p\dagger} &= -\frac{im_k k_B T}{\hbar} \left(e^{-\frac{\mathcal{H}_0}{k_B T}} r_{sk} e^{+\frac{\mathcal{H}_0}{k_B T}} - r_{sk} \right), \\ \Xi_{sk}^q &= -\frac{im_k k_B T}{\hbar} \left(e^{+\frac{\mathcal{H}_0}{k_B T}} p_{sk} e^{-\frac{\mathcal{H}_0}{k_B T}} - p_{sk} \right), & \Xi_{sk}^{q\dagger} &= \frac{im_k k_B T}{\hbar} \left(e^{-\frac{\mathcal{H}_0}{k_B T}} p_{sk} e^{+\frac{\mathcal{H}_0}{k_B T}} - p_{sk} \right), \end{aligned} \quad (62)$$

where we also show the adjoint operators.

Now, we recall that any non-Hermitian operator $\mathcal{A} \neq \mathcal{A}^\dagger$ can always be written in the form $\mathcal{A} = \mathcal{R} + i\mathcal{I}$, where \mathcal{R} and \mathcal{I} are Hermitian operators, with $\mathcal{R} = \mathcal{R}^\dagger$ and $\mathcal{I} = \mathcal{I}^\dagger$. The relations $\mathcal{R} = \frac{1}{2}(\mathcal{A} + \mathcal{A}^\dagger)$ and $\mathcal{I} = \frac{1}{2i}(\mathcal{A} - \mathcal{A}^\dagger)$ can be easily proved. The first friction operator Ξ_{sk}^p can therefore be decomposed in the form $\Xi_{sk}^p = \mathcal{A}_{sk}^p + i\mathcal{B}_{sk}^p$, where

$$\mathcal{A}_{sk}^p = \frac{im_k k_B T}{2\hbar} \left(e^{+\frac{\mathcal{H}_0}{k_B T}} r_{sk} e^{-\frac{\mathcal{H}_0}{k_B T}} - e^{-\frac{\mathcal{H}_0}{k_B T}} r_{sk} e^{+\frac{\mathcal{H}_0}{k_B T}} \right), \quad (63)$$

$$\mathcal{B}_{sk}^p = \frac{m_k k_B T}{2\hbar} \left(e^{+\frac{\mathcal{H}_0}{k_B T}} r_{sk} e^{-\frac{\mathcal{H}_0}{k_B T}} + e^{-\frac{\mathcal{H}_0}{k_B T}} r_{sk} e^{+\frac{\mathcal{H}_0}{k_B T}} - 2r_{sk} \right). \quad (64)$$

Similarly, the second friction operator Ξ_{sk}^q can be decomposed in the form $\Xi_{sk}^q = \mathcal{A}_{sk}^q + i\mathcal{B}_{sk}^q$, where

$$\mathcal{A}_{sk}^q = -\frac{im_k k_B T}{2\hbar} \left(e^{+\frac{\mathcal{H}_0}{k_B T}} p_{sk} e^{-\frac{\mathcal{H}_0}{k_B T}} - e^{-\frac{\mathcal{H}_0}{k_B T}} p_{sk} e^{+\frac{\mathcal{H}_0}{k_B T}} \right), \quad (65)$$

$$\mathcal{B}_{sk}^q = -\frac{m_k k_B T}{2\hbar} \left(e^{+\frac{\mathcal{H}_0}{k_B T}} p_{sk} e^{-\frac{\mathcal{H}_0}{k_B T}} + e^{-\frac{\mathcal{H}_0}{k_B T}} p_{sk} e^{+\frac{\mathcal{H}_0}{k_B T}} - 2p_{sk} \right). \quad (66)$$

These expressions are particularly useful when the operators are represented in the energy basis induced by the eigenvector equation $\mathcal{H}_0 \varphi_n(\vec{q}) = E_n \varphi_n(\vec{q})$. Under this assumption, the representation of the friction operators is obtained in the following form:

$$\begin{aligned}
 \mathcal{A}_{sk,\ell j}^p &= p_{sk,\ell j} \frac{\sinh\left(\frac{E_\ell - E_j}{k_B T}\right)}{\frac{E_\ell - E_j}{k_B T}}, & \mathcal{B}_{sk,\ell j}^p &= \frac{m_k k_B T}{\hbar} r_{sk,\ell j} \left[\cosh\left(\frac{E_\ell - E_j}{k_B T}\right) - 1 \right], \\
 \mathcal{A}_{sk,\ell j}^q &= m_k \left(\frac{\partial V_0}{\partial r_{sk}} \right)_{\ell j} \frac{\sinh\left(\frac{E_\ell - E_j}{k_B T}\right)}{\frac{E_\ell - E_j}{k_B T}}, & \mathcal{B}_{sk,\ell j}^q &= -\frac{m_k k_B T}{\hbar} p_{sk,\ell j} \left[\cosh\left(\frac{E_\ell - E_j}{k_B T}\right) - 1 \right].
 \end{aligned} \tag{67}$$

These expressions are important because they show once again that in the classical limit ($\hbar \rightarrow 0$ or $E_\ell - E_j \rightarrow 0$) we find the limiting values $\Xi_{sk}^p = \mathcal{A}_{sk}^p + i\mathcal{B}_{sk}^p \rightarrow p_{sk}$ and $\Xi_{sk}^q = \mathcal{A}_{sk}^q + i\mathcal{B}_{sk}^q \rightarrow m_k \frac{\partial V_0}{\partial r_{sk}}$, as discussed for the classical Fokker–Planck equation. As already mentioned, the analytical expressions for the friction operators are quite manageable in this case, but they lose the Hermitian character that is typical of genuine physical observables.

5.1. Application to the quantum HO

We apply this formalism to the one-dimensional HO to study the deviations from the previous case. As before, we consider the Hamiltonian of the system in the form $\mathcal{H}_0 = \frac{1}{2m}p^2 + \frac{1}{2}m\omega^2q^2$, and we obtain the explicit form of the friction operators as

$$\Xi^p = \frac{\sinh\left(\frac{\hbar\omega}{k_B T}\right)}{\frac{\hbar\omega}{k_B T}} p + im\omega \frac{\cosh\left(\frac{\hbar\omega}{k_B T}\right) - 1}{\frac{\hbar\omega}{k_B T}} q, \tag{68}$$

$$\Xi^q = m^2\omega^2 \frac{\sinh\left(\frac{\hbar\omega}{k_B T}\right)}{\frac{\hbar\omega}{k_B T}} q - im\omega \frac{\cosh\left(\frac{\hbar\omega}{k_B T}\right) - 1}{\frac{\hbar\omega}{k_B T}} p. \tag{69}$$

In this case, the friction operators are given by a linear combination of the operators p and q . By comparing them with equation (41), it is observed that in any case when $\frac{\hbar\omega}{k_B T} \rightarrow 0$ the two operators converge to p and $m^2\omega^2q$, respectively. The obtained operators in equations (68) and (69) can be inserted into the quantum master equation stated by equation (59), to eventually obtain

$$\begin{aligned}
 \frac{d\rho}{dt} &= \frac{1}{i\hbar} [\mathcal{H}_0, \rho] - \frac{k_B T \beta_p m}{\hbar^2} [q, [q, \rho]] + \frac{\beta_p}{2i\hbar} \frac{\sinh\left(\frac{\hbar\omega}{k_B T}\right)}{\frac{\hbar\omega}{k_B T}} [q, p\rho + \rho p] \\
 &\quad - \frac{k_B T \beta_q m}{\hbar^2} [p, [p, \rho]] - \frac{m^2\omega^2 \beta_q}{2i\hbar} \frac{\sinh\left(\frac{\hbar\omega}{k_B T}\right)}{\frac{\hbar\omega}{k_B T}} [p, q\rho + \rho q] \\
 &\quad - \frac{m\omega\beta_p}{2\hbar} \frac{\cosh\left(\frac{\hbar\omega}{k_B T}\right) - 1}{\frac{\hbar\omega}{k_B T}} [q, [q, \rho]] - \frac{m\omega\beta_q}{2\hbar} \frac{\cosh\left(\frac{\hbar\omega}{k_B T}\right) - 1}{\frac{\hbar\omega}{k_B T}} [p, [p, \rho]].
 \end{aligned} \tag{70}$$

This equation can be compared with equation (44), and we can identify the crucial parameters for verifying its Lindblad character. First of all, we have that $\mathcal{D}_{qp} = 0$, and moreover we get

$$\mathcal{D}_{pp} = k_B T \beta_p m + \frac{m \hbar \omega \beta_p \cosh \eta - 1}{2 \eta}, \quad (71)$$

$$\mathcal{D}_{qq} = k_B T \beta_q m + \frac{m \hbar \omega \beta_q \cosh \eta - 1}{2 \eta}, \quad (72)$$

$$\lambda + \mu = \beta_p \frac{\sinh \eta}{\eta}, \quad \lambda - \mu = m^2 \omega^2 \beta_q \frac{\sinh \eta}{\eta}, \quad (73)$$

where we have defined $\eta = \frac{\hbar \omega}{k_B T}$ to compact the notation. As in the previous case, since both \mathcal{D}_{pp} and \mathcal{D}_{qq} must be strictly positive (see equations (45) and (46)), we obtain from equations (71) and (72) that both β_p and β_q must be strictly positive. Again, this proves that we must include the friction and noise terms in both Hamilton–Langevin equations (see equations (1) and (2)). We now investigate the condition in equation (47). By defining again $x = \beta_p / (m^2 \omega^2 \beta_q)$, this relation can be rewritten as

$$4x(1 + \cosh \eta)^2 \geq (x + 1)^2 \sinh^2 \eta, \quad (74)$$

which is equivalent to

$$x^2 \sinh^2 \eta - x(8 + 8 \cosh \eta + 2 \sinh^2 \eta) + \sinh^2 \eta \leq 0. \quad (75)$$

This second-degree inequality leads to a discriminant $\Delta = 32(1 + \cosh \eta)^3 = 256 \cosh^6(\frac{\eta}{2}) = 256 \cosh^6 \xi$, where $\xi = \frac{\hbar \omega}{2k_B T}$, as before. Hence, we determine the two solutions as

$$x_{1,2} = \left[\frac{\cosh(\frac{\eta}{2}) \pm 1}{\sinh(\frac{\eta}{2})} \right]^2 = \left(\frac{\cosh \xi \pm 1}{\sinh \xi} \right)^2, \quad (76)$$

where we use the standard relations $\cosh \eta = \sinh^2 \xi + \cosh^2 \xi$ and $\sinh \eta = 2 \sinh \xi \cosh \xi$.

Importantly, these solutions coincide with those obtained in equation (51). Hence, also in this second case, we recover the conditions under which the equation attains the Lindblad form, which are precisely the same as those derived in the first case, expressed in equation (52) or (53). Remarkably, this condition turns out to be independent of the specific choice of friction operators, suggesting that it could represent a more general, possibly universal, result.

6. Quantum stochastic thermodynamics

In this section we construct the thermodynamic formulation starting from the evolution equation for the density matrix introduced in equation (23). For the sake of clarity, and without loss of generality, we confine our discussion to the case of Hamiltonian friction operators, which are analytically tractable but also the most relevant from a physical standpoint. Within this framework, we establish the first and second laws of

thermodynamics after introducing the notions of internal energy and entropy associated with the system. The same line of analysis can be extended to the second case with non-Hermitian friction operators; nevertheless, we refrain from presenting it here for conciseness, as it yields results that are essentially analogous to those described below.

6.1. First law of thermodynamics

To retrieve the first law of thermodynamics, we firstly introduce the internal energy \mathcal{E} of the system, defined as the expectation value of the Hamiltonian operator, $\mathcal{E} = \text{Tr}(\mathcal{H}_0 \varrho)$. The time evolution of this internal energy is

$$\frac{d\mathcal{E}}{dt} = \frac{d\text{Tr}(\mathcal{H}_0 \varrho)}{dt} = \text{Tr}\left(\mathcal{H}_0 \frac{d\varrho}{dt}\right). \tag{77}$$

We need to substitute here the terms coming from equation (23). The classical Liouvillian term leads to $\text{Tr}(\mathcal{H}_0 [\mathcal{H}_0, \varrho]) = 0$, because of the cyclic property of the trace. Concerning the effect of external forces, we need to develop $\text{Tr}(\mathcal{H}_0 [r_{sk}, \varrho]) = \text{Tr}([\mathcal{H}_0, r_{sk}] \varrho)$, where we use again the cyclic property of the trace. We can now use relation $[r_{sk}, \mathcal{H}_0] = \frac{i\hbar}{m_k} p_{sk}$, and we get $\text{Tr}(\mathcal{H}_0 [r_{sk}, \varrho]) = -i\hbar \mathbb{E}\{p_{sk}\} / m_k$. An arbitrary noise term delivers the contribution

$$\begin{aligned} \text{Tr}(\mathcal{H}_0 [r_{sk}, [r_{sk}, \varrho]]) &= \text{Tr}([\mathcal{H}_0, r_{sk}] [r_{sk}, \varrho]) \\ &= -\frac{i\hbar}{m_k} \text{Tr}(p_{sk} [r_{sk}, \varrho]) = -\frac{i\hbar}{m_k} \text{Tr}([p_{sk}, r_{sk}] \varrho) = -\frac{\hbar^2}{m_k}, \end{aligned} \tag{78}$$

or

$$\begin{aligned} \text{Tr}(\mathcal{H}_0 [p_{sk}, [p_{sk}, \varrho]]) &= \text{Tr}([\mathcal{H}_0, p_{sk}] [p_{sk}, \varrho]) \\ &= i\hbar \text{Tr}\left(\frac{\partial V_0}{\partial r_{sk}} [p_{sk}, \varrho]\right) = i\hbar \text{Tr}\left(\left[\frac{\partial V_0}{\partial r_{sk}}, p_{sk}\right] \varrho\right) \\ &= -\hbar^2 \mathbb{E}\left\{\frac{\partial^2 V_0}{\partial r_{sk}^2}\right\}. \end{aligned} \tag{79}$$

Moreover, the arbitrary friction contribution corresponds to the term

$$\begin{aligned} \text{Tr}(\mathcal{H}_0 [r_{sk}, \Theta_{sk}^p \varrho + \varrho \Theta_{sk}^p]) &= \text{Tr}([\mathcal{H}_0, r_{sk}] (\Theta_{sk}^p \varrho + \varrho \Theta_{sk}^p)) \\ &= -\frac{i\hbar}{m_k} \text{Tr}(p_{sk} (\Theta_{sk}^p \varrho + \varrho \Theta_{sk}^p)) \\ &= -\frac{i\hbar}{m_k} \mathbb{E}\{p_{sk} \Theta_{sk}^p + \Theta_{sk}^p p_{sk}\}, \end{aligned}$$

or

$$\begin{aligned} \text{Tr}(\mathcal{H}_0 [p_{sk}, \Theta_{sk}^q \varrho + \varrho \Theta_{sk}^q]) &= \text{Tr}([\mathcal{H}_0, p_{sk}] (\Theta_{sk}^q \varrho + \varrho \Theta_{sk}^q)) \\ &= i\hbar \text{Tr} \left(\frac{\partial V_0}{\partial r_{sk}} (\Theta_{sk}^q \varrho + \varrho \Theta_{sk}^q) \right) \\ &= i\hbar \mathbb{E} \left\{ \frac{\partial V_0}{\partial r_{sk}} \Theta_{sk}^q + \Theta_{sk}^q \frac{\partial V_0}{\partial r_{sk}} \right\}. \end{aligned}$$

Summing up all contributions, we obtain the following result:

$$\begin{aligned} \frac{d\mathcal{E}}{dt} &= \sum_{k=1}^N \sum_{s=x,y,z} f_{sk} \frac{1}{m_k} \mathbb{E}\{p_{sk}\} \\ &+ 2\beta_p \left[\frac{3}{2} N k_B T - \sum_{k=1}^N \sum_{s=x,y,z} \frac{1}{2m_k} \mathbb{E} \left\{ \frac{p_{sk} \Theta_{sk}^p + \Theta_{sk}^p p_{sk}}{2} \right\} \right] \\ &+ \beta_q \left[k_B T \sum_{k=1}^N \sum_{s=x,y,z} m_k \mathbb{E} \left\{ \frac{\partial^2 V_0}{\partial r_{sk}^2} \right\} - \sum_{k=1}^N \sum_{s=x,y,z} \mathbb{E} \left\{ \frac{\frac{\partial V_0}{\partial r_{sk}} \Theta_{sk}^q + \Theta_{sk}^q \frac{\partial V_0}{\partial r_{sk}}}{2} \right\} \right]. \end{aligned} \quad (80)$$

This represents the first law of thermodynamics, where we can identify the average rate of work $\frac{d\mathbb{E}\{L\}}{dt}$ done on the system with the average power $\sum_{k=1}^N \vec{f}_k \cdot \mathbb{E}\{\vec{p}_k\}/m_k$ of the external forces. This term is identical to the one obtained in the classical analysis of the problem. The second and third terms in equation (80) represent the average rate of heat $\frac{d\mathbb{E}\{Q\}}{dt}$ entering the system. We know that Hermitian operators Θ_{sk}^p take the role of classical momenta p_{sk} . Similarly, Hermitian operators Θ_{sk}^q are the quantum counterpart of the classical terms $m_k \frac{\partial V_0}{\partial r_{sk}}$. Therefore, the term $\sum_{k=1}^N \sum_{s=x,y,z} \frac{1}{2m_k} \mathbb{E} \left\{ \frac{p_{sk} \Theta_{sk}^p + \Theta_{sk}^p p_{sk}}{2} \right\}$ represents the quantum modified average kinetic energy of the system, corresponding to the classical term $\sum_{k=1}^N \frac{1}{2m_k} \mathbb{E}\{\vec{p}_k \cdot \vec{p}_k\}$. Moreover, the quantum term $\sum_{k=1}^N \sum_{s=x,y,z} \mathbb{E} \left\{ \left(\frac{\partial V_0}{\partial r_{sk}} \Theta_{sk}^q + \Theta_{sk}^q \frac{\partial V_0}{\partial r_{sk}} \right) / 2 \right\}$ corresponds to the classical contribution $\sum_{k=1}^N \sum_{s=x,y,z} m_k \mathbb{E} \left\{ \left(\frac{\partial V_0}{\partial r_{sk}} \right)^2 \right\}$. Therefore, it can be affirmed that the quantum version of the first law perfectly corresponds to the classical one, stated in equation (11).

It is worth noting that the friction coefficients β_p and β_q determine the characteristic rate of relaxation toward equilibrium, namely the rate at which equipartition is established. Indeed, the two bracketed terms multiplying the coefficients β_p and β_q in equation (80) identically vanish at thermodynamic equilibrium. The corresponding identities thus obtained can be interpreted as two distinct formulations of the quantum equipartition theorem. They can be written as follows:

$$\frac{1}{2} k_B T = \frac{1}{2m_k} \mathbb{E} \left\{ \frac{p_{sk} \Theta_{sk}^p + \Theta_{sk}^p p_{sk}}{2} \right\}, \quad (81)$$

$$k_B T m_k \mathbb{E} \left\{ \frac{\partial^2 V_0}{\partial r_{sk}^2} \right\} = \mathbb{E} \left\{ \frac{\frac{\partial V_0}{\partial r_{sk}} \Theta_{sk}^q + \Theta_{sk}^q \frac{\partial V_0}{\partial r_{sk}}}{2} \right\}. \tag{82}$$

These two relations represent the quantum version of equation (12), and they can be directly proved by using the equilibrium density matrix stated in equation (24). The proof of equation (81) can be found in [87], and the proof of equation (82) can be performed in a very similar way (omitted here for brevity).

6.2. Second law of thermodynamics

In this section, we develop a balance equation for the von Neumann entropy of the system defined as follows:

$$\mathcal{S} = -k_B \text{Tr}(\varrho \ln \varrho) = -k_B \mathbb{E}(\ln \varrho). \tag{83}$$

To begin, we calculate the time derivative of entropy

$$\frac{d\mathcal{S}}{dt} = -k_B \text{Tr} \left(\frac{d\varrho}{dt} \ln \varrho + \varrho \frac{d}{dt} \ln \varrho \right), \tag{84}$$

and we remember that $\text{Tr}(\varrho \frac{d}{dt} \ln \varrho) = 0$ (see [87]). Hence, we obtain a simpler relation

$$\frac{d\mathcal{S}}{dt} = -k_B \text{Tr} \left(\frac{d\varrho}{dt} \ln \varrho \right). \tag{85}$$

The entropy balance can be further elaborated by considering the density matrix evolution given in equation (23). The Hamiltonian contribution leads to the following term:

$$\text{Tr}([\mathcal{H}_0, \varrho] \ln \varrho) = \text{Tr}(\mathcal{H}_0 \varrho \ln \varrho - \varrho \mathcal{H}_0 \ln \varrho) = \text{Tr}(\mathcal{H}_0 [\varrho, \ln \varrho]) = 0, \tag{86}$$

where we apply the cyclic property of the trace, and recall that ϱ commutes with $\ln \varrho$. The contribution of external forces is also zero, in fact

$$\text{Tr}([r_{sk}, \varrho] \ln \varrho) = \text{Tr}(r_{sk} \varrho \ln \varrho - \varrho r_{sk} \ln \varrho) = \text{Tr}(r_{sk} [\varrho, \ln \varrho]) = 0. \tag{87}$$

To complete the entropy balance, we rewrite equation (23) in a compact form

$$\frac{d\varrho}{dt} = \frac{1}{i\hbar} [\mathcal{H}_0, \varrho] + \mathcal{A} \varrho + \mathcal{R} \varrho = \mathcal{L} \varrho, \tag{88}$$

where $\mathcal{A} \varrho$ denotes the contribution of the external force, $\mathcal{R} \varrho$ encompasses the friction and noise terms (i.e. the quantum Langevin bath) and $\mathcal{L} \varrho$ represents the sum of all contributions in the evolution equation. Since the Hamiltonian and external force contributions vanish in the entropic balance, we may then write

$$\frac{d\mathcal{S}}{dt} = -k_B \text{Tr}(\mathcal{R} \varrho \ln \varrho). \tag{89}$$

Similarly, the average heat rate defined in the previous section can be written as

$$\frac{d\mathbb{E}\{Q\}}{dt} = \text{Tr}(\mathcal{R}\varrho\mathcal{H}_0) = k_B T \text{Tr}\left(\mathcal{R}\varrho\frac{\mathcal{H}_0}{k_B T}\right). \quad (90)$$

Therefore, we can write the second law of thermodynamics as follows:

$$\frac{d\mathcal{S}}{dt} = \frac{1}{T} \frac{d\mathbb{E}\{Q\}}{dt} + \frac{d\mathcal{S}_p}{dt}, \quad (91)$$

where

$$\frac{d\mathcal{S}_p}{dt} = -k_B \text{Tr}\left[\mathcal{R}\varrho\left(\ln\varrho + \frac{\mathcal{H}_0}{k_B T}\right)\right]. \quad (92)$$

The term $\frac{d\mathcal{S}_f}{dt} = \frac{1}{T} \frac{d\mathbb{E}\{Q\}}{dt}$ represents the entropy flow, that is, the amount of entropy entering the system due to heat exchange. The term $\frac{d\mathcal{S}_p}{dt}$ represents the production of entropy, due to the irreversibility of the thermodynamic transformation. It must always be positive for consistency with classical thermodynamics.

The entropy production term can be simplified by introducing the asymptotic canonical distribution $\varrho_{\text{eq}} = \frac{1}{Z_{\text{qu}}} e^{-\frac{\mathcal{H}_0}{k_B T}}$. Its logarithm is given by $\ln\varrho_{\text{eq}} = \left(\ln\frac{1}{Z_{\text{qu}}}\right)I - \frac{\mathcal{H}_0}{k_B T}$ (see [87]). Since the term $\left(\ln\frac{1}{Z_{\text{qu}}}\right)I$ does not contribute to entropy production, owing to $\text{Tr}[\mathcal{R}\varrho] = 0$, the quantity $\frac{d\mathcal{S}_p}{dt}$ can be expressed in the following form:

$$\frac{d\mathcal{S}_p}{dt} = k_B \text{Tr}[\mathcal{R}\varrho(\ln\varrho_{\text{eq}} - \ln\varrho)]. \quad (93)$$

We now demonstrate that the rate of entropy production remains strictly positive throughout the relaxation toward equilibrium. To this end, we consider the system in the absence of any externally applied force, whose dynamics is governed by the evolution equation $\frac{d\varrho}{dt} = \frac{1}{i\hbar}[\mathcal{H}_0, \varrho] + \mathcal{R}\varrho = \mathcal{L}\varrho$. From equation (93), an equivalent expression for the entropy production can be written as:

$$\frac{d\mathcal{S}_p}{dt} = k_B \text{Tr}[\mathcal{L}\varrho(\ln\varrho_{\text{eq}} - \ln\varrho)]. \quad (94)$$

Here, the relaxation operator \mathcal{R} has been replaced by \mathcal{L} since $\text{Tr}([\mathcal{H}_0, \varrho]\ln\varrho_{\text{eq}}) = \text{Tr}([\mathcal{H}_0, \varrho]\ln\varrho) = 0$. We note that the evolution equation $\frac{d\varrho}{dt} = \mathcal{L}\varrho$ admits the formal solution $\varrho(t) = e^{\mathcal{L}t}\varrho(0)$. Moreover, we can define the quantum relative entropy of ϱ_1 with respect to ϱ_2 as follows:

$$\mathcal{S}(\varrho_1|\varrho_2) \equiv \text{Tr}[\varrho_1 \ln\varrho_1 - \varrho_1 \ln\varrho_2]. \quad (95)$$

This represents a distance measure between the states described by the two density matrices ϱ_1 and ϱ_2 [143]. We recall that Klein's inequality states that the quantum relative entropy $\mathcal{S}(\varrho_1|\varrho_2)$ is non-negative, and it is zero if and only if $\varrho_1 = \varrho_2$ [144]. We will use this result in the following developments. To better understand the structure

of equation (94), assuming that $\varrho = \varrho(t)$, we perform the following calculation:

$$\begin{aligned}
 -\frac{d}{d\tau} \mathcal{S}(e^{\mathcal{L}\tau} \varrho | \varrho_{\text{eq}}) \Big|_{\tau=0} &= \frac{d}{d\tau} \left[\text{Tr} \left(e^{\mathcal{L}\tau} \varrho \ln \varrho_{\text{eq}} \right) - \text{Tr} \left(e^{\mathcal{L}\tau} \varrho \ln e^{\mathcal{L}\tau} \varrho \right) \right] \Big|_{\tau=0} \\
 &= \left[\text{Tr} \left(e^{\mathcal{L}\tau} \mathcal{L} \varrho \ln \varrho_{\text{eq}} \right) - \text{Tr} \left(e^{\mathcal{L}\tau} \mathcal{L} \varrho \ln e^{\mathcal{L}\tau} \varrho \right) - \text{Tr} \left(e^{\mathcal{L}\tau} \varrho \frac{d}{d\tau} \ln e^{\mathcal{L}\tau} \varrho \right) \right] \Big|_{\tau=0}, \quad (96)
 \end{aligned}$$

where the last term is zero since we know that $\text{Tr} \left(\varrho \frac{d}{dt} \ln \varrho \right) = 0$ for any density matrix ϱ . Therefore, we obtain

$$-\frac{d}{d\tau} \mathcal{S}(e^{\mathcal{L}\tau} \varrho | \varrho_{\text{eq}}) \Big|_{\tau=0} = \text{Tr}(\mathcal{L} \varrho \ln \varrho_{\text{eq}} - \mathcal{L} \varrho \ln \varrho), \quad (97)$$

which means that the rate of entropy production can be determined through the expression

$$\frac{d\mathcal{S}_p}{dt} = -k_B \frac{d}{d\tau} \mathcal{S}(e^{\mathcal{L}\tau} \varrho | \varrho_{\text{eq}}) \Big|_{\tau=0}, \quad (98)$$

which was first proven in [26]. The latter can be further elaborated as follows:

$$\begin{aligned}
 \frac{d\mathcal{S}_p}{dt} &= -k_B \lim_{\Delta \rightarrow 0} \frac{\mathcal{S}(e^{\mathcal{L}(\tau+\Delta)} \varrho | \varrho_{\text{eq}}) - \mathcal{S}(e^{\mathcal{L}\tau} \varrho | \varrho_{\text{eq}})}{\Delta} \Big|_{\tau=0} \\
 &= -k_B \lim_{\Delta \rightarrow 0} \frac{\mathcal{S}(e^{\mathcal{L}\Delta} \varrho | \varrho_{\text{eq}}) - \mathcal{S}(\varrho | \varrho_{\text{eq}})}{\Delta} \\
 &= -k_B \lim_{\Delta \rightarrow 0} \frac{\mathcal{S}(e^{\mathcal{L}\Delta} \varrho | e^{\mathcal{L}\Delta} \varrho_{\text{eq}}) - \mathcal{S}(\varrho | \varrho_{\text{eq}})}{\Delta}, \quad (99)
 \end{aligned}$$

where we used the property $e^{\mathcal{L}\Delta} \varrho_{\text{eq}} = \varrho_{\text{eq}}$, defining the equilibrium solution.

The result in equation (99) is significant since it expresses the entropic production as the difference between the relative entropies $\mathcal{S}(e^{\mathcal{L}\Delta} \varrho | e^{\mathcal{L}\Delta} \varrho_{\text{eq}})$ and $\mathcal{S}(\varrho | \varrho_{\text{eq}})$. We recall an important property: the relative entropy decreases monotonically under the action of any completely positive, trace-preserving map Φ acting on the density matrix

$$\mathcal{S}(\Phi \varrho_1 | \Phi \varrho_2) \leq \mathcal{S}(\varrho_1 | \varrho_2). \quad (100)$$

This inequality is called monotonicity of the quantum relative entropy, and it was first proved by Lindblad [21, 22]. Therefore, the rate of entropy production in equation (99) is non-negative if the operator $e^{\mathcal{L}\Delta}$ is completely positive and trace-preserving.

It is known that the equation describing a density matrix provides a completely positive and trace-preserving evolution if and only if it can be put into the so-called Lindblad form [23–25]. Thus, if we assume that our equation generates a completely positive and trace-preserving evolution (we prove this point only for the HO), the entropy production rate will always be non-negative

$$\frac{d\mathcal{S}_p}{dt} = -k_B \lim_{\Delta \rightarrow 0} \frac{\mathcal{S}(e^{\mathcal{L}\Delta} \varrho | e^{\mathcal{L}\Delta} \varrho_{\text{eq}}) - \mathcal{S}(\varrho | \varrho_{\text{eq}})}{\Delta} \geq 0. \quad (101)$$

We note that the non-negativity of quantum entropy production has been established in the literature through a variety of approaches and methodologies, which nonetheless lead to conclusions consistent with the result obtained here [26–32].

To show a further connection with non-equilibrium thermodynamics, we also introduce the Helmholtz free energy $\mathcal{F} = \mathcal{E} - T\mathcal{S}$ and study its evolution. Recalling the previously discussed relation $\mathcal{H}_0 = -k_B T \ln \rho_{\text{eq}} + k_B T \left(\ln \frac{1}{Z_{\text{qu}}} \right) I$, we obtain

$$\mathcal{F} = k_B T \text{Tr}(\rho \ln \rho - \rho \ln \rho_{\text{eq}}) - k_B T \ln Z_{\text{qu}}. \quad (102)$$

It can be seen that at equilibrium the free energy takes on the asymptotic value $\mathcal{F} = -k_B T \ln Z_{\text{qu}}$, which corresponds to the standard expression of equilibrium statistical mechanics. The first part of equation (102) can be identified with a relative entropy, and we can indeed write

$$\mathcal{F} = k_B T \mathcal{S}(\rho | \rho_{\text{eq}}) - k_B T \ln Z_{\text{qu}}. \quad (103)$$

On the one hand we can use the previously mentioned Klein inequality $\mathcal{S}(\rho | \rho_{\text{eq}}) \geq 0$, and immediately see that free energy always takes values larger than its equilibrium value

$$\mathcal{F} \geq -k_B T \ln Z_{\text{qu}}. \quad (104)$$

In contrast, the free energy always decreases as time increases since

$$\frac{d\mathcal{F}}{dt} = -\frac{1}{T} \frac{d\mathcal{S}_p}{dt}. \quad (105)$$

This underlines that a negative free energy change is a necessary condition for spontaneity (irreversibility). Altogether, our analysis confirms the complete consistency between the quantum formalism and macroscopic non-equilibrium thermodynamics.

7. Numerical results

In this final section we describe the implementation and the results obtained for the evolution equation of the density matrix for the HO. The HO evolution equation is projected onto the energy basis and solved numerically to observe the thermodynamics of the system during its relaxation towards thermal equilibrium.

The first results are displayed in figure 2, where we plot the evolution of the main quantities over time for different initial conditions, taking a 16×16 density matrix as a practical example of implementation. In this figure, one can compare five different models. The solid blue lines correspond to the model with Hermitian friction operators, with $\beta_p = m^2 \omega^2 \beta_q$ (ensuring complete positivity) (see equation (42)). The solid red lines correspond to the model with non-Hermitian friction operators, with $\beta_p = m^2 \omega^2 \beta_q$ (ensuring complete positivity) (see equation (70)). The dashed blue and

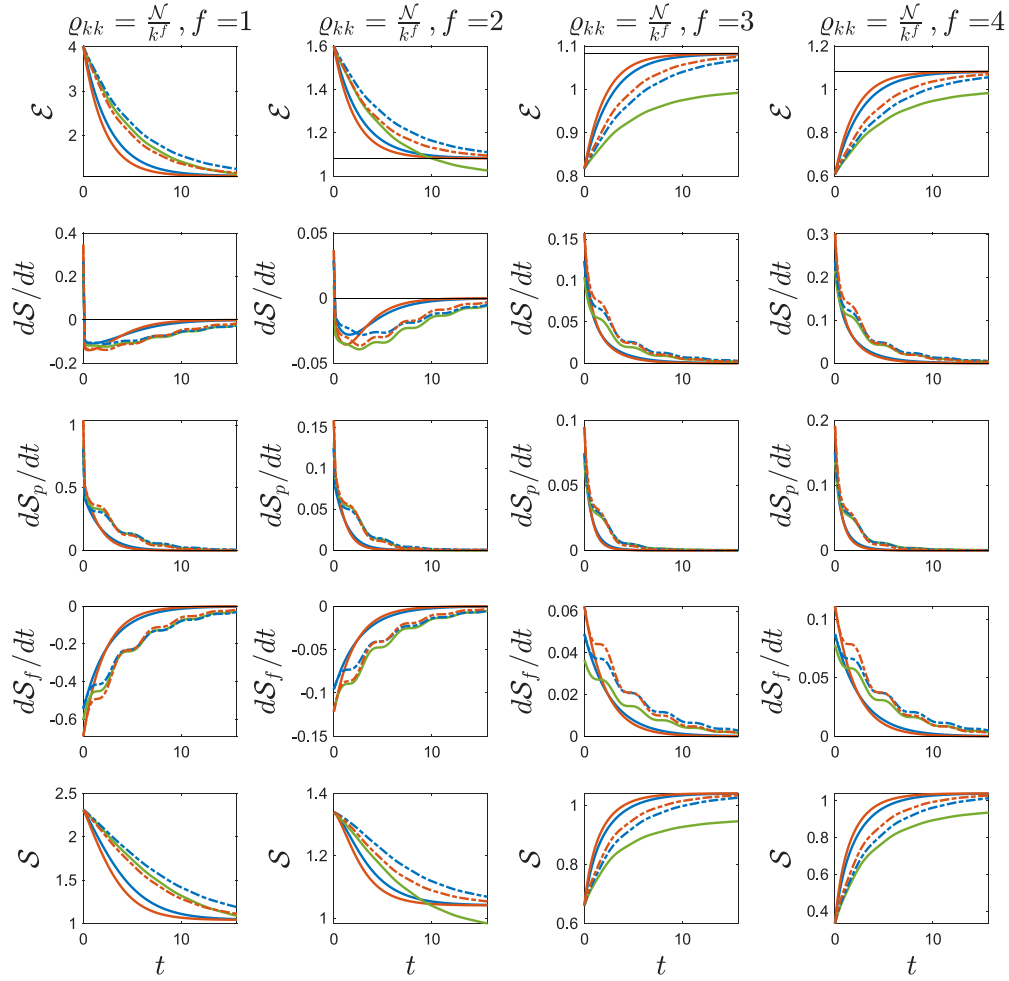


Figure 2. Results for the quantum harmonic oscillator in contact with a thermal bath. Each column represents the plots corresponding to an initial density matrix (16×16) given by $\rho_{kk}(0) = \mathcal{N}/k^f$, with $f = 1, 2, 3, 4$ (\mathcal{N} is a normalizing factor). In the first row, we show the total energy \mathcal{E} , which must converge to $\frac{1}{2}\hbar\omega + \hbar\omega/(e^{\frac{\hbar\omega}{k_B T}} - 1)$. In the following rows, one can find the behavior of the total entropy rate $\frac{d\mathcal{S}}{dt}$, the entropy production rate $\frac{d\mathcal{S}_p}{dt}$, which is always positive, and the entropy flow rate $\frac{d\mathcal{S}_f}{dt}$. In the last row, we plot the entropy \mathcal{S} . Solid blue and red lines correspond to Hermitian and non-Hermitian friction operators with $\beta_p = m^2\omega^2\beta_q$. Dashed blue and red lines correspond to Hermitian and non-Hermitian friction operators with $\beta_q = 0$. Solid green lines correspond to the Caldeira–Leggett model. We adopted the parameters $\hbar = 1$, $k_B = 1$, $T = 1$, $\beta_p = 0.2$, $\omega = 1$ and $m = 1$ in arbitrary units. We calculated 1000 times the exponential of a 256×256 matrix with a time step $\pi/200$.

red lines correspond to models with Hermitian and non-Hermitian friction operators, respectively, when $\beta_q = 0$. Notably, the blue dashed lines describe the model discussed in [87] and the red dashed lines the model introduced in [127–129]. In these cases,

complete positivity is not guaranteed. Finally, the solid green lines correspond to the Caldeira–Leggett model [13–15], where $\beta_q = 0$ and $\Theta^p = p$. In this case, neither complete positivity nor thermodynamic consistency is guaranteed.

In figure 2, we consider as the initial condition a mixed state composed of energy eigenfunctions with probability $p_k = \mathcal{N}/k^f$ for chosen values of the parameter f (\mathcal{N} is a normalizing factor, and $k = 1$ corresponds to the fundamental state). The initial density matrix takes the form $\rho_{kk}(0) = \mathcal{N}/k^f$, $\rho_{kh}(0) = 0$ if $h \neq k$. It is observed that for large f the probability distribution decays sharply with k , restricting the system to low-energy states and yielding a correspondingly low initial energy. In contrast, for small f , the decay is slower, enabling substantial occupation of high-energy states and resulting in a higher initial energy. Recall that the asymptotic mean energy at thermal equilibrium is given by $\frac{1}{2}\hbar\omega + \hbar\omega/(e^{\frac{\hbar\omega}{k_B T}} - 1)$. In this construction, the selected superpositions of states are employed to define two initial conditions whose energies exceed the thermal equilibrium value, and two others whose energies lie below it. The first two cases (with $f = 1, 2$) are shown in the first two columns of figure 2, and the other two (with $f = 3, 4$) in the next two columns.

In the panels of the first row we observe the evolution of the internal energy. In the first two columns, the total energy decreases because of the outgoing heat, and in the other two the energy increases because of the incoming heat. These heat flows generate an entropy flow rate that can be negative or positive. This is evident in the panels of the fourth row of figure 2, where the entropy flow rate is negative in the first two cases and positive in the other two. The entropy production rate is always positive, in accordance with the second law of thermodynamics (see the third row of figure 2 and equation (101)). This term, in fact, corresponds to the irreversibility and spontaneity of the process rather than the direction of heat flow. The total entropy rate can also have a sign that depends on the initial conditions and the state of progress of the relaxation process (see the second row in figure 2). In the last row of the figure we show the evolution of the total entropy \mathcal{S} , which may increase or decrease depending on thermal fluxes.

From these results, we conclude that the Caldeira–Leggett model does not comply with thermodynamics, as the asymptotic internal energy does not match the value predicted by the canonical quantum distribution. The other models appear to be consistent with thermodynamics, as they comply with all the evolutions predicted by the first and second laws, as discussed in section 6. Moreover, we checked that all eigenvalues of ρ remain positive during the time evolution of the previous system.

Nevertheless, these observations correspond to initial conditions specified by particular mixed states. If we instead consider pure initial states we obtain the results shown in figure 3, which reveal other interesting phenomena. Here, we consider the four initial conditions corresponding to the pure states characterized by the first four energy states of the HO. This means that we consider the initial density matrix taking the form $\rho_{ss}(0) = 1$ for $s = 1, 2, 3$ or 4 , $\rho_{kk}(0) = 0$ if $k \neq s$, and $\rho_{kh}(0) = 0$ if $h \neq k$. These four initial conditions lead to the evolutions shown in figure 3, where we exhibit the same physical quantities considered in figure 2 for a short interval of time. The evolution of energy shows no significant changes, and even in this case only the Caldeira–Leggett model does not respect the correct energetic thermodynamic asymptotic value. In the entropy

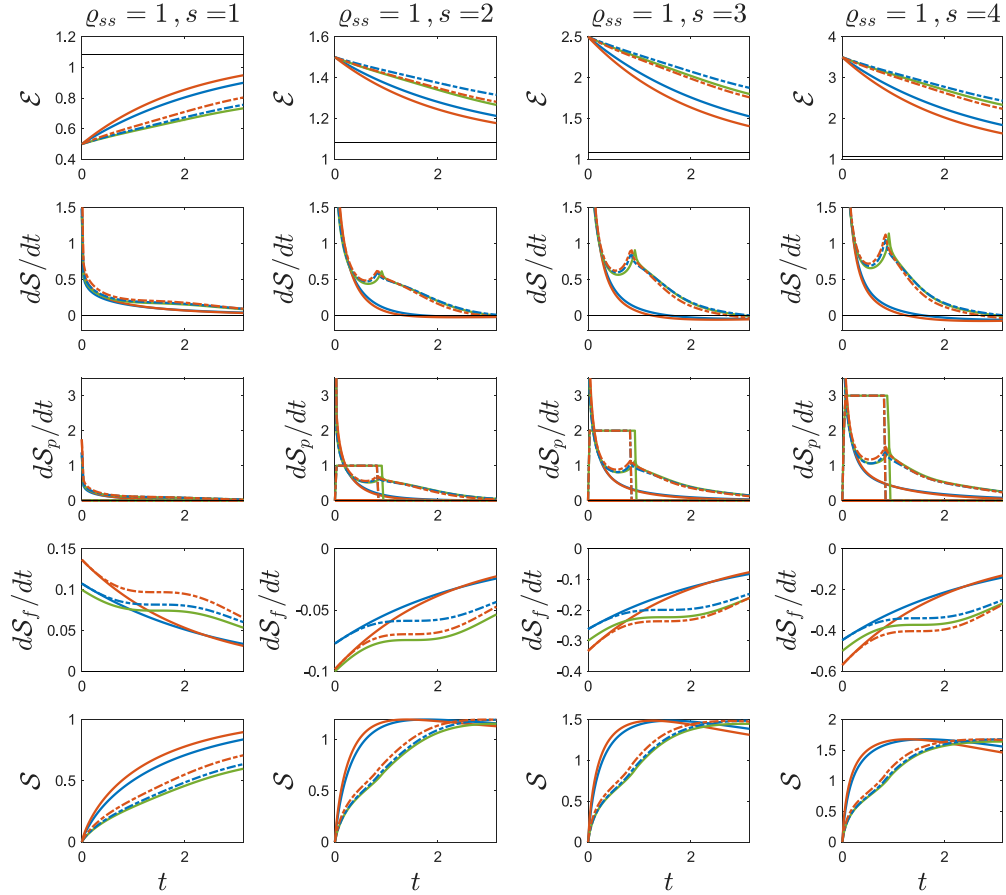


Figure 3. Results for a quantum harmonic oscillator in contact with a thermal bath. Each column represents the plots corresponding to an initial density matrix (16×16) given by $\varrho_{ss}(0) = 1$, with $s = 1, 2, 3, 4$ (\mathcal{N} is a normalizing factor, $\varrho_{kk}(0) = 0$ if $k \neq s$). In the first row, we show the total energy \mathcal{E} , which must converge to $\frac{1}{2}\hbar\omega + \hbar\omega/(e^{\frac{\hbar\omega}{k_B T}} - 1)$. In the following rows, one can find the behavior of the total entropy rate $\frac{d\mathcal{S}}{dt}$, the entropy production rate $\frac{d\mathcal{S}_p}{dt}$, which is always positive, and the entropy flow rate $\frac{d\mathcal{S}_f}{dt}$. In the last row, we plot the entropy \mathcal{S} . In the third row, we also show the number of negative eigenvalues of $\varrho(t) = 1$, revealing the positivity violation. Solid blue and red lines correspond to Hermitian and non-Hermitian friction operators with $\beta_p = m^2\omega^2\beta_q$. Dashed blue and red lines correspond to Hermitian and non-Hermitian friction operators with $\beta_q = 0$. Solid green lines correspond to the Caldeira–Leggett model. We adopted the parameters $\hbar = 1$, $k_B = 1$, $T = 1$, $\beta_p = 0.2$, $\omega = 1$ and $m = 1$ in arbitrary units. We calculated 1000 times the exponential of a 256×256 matrix with a time step $\pi/1000$.

rate and entropy production rate plots (second and third rows), we observe (in the last three columns) the presence of small peaks that need to be understood. To this end, in the entropy production plots we have also superimposed the time evolution of the number of negative eigenvalues of the density matrix. We see that the three models with $\beta_q = 0$ (with Hermitian and non-Hermitian friction operators, and the Caldeira–Leggett

model) have some unphysical negative eigenvalues in the first time interval, showing the incomplete positivity of these models, at least for these initial conditions. This is consistent with what was demonstrated previously: the evolution equation can be of the Lindblad type only if $\beta_p > 0$ and $\beta_q > 0$. Once again, we see that it is essential to include the friction and noise terms in the second classical Hamilton equation (equation (2)), in order for the canonical quantization to work correctly. The peaks observed in the three models with $\beta_q = 0$ are therefore artifacts of the lack of positivity of the density matrix, and are in fact absent in the two models with $\beta_q > 0$ (solid blue and red lines).

We therefore conclude that the two models defined in equations (42) and (70)—with $\beta_p > 0$, $\beta_q > 0$ and equation (52) or (53) satisfied—are correct from the thermodynamic point of view (positive entropy production) and also from the mathematical point of view (complete positivity). Moreover, these two properties are closely related to each other through the monotonicity of quantum relative entropy, as discussed in section 6. Should one want to distinguish between equations (42) and (70), it may be said that equation (42) is preferable because it adopts Hermitian friction operators and can therefore be associated with real physical observables. An important issue that remains open at present is the verification of the complete positivity of the general models defined in equations (23) and (59) for an arbitrary potential acting on the quantum system and not only for the HO.

8. Conclusions

In this work we have developed a unified classical-to-quantum framework for the stochastic description of open systems grounded in a generalized Langevin dynamics where friction and noise act symmetrically on both Hamilton equations. At the classical level, this structure leads to a generalized Klein–Kramers equation that preserves the canonical Gibbs distribution and is fully consistent with the first and second laws of thermodynamics. This result substantiates the physical relevance of including both dissipative and stochastic contributions in the equations for position and momentum, revealing a minimally required symmetry for thermodynamic consistency.

By applying canonical quantization to the classical Klein–Kramers operator, we derive two distinct quantum master equations, corresponding respectively to Hermitian and non-Hermitian friction operators. Despite their structural differences, both formulations yield Lindblad-type dynamics for the HO under the same universal constraint on the friction coefficients. Remarkably, this constraint is independent of the choice of operator representation, suggesting that complete positivity in the quantum regime consistently mirrors the classical requirement of symmetric dissipation and noise. This generality strengthens the conceptual bridge between classical and quantum descriptions of non-equilibrium statistical mechanics. Moreover, it is interesting to note that the QOME used in countless applications can be expressed in the form predicted by our approach.

Our results demonstrate that friction and noise must be included in both Hamilton equations to guarantee a fully thermodynamically consistent and completely positive quantum evolution. The formalism naturally provides generalized quantum expressions for heat, work and entropy production, leading to compact formulations of the quantum

first and second laws, closely connected with the monotonicity of quantum relative entropy.

The methodology introduced here can be readily adapted to a broad class of nanoscale and mesoscopic systems of current interest, ranging from quantum dots to optomechanical platforms. It thus offers a robust and physically transparent foundation for exploring quantum thermodynamics in regimes where stochasticity, dissipation and quantum coherence interplay in essential ways.

A natural perspective for future research is to establish that the symmetry of friction and noise in the Hamilton equations, for arbitrary potential energy landscapes, systematically leads—through canonical quantization—to master equations of Lindblad type, and therefore to completely positive quantum evolutions. This question can be approached by analyzing additional simple models for which the energy basis allows fully analytic expressions for all operators, such as the infinite potential well, and then extending the analysis to general potential energies. Depending on the complexity of the potential, this program may be pursued analytically or numerically. Another promising line of investigation concerns the generalization of the present models to non-Markovian dynamics, in which memory effects become relevant.

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