PHYSICAL REVIEW A **98**, 042133 (2018)

Friction as a consistent quantum-mechanical concept

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(Received 20 April 2018; revised manuscript received 24 September 2018; published 29 October 2018)

A quantum analog of friction (understood as a completely positive, Markovian, translation-invariant, phenomenological model of dissipation) is known to be at odds with detailed balance in the thermodynamic limit. We show that this is not the case for quantum systems with internal (e.g., spin) states nonadiabatically coupled to translational dynamics. For such systems, a quantum master equation is derived which phenomenologically accounts for the frictional effect of a uniform zero-temperature environment. A simple analytical example is provided. Conjectures regarding the finite-temperature case are also formulated. The results are important for efficient simulations of complex molecular dynamics and quantum reservoir engineering applications.

DOI: 10.1103/PhysRevA.98.042133

I. INTRODUCTION

When dealing with complex dissipative environments, modern quantum scientists substantially rely on intuition, like ancient craftsmen taming the elements to build mills or sailing vessels. Specifically, there is vast experimental evidence that quantum effects play a pivotal role even in such complex and manifestly dissipative processes as photosynthesis [1–3]. However, it not clear how coherent quantum dynamics is induced and guided by dissipative interactions. Despite several recent conceptual breakthroughs in the areas of quantum reservoir engineering[1] and topologically protected phases of matter [6], the analysis of coherent dynamics in real-world open systems is impeded by a prohibitively complex microscopic modeling of nonperturbative system-bath interactions.

In classical mechanics, the similar curse of dimensionality is escaped from by introducing friction, a phenomenological nonconservative force resisting the relative motion of objects and converting their kinetic energies into heat [7]. Despite being very simple, the concept of friction is proven useful even in explaining some quantum-level dynamics involving strong system-bath couplings, such as in the case of simple chemical reactions in liquid solutions [8]. However, there is no unique way to quantize nonconservative forces [7]. As result, existing phenomenological quantum dissipative models, be they quantum optical master equation [9], Föster, or Redfield models [10,11], depend on the system Hamiltonian in a complex way. This dependence cannot be simplified to a few friction and diffusion coefficients, especially in the low-temperature regime. Furthermore, to ensure that the surrounding physical bath stays unchanged, the quantum dissipation model must be nontrivially readjusted each time the Hamiltonian is altered (e.g., by an external field or as a result of chemical reactions). Furthermore, the models discussed describe the relaxation dynamics in terms of interstate transition rates. This picture is not natural when dealing with the dynamics of essentially semiclassical vibration wave packets in many photochemical reactions.

To mitigate the above complications, we develop in this paper a phenomenological quantum dissipation model possessing favorable features of classical friction. For brevity, we refer to this model as "quantum friction."[2] We restrict our analysis to the simplest case of a homogeneous environment at a zero temperature and master equations linear with respect to the system density matrix. It is explained in detail elsewhere that the corresponding quantum friction model must satisfy the following four criteria [13,14]:

(i) Markovianity,
(ii) positivity,
(iii) translation invariance, and
(iv) an asymptotic approach to the canonical equilibrium state.

Specifically, the Markovianity ensures that the quantum friction is memoryless. Positivity guarantees that the model is quantum-mechanically consistent, i.e., that any initial positive density matrix remain positive at all times. Translation invariance makes quantum friction coordinate independent, because the corresponding classical friction is a velocity-only–dependent force.

The problem of finding a phenomenological model obeying these four criteria has a long history and has been the subject of many controversies over the years (see, e.g.,

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[1] For instance, it was proven that quantum information processing can be fully dissipation driven [4]. Furthermore, dissipation enables optical and mechanical nonreciprocal couplings—a key ingredient for implementing a quantum analog of a sailing vessel [5].

[2] We want to disambiguate our broad notion of "quantum friction" from its narrow meaning of the force acting on atoms flying near surfaces [12].

2469-9926/2018/98(4)/042133(7)

Refs. [15–17]). As early as 1976, Lindblad demonstrated that this problem has no resolution for a harmonic oscillator [18]. Subsequent failed searches forced Kohen *et al.* to conjecture in their 1997 review [19] that the incompatibility of all four criteria is a generic property, although with the sagacious comment: "except in special cases," which were not known at that time. Later, free quantum Brownian motion was identified by Vacchini [20] to be such a special case. We have proven that no other exceptions exist among quantum systems with N_{ext} translation degrees of freedom [14].

In this paper, we report a class of "special cases" with all four criteria satisfied at zero temperature. These are systems with *internal* degrees of freedom, such as spin. The explicit forms of quantum friction dissipators are derived for such systems.

This paper is organized as follows: We start by formalizing the four-criterion problem in Sec. II. A constructive proof of existence of its solution at zero temperature for systems with internal degrees of freedom is presented in Sec. III. The corresponding quantum friction dissipators are also derived and analyzed in detail. The results obtained are illustrated on the simplest analytically tractable example of a two-dimensional harmonic oscillator in Sec. IV. In the following Sec. V we discuss the conjectures regarding the existence of quantum friction at finite temperatures. The paper concludes with a brief summary and outlook.

II. FORMULATION OF THE PROBLEM

The object of our analysis will be the quantum systems with $\widetilde{N}_{\text{int}} > 1$ internal states $|\widetilde{i}\rangle$ coupled to $N_{\text{ext}} \neq 0$ translation degrees of freedom. (Hereafter, the tilde $\widetilde{}$ marks quantities associated with internal states.) An example of such a system is a molecule with the following vibronic model Hamiltonian:

$$\hat{H} = \underbrace{\sum_{k=1}^{N_{\text{ext}}} \frac{1}{2\mu_k}\hat{p}_k^2 + V(\hat{\boldsymbol{x}})}_{\text{vibrational part}} + \underbrace{\sum_{i=1}^{\widetilde{N}_{\text{int}}} \widetilde{E}_i |\widetilde{i}\rangle\langle\widetilde{i}|}_{\text{spin or electronic part}} + \underbrace{\sum_{i\neq j} g_{i,j}|\widetilde{i}\rangle\langle\widetilde{j}|}_{\text{spin or electronic couplings}} + \underbrace{\sum_{i=1}^{\widetilde{N}_{\text{int}}} \delta V_i(\hat{\boldsymbol{x}})|\widetilde{i}\rangle\langle\widetilde{i}|}_{\text{vibronic couplings}}. \tag{1}$$

Here the sets of nuclear coordinates $\hat{\boldsymbol{x}} = \{\hat{x}_1, \ldots, \hat{x}_{N_{\text{ext}}}\}$ and momenta $\hat{\boldsymbol{p}} = \{\hat{p}_1, \ldots, \hat{p}_{N_{\text{ext}}}\}$ represent the translational degrees of freedom and the "internal" states $|\widetilde{i}\rangle$ correspond to different electronic and/or spin states of the molecule. The symbols $g_{i,j}$, $V_i(\hat{\boldsymbol{x}})$, and $\widetilde{E}_i$ denote the coupling constants, coupling operators, and internal-state eigenenergies, respectively. Assume that the molecule is immersed in a homogeneous environment (such as a gaseous media or uniform solvent) at zero temperature. Our goal is to construct a phenomenological model of the dissipative backaction of such an environment on the system which satisfies the criteria i–iv of quantum friction.

The question of which dissipative processes simultaneously satisfy criteria i and ii was resolved by Lindblad [21]. The answer is a master equation now bearing his name:

$$\frac{\partial}{\partial t}\hat{\rho} = \mathscr{L}[\hat{\rho}], \quad \mathscr{L} = \mathscr{L}_0 + \mathscr{L}_{\text{rel}} \tag{2}$$

where the superoperator $\mathscr{L}_0[\odot] = \frac{i}{\hbar}[\odot, \hat{H}]$ accounts for unitary evolution of the system isolated from environment, and the dissipation term $\mathscr{L}_{\text{rel}}$ describing the system-environment couplings is

$$\mathscr{L}_{\text{rel}} = \sum_{k=1}^{N_{\text{lbd}}} \mathscr{L}^{\text{lbd}}_{\hat{A}_k}, \tag{3a}$$

$$\mathscr{L}^{\text{lbd}}_{\hat{L}}[\hat{\rho}] \overset{\text{def}}{=} \hat{L}\hat{\rho}\hat{L}^\dagger - \frac{1}{2}(\hat{L}^\dagger\hat{L}\hat{\rho} + \hat{\rho}\hat{L}^\dagger\hat{L}). \tag{3b}$$

The goal of this work is to identify the conditions under which the dissipator $\mathscr{L}_{\text{rel}}$ defined by Eq. (3a) additionally obeys the criteria iii and iv.

The translation invariance criterion iii with respect to the nth coordinate is formally defined as

$$[\hat{p}_n, \mathscr{L}_{\text{rel}}[\hat{\rho}]] = \mathscr{L}_{\text{rel}}[[\hat{p}_n, \hat{\rho}]]. \tag{3c}$$

A general recipe for imposing this criterion on the Lindblad term (3a) was found by Holevo [22,23] and further analyzed in applications by Vacchini [24,25]. Specifically, to satisfy Eq. (3c) it is necessary and sufficient that the Lindblad operators $\hat{A}_k$ in Eq. (3a) take the forms

$$\hat{A}_k \overset{\text{def}}{=} e^{-i\boldsymbol{\kappa}_k\hat{\boldsymbol{x}}}\hat{f}_k(\hat{\boldsymbol{p}}). \tag{3d}$$

Here $\hat{f}_k(\boldsymbol{p}) \in \mathbb{C}^{\widetilde{N}_{\text{int}}\times\widetilde{N}_{\text{int}}}$ and $\boldsymbol{\kappa}_k \in \mathbb{R}^{N_{\text{ext}}}$ are arbitrary parameters and matrix-valued functions. They generally should be treated as a phenomenological quantities and can be deduced from empirical fits to time evolution of higher-order averages, e.g., $\langle\hat{\boldsymbol{x}}^2\rangle$, $\langle\hat{\boldsymbol{p}}^2\rangle$. In the cases when the dissipative term $\mathscr{L}_{\text{rel}}$ describes random collisions with light environmental particles, the values of $\hbar\boldsymbol{\kappa}_k$ and $\hat{f}_k(\boldsymbol{p})$ can be associated with the characteristic momentum exchange in a collision event and the scattering amplitude in momentum space [14].

It is worth showing why the dissipative dynamics satisfying criteria i–iii deserves the name quantum friction. The average positions and momenta of a wave packet, evolving according to Eqs. (3), satisfy equations

$$\frac{d}{dt}\langle\hat{p}_n\rangle = \frac{i}{\hbar}\langle[\hat{H}, \hat{p}_n]\rangle + \langle\hat{F}^{\text{fr}}_n\rangle, \tag{4a}$$

$$\frac{d}{dt}\langle\hat{x}_n\rangle = \frac{i}{\hbar}\langle[\hat{H}, \hat{x}_n]\rangle + \langle\hat{G}^{\text{fr}}_n\rangle, \tag{4b}$$

where

$$\hat{\boldsymbol{F}}^{\text{fr}}(\hat{\boldsymbol{p}}) = -\sum_k \hbar\boldsymbol{\kappa}_k\hat{f}^\dagger_k(\hat{\boldsymbol{p}})\hat{f}_k(\hat{\boldsymbol{p}}) \tag{5}$$

defines the position-independent force $\langle\hat{\boldsymbol{F}}^{\text{fr}}\rangle$ which, under a proper choice of operators $\hat{f}^\dagger_k(\hat{\boldsymbol{p}})$, acts in the direction opposite to momenta $\langle\hat{\boldsymbol{p}}\rangle$, similarly to the conventionally defined classical friction. Note, however, that this force is paired with term $\langle\hat{\boldsymbol{G}}^{\text{fr}}\rangle$ in Eq. (4b), where

$$\hat{G}^{\text{fr}}_n(\hat{\boldsymbol{p}}) = \frac{1}{2}i\hbar\sum_k\left(\hat{f}^\dagger_k(\hat{\boldsymbol{p}})\frac{\partial\hat{f}_k(\hat{\boldsymbol{p}})}{\partial\hat{p}_n} - \frac{\partial\hat{f}^\dagger_k(\hat{\boldsymbol{p}})}{\partial\hat{p}_n}\hat{f}_k(\hat{\boldsymbol{p}})\right). \tag{6}$$

The presence of the term $\langle \hat{\boldsymbol{G}}^{\text{fr}} \rangle$ can be physically attributed to changed effective masses of moving particles "dressed" by the environment. This term is of the same nature as the "position diffusion," a well-known peculiarity of quantum Brownian motion [26].

Recall that the classical frictional forces are accompanied by thermal fluctuations satisfying the fluctuation-dissipation theorem. Similarly, criteria i–iii are not sufficient to define thermodynamically consistent quantum friction, and the additional criterion Iiv is required to ensure detailed balance at thermal equilibrium:

$$\mathscr{L}_{\text{rel}}\big[\hat{\rho}_T^{\text{th}}\big] = 0. \tag{7}$$

Here $\hat{\rho}_T^{\text{th}} = \hat{\rho}|_{t\to\infty} \propto e^{-\frac{\hat{H}}{k_B T}}$ is the stationary Gibbs system state corresponding to temperature T. It is worth stressing that Eq. (7) implies nonvanishing thermal fluctuations even at the zero bath temperature.

The criteria i, ii, and iv are fulfilled, e.g., by the quantum optical master equation [9]. A variety of other models are known where some three out of four criteria i–iv are satisfied (see Ref. [19] for detailed review). However except for free Brownian motion [20], no model is known which satisfies both Eqs. (3) and (7). The nonexistence of such a model for the case $\widetilde{N}_{\text{int}} = 1$ was rigorously proven by us recently [14]. In particular, we have shown that the criteria i–iii are compatible only with the following weaker variant of the condition (7):

$$\text{Tr}\left[\hat{\rho}_{T'}^{\text{th}} \mathscr{L}_{\text{rel}}\big[\hat{\rho}_T^{\text{th}}\big]\right] = 0 \text{ for any } T', \tag{8}$$

which we refer to as the *relaxed thermalization* (RT) condition.

The condition (8) always holds when Eq. (7) is satisfied. In fact, it can be shown that Eq. (8) only guarantees that the steady state of the model coincides with the true equilibrium $\hat{\rho}_T^{\text{th}}$ up to first order in system-bath couplings. Thus, Eq. (8) is expected to approximate reasonably well the exact thermalization criterion (7) when the bath-induced decay and decoherence times are large compared with all the characteristic dynamical timescales of the system [14].

III. RECONCILING THE FOUR-CRITERION CLASH AT ZERO TEMPERATURE

In this section, we prove the existence of quantum friction simultaneously satisfying criteria i–iv for systems characterized by the Hamiltonian (1) with $\widetilde{N}_{\text{int}} > 1$. Our methodology is to first figure out the necessary requirements to satisfy the criteria i – iii and RT criterion (8) for $\widetilde{N}_{\text{int}} > 1$ and then to identify whether the RT criterion can be upgraded to the exact thermalization condition (7).

As discussed in the previous section, the dissipator $\mathscr{L}_{\text{rel}}$ satisfying criteria i–iii needs to have the form defined by Eqs. (3). In the case $T = 0$, substitution of Eqs. (3) allows us to cast Eq. (8) into N_{lbd} independent extremal conditions

$$J_k = \text{Tr}\left[\hat{\rho}_0^{\text{th}} \mathscr{L}_{\hat{A}_k}^{\text{lbd}}\big[\hat{\rho}_0^{\text{th}}\big]\right] \to \max \;\; (k = 1, \dots, N_{\text{lbd}}). \tag{9}$$

Specifically, Eq. (9) can be obtained from Eq. (8) and equalities $\text{Tr}[\mathscr{L}_{\hat{A}_k}^{\text{lbd}}[\hat{\rho}]] = 0$, which guarantee that $J_k \leqslant 0$ for any k. Hence, Eq. (8) can be satisfied only when all J_k take their maximal values $J_k = 0$.

Let $|n\rangle$ and E_n be the system Hamiltonian eigenstates and eigenvalues, respectively. Each of these states can be represented in the form

$$|n\rangle = \sum_{i=1}^{\widetilde{N}_{\text{int}}} |\widetilde{i}\rangle\, |\Psi_{n,i}\rangle, \tag{10}$$

where $|\Psi_{n,i}\rangle$ are the vibrational parts of the eigenstates. Note that $|\Psi_{n,i}\rangle$ are neither normalized nor orthogonal. Below we deal with their momentum wave functions $\Psi_{n,i}(\boldsymbol{p})$ and also with the operators $\Psi_{n,i}(\hat{\boldsymbol{p}})$ obtained via the substitution $\boldsymbol{p} \to \hat{\boldsymbol{p}}$. In addition, we will use the notation $|\varphi_{k,n}\rangle = \hat{A}_k\, |n\rangle$. The expressions for J_k in Eq. (9) can now be rewritten as

$$J_k = |\langle 0|\varphi_{k,0}\rangle|^2 - \langle \varphi_{k,0}|\varphi_{k,0}\rangle. \tag{11}$$

Here we accounted for the fact that the thermodynamic equilibrium at $T = 0$ corresponds to the ground state $\hat{\rho}_0^{\text{th}} = |0\rangle\langle 0|$. The Cauchy-Schwarz inequality requires that

$$|\langle 0|\varphi_{k,0}\rangle|^2 \leqslant \langle \varphi_{k,0}|\varphi_{k,0}\rangle\langle 0|0\rangle = \langle \varphi_{k,0}|\varphi_{k,0}\rangle, \tag{12}$$

where the equality holds if and only if $|0\rangle \propto |\varphi_{k,0}\rangle$. Hence, it follows from Eqs. (9) and (11) that

$$J_k = 0 \text{ iff } \hat{A}_k\, |0\rangle = \alpha_k\, |0\rangle \text{ for all } k \;(\alpha_k \in \mathbb{C}). \tag{13}$$

Equations (13) can always be resolved with respect to $\hat{A}_k$. The general solution can be written in terms of operators $\hat{f}_k(\hat{\boldsymbol{p}})$ introduced in Eq. (3d) as

$$\hat{f}_k(\hat{\boldsymbol{p}}) = \hat{f}_{0,k}(\hat{\boldsymbol{p}}) + \alpha_k \sum_{i=1}^{\widetilde{N}_{\text{int}}} \frac{\Psi_{0,i}(\hat{\boldsymbol{p}} - \hbar\boldsymbol{\kappa}_k)}{\Psi_{0,i}(\hat{\boldsymbol{p}})} |\widetilde{i}\rangle\langle\widetilde{i}|, \tag{14a}$$

where $\hat{f}_{0,k}(\hat{\boldsymbol{p}})$ is the position-independent operator satisfying the equation

$$\hat{f}_{0,k}(\hat{\boldsymbol{p}})\, |0\rangle = 0. \tag{14b}$$

For instance, the general solution for $\hat{f}_{0,k}$ in the case of a two-level internal subsystem ($\widetilde{N}_{\text{int}} = 2$) can be represented as

$$\hat{f}_{0,k}(\hat{\boldsymbol{p}}) = \sum_{i,j=0}^{1} (-1)^{i-j} G_{1-i,k}(\hat{\boldsymbol{p}}) \Psi_{0,i}^{*}(\hat{\boldsymbol{p}}) \Psi_{0,j}(\hat{\boldsymbol{p}}) |\widetilde{1-i}\rangle\langle\widetilde{1-j}|, \tag{15}$$

where $G_{0,k}(\boldsymbol{p}) \in \mathbb{C}$ and $G_{1,k}(\boldsymbol{p}) \in \mathbb{C}$ are arbitrary functions.

One can notice that the operators (15) always contain off-diagonal terms between different internal states $|\widetilde{i}\rangle$. Hence, the population of internal states is conserved when $\hat{f}_{0,k} = 0$ for all k. In the case when $|\widetilde{i}\rangle$ represent the electronic states of a molecule, the latter model can represent instantaneous events (e.g., the direct collisions of light particles with the molecule's nuclei) not involving electrons.

Equations (14) answer the question of when criteria i–iii can be satisfied together with the relaxed thermalization condition (8). Let us now turn to the conditions required to satisfy strict thermalization condition iv [Eq. (7)]. The substitution of Eqs. (14) allows us to rewrite condition (7) as

$$\sum_{k=1}^{N_{\text{lbd}}} \alpha_k^2\, |0\rangle = \sum_{k=1}^{N_{\text{lbd}}} \hat{f}_k(\hat{\boldsymbol{p}})^{\dagger} \hat{f}_k(\hat{\boldsymbol{p}})\, |0\rangle = \sum_{k=1}^{N_{\text{lbd}}} \alpha_k \hat{A}_k^{\dagger}(\hat{\boldsymbol{p}})\, |0\rangle\,.$$

It is easier to analyze this relation after multiplying both sides by the operator $\sum_{j=0}^{\widetilde{N}_{\text{int}}} |\widetilde{0}\rangle\langle\widetilde{j}|\Psi_{0,j}(\hat{\boldsymbol{p}})$, which gives

$$\forall\, \boldsymbol{p} : \sum_{k=1}^{N_{\text{lbd}}} \alpha_k^2 \sum_{j=1}^{\widetilde{N}_{\text{int}}} (|\Psi_{0,j}(\boldsymbol{p})|^2 - |\Psi_{0,j}(\boldsymbol{p} - \hbar\boldsymbol{\kappa}_k)|^2) = 0. \quad (16)$$

As discussed in Ref. [14], the effect of the part of Lindblad operator $\hat{A}_k$ proportional to α_k can be associated with an instantaneous inelastic collision with a massless particle, such as a photon, having momentum $\hbar\boldsymbol{\kappa}_k$. In light of this interpretation, the exact thermalization condition (16) requires invariance of the momentum distribution with respect to the entire sequence of such collisions described by operator $\mathscr{L}_{\text{rel}}$. Apart from exceptional cases, the condition (16) can be satisfied if and only if either $\alpha_k = 0$ or $\boldsymbol{\kappa}_k = 0$ for each k. Note, however, that the terms $\mathscr{L}_{\hat{A}_k}^{\text{lbd}}$ corresponding to $\boldsymbol{\kappa}_k = 0$ do not contribute to friction $\hat{\boldsymbol{F}}^{\text{fr}}$ in Eq. (4a). In other words, despite the underlying dissipative process formally satisfies criteria i–iii of quantum friction, it does not involve direct momentum transfer between the system and the bath. Hence, it cannot be physically interpreted as a frictional process and, thus, is out of scope for our programme.

The remaining possibility to obey condition (16) by setting $\alpha_k = 0$ and $\boldsymbol{\kappa}_k \neq 0$ in Eqs. (14) leads to an exactly thermalizable dissipator $\mathscr{L}_{\text{rel}}$ satisfying Eq. (7). This finding that all four criteria i–iv can be simultaneously satisfied is the central result of this work. For example, in the case of the two-level internal subspace considered above, this is achieved by setting $\alpha_k = 0$ in Eq. (14a) and choosing arbitrary functions $G_{0,k}(\boldsymbol{p})$, $G_{1,k}(\boldsymbol{p})$ and vectors $\boldsymbol{\kappa}_k$ in Eq. (15). It is worth stressing, however, that unlike classical friction, this solution leads to the nonvanishing term $\langle\hat{\boldsymbol{G}}^{\text{fr}}\rangle$ in Eq. (4b).

What makes quantum friction possible in the case $\widetilde{N}_{\text{int}} > 1$? Our formal results admit the following physical interpretation: The very notion of friction is implicitly attached to the classical concept of bath. When considering classical dynamics, it is sufficient to treat the bath as an infinite heat tank at constant temperature. However, this model fails to account for proximity effects responsible for spatial and/or temporal system-bath correlations. These correlations turned out to be crucial for quantum thermalization [14]: Without them, microscopic perpetual motion would be possible. Internal degrees of freedom enable quantum friction by serving as an ancilla subsystem to phenomenologically mimic proximity effects on translation degrees of freedom. We have seen that the thermalizability criterion iv can be fulfilled even if this ancilla subsystem consists of just two quantum states. However, a very essence of proximity effects implies that this mechanism can work only when the external and ancilla internal degrees of freedom are coupled nonadiabatically. This implies that the system ground state $|0\rangle$ is such that $|\Psi_{0,i}\rangle \not\propto |\Psi_{0,j\neq i}\rangle$ and $|\Psi_{0,i}\rangle \neq 0$ for all i and j. If this condition is satisfied, quantum friction simultaneously thermalizes *both* the external degrees of freedom and the ancilla subsystem. Otherwise, neither of these degrees of freedom can be thermalized, as can be seen, e.g., from Eq. (15) in the case of $|\Psi_{0,1}\rangle = 0$.

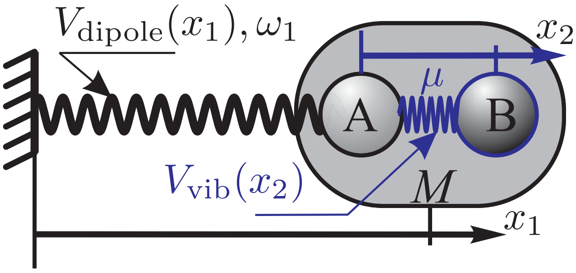

FIG. 1. The ball-and-spring model of a quantum damped harmonic oscillator [Eq. (17)] with an additional internal structure represented by the molecular stretching mode x_2 (see Sec. IV for details).

IV. AN ILLUSTRATION: THE DAMPED HARMONIC OSCILLATOR

Let us illustrate the conclusions of the previous section by quantizing the familiar classical model of a damped harmonic oscillator,

$$\ddot{x}_1 + 2\gamma(\dot{x}_1)\dot{x}_1 + \omega_1^2 x_1 = 0, \quad (17)$$

where ω_1 and $\gamma = \gamma(\dot{x}_1)$ are the oscillator's frequency and frictional damping rate, respectively. Recall that, according to Lindblad's celebrated result [18], the model (17) cannot be quantized within criteria i–iv imposed on the friction term under the assumption that an oscillating body is a structureless point particle. Here we assume that the oscillating body is a pre-aligned diatomic molecule AB of mass M with one internal harmonic degree of freedom: a stretching vibrational mode x_2 characterized by the reduced effective mass μ and potential energy $\hat{V}_{\text{vib}} \propto \hat{x}_2^2$.

Consider the dynamics of such a molecule in a harmonic dipole trap, as shown in Fig. 1, assuming that the long-term thermalization dynamics is guided by an effective friction force (e.g., due to radiation decay), which stirs the system into thermodynamic equilibrium with an environment. Assuming that atom A is a primary contributor to the induced dipole moment, the system Hamiltonian can be written in the form

$$\hat{H} = \frac{\hat{p}_1^2}{2M} + \frac{\hat{p}_2^2}{2\mu} + \hat{V}_{\text{dipole}} + \hat{V}_{\text{vib}}, \quad (18)$$

where x_1 in an external center-of-mass molecular coordinate and $\hat{V}_{\text{dipole}} \simeq \frac{M\omega_1^2}{2}(\hat{x}_1 - \frac{\mu}{m_1}\hat{x}_2)^2$ is a laser-induced trapping potential. It is convenient to rewrite the Hamiltonian (18) in the normal mode representation:

$$\hat{H} = \sum_{l=1}^{2} \hbar\omega_l \hat{a}_l'^{\dagger}\hat{a}_l'. \quad (19)$$

Here $\hat{a}_l'$ is the annihilation operator for the lth normal mode:

$$\hat{a}_l' = \frac{1}{\sqrt{2}}\left(\frac{1}{\hbar\sqrt{\beta_l'}}\hat{x}_l' + i\sqrt{\beta_l'}\hat{p}_l'\right) \quad [\beta_l' = (\hbar\omega_l)^{-1}], \quad (20)$$

and the operators $\hat{x}_l'$ and $\hat{p}_l'$ of normal coordinates and momenta are defined as

$$\hat{x}_1' = \sqrt{m_1}\cos(\varphi)\hat{x}_1 - \sqrt{m_2}\sin(\varphi)\hat{x}_2,$$
$$\hat{x}_2' = \sqrt{m_1}\sin(\varphi)\hat{x}_1 + \sqrt{m_2}\cos(\varphi)\hat{x}_2,$$
$$\hat{p}_1' = \frac{\cos(\varphi)}{\sqrt{m_1}}\hat{p}_1 - \frac{\sin(\varphi)}{\sqrt{m_2}}\hat{p}_2, \quad \hat{p}_2' = \frac{\sin(\varphi)}{\sqrt{m_1}}\hat{p}_1 + \frac{\cos(\varphi)}{\sqrt{m_2}}\hat{p}_2. \tag{21}$$

We are interested in the situation when the external and internal motions are coupled, i.e., when $\varphi \neq 0, \pi$.

Let us derive the phenomenological frictional dissipator for the case of a cold environment $T = 0$. According to the conclusions of Sec. III, the dissipator of interest should be of the form (3) with

$$\hat{A}_k = e^{-i\kappa_k \hat{x}_1} f_k(\hat{p}_1, \hat{p}_2, \hat{x}_2) \tag{22}$$

and satisfy Eq. (13).

It is helpful to introduce the operators

$$\hat{\mathfrak{a}}_1 = \mathfrak{a}_1(\hat{x}_1, \hat{p}_1, \hat{p}_2) = \sqrt{2}\left(\hat{a}_2'\sqrt{\beta_2'}\sin(\varphi) + \hat{a}_1'\sqrt{\beta_1'}\cos(\varphi)\right),$$
$$\hat{\mathfrak{a}}_2 = \mathfrak{a}_2(\hat{x}_2, \hat{p}_1, \hat{p}_2) = \sqrt{2}\left(\hat{a}_2'\sqrt{\beta_2'}\cos(\varphi) - \hat{a}_1'\sqrt{\beta_1'}\sin(\varphi)\right), \tag{23}$$

which satisfy

$$\hat{\mathfrak{a}}_{1,2}|0\rangle = 0. \tag{24}$$

Here $|0\rangle$ is the system's ground state and also the equilibrium Gibbs state for $T = 0$. It can be written in the momentum representation as

$$\langle p_1', p_2'|0\rangle \propto \exp\left(-\sum_{l=1}^{2}\frac{1}{2}\beta_l' p_l'^2\right). \tag{25}$$

The general solution of the equation $\hat{A}_k\,|0\rangle = \alpha_k\,|0\rangle$ compliant with the translation invariance condition (3c) with respect to x_1 is

$$\hat{A}_k = e^{-i\kappa_k \hat{x}_1}\hat{G}_k'\hat{\mathfrak{a}}_2 + \alpha_k e^{-i\hbar\kappa_k \frac{1}{\sqrt{m_1}}\hat{\mathfrak{a}}_1}. \tag{26}$$

Here $\hat{G}_k' = G_k'(\hat{p}_1, \hat{p}_2, \hat{x}_2)$ is an arbitrary operator independent of $\hat{x}_1$. Equation (26) is nothing but the specialization of the general solution (14). It obeys the exact thermalization condition (7) if $\alpha_k = 0$ for all k and satisfies only RT condition (8) otherwise.

As expected, the dissipator $\mathscr{L}_{\text{rel}}$ corresponding to solution (26) with $\alpha_k = 0$ vanishes when the internal and external degrees of freedom are dynamically decoupled (e.g., when $\widetilde{N}_{\text{int}} = 1$ or $\varphi = 0$). However, the solutions of both Eqs. (14a) and (26) with $\alpha_k \neq 0$ do exist even in the latter case. A simple computation shows that these solutions reduce to $f_k(\hat{p}_1) \propto \exp\left(\frac{\hat{p}_1\kappa_k}{m_1\omega_1}\right)$ obtained in Ref. [14]. The latter solution [and, more generally, the last term in Eq. (26)] indicate that the system-environment correlations are minimized (for any given $\boldsymbol{\kappa}_k$) when the associated effective force $\langle \boldsymbol{G}_k^{\text{fr}}\rangle$ depends exponentially on momenta $\hat{\boldsymbol{p}}$. Interestingly that unlike typical classical friction forces anti-aligned with momenta, the last term in Eq. (26) has a long exponentially vanishing "endothermic" tail representing a force aligned with p_1. For further discussion on the physics of these tails, see Ref. [14].

In contrast, the solution (26) with $\alpha_k = 0$ represents an arbitrary nonlinear friction force acting on the external degree of freedom x_1. Importantly, this force exists due to the dissipative coupling between the external and internal degrees of freedom. The origin for this coupling can be illustrated by the classical ball-and-spring model of a diatomic molecule where each ball is subjected to an independent nonlinear friction force. In this model, the total effective friction force applied to the system's center of mass depends on the relative velocity of the balls, whereas the decay of the internal oscillation depends on the center-of-mass velocity. The hallmark of the quantum friction is inability to cancel these interdependencies out even for the linear friction $F_1^{\text{fr}} \propto p_1$.

V. DISCUSSION OF FINITE-TEMPERATURE CASE

So far, our analysis has been restricted to interactions of quantum systems with baths cooled down to the zero temperature. An existence of quantum friction forces at finite temperatures is an open question beyond the scope of this work. Nevertheless, we would like to briefly discuss insights that might help to find the answer.

First, note that, in the case $T = 0$, the exactly thermalizable frictional dissipator [defined by Eqs. (3) and (14) with $\alpha_k = 0$] has the property that each individual term $\mathscr{L}_{\hat{A}_k}^{\text{lbd}}$ independently satisfies condition (7). However, the analogous property cannot hold at finite temperatures for any Lindblad operator $\hat{A}_k$ of the form (3d),

$$\forall\, T \neq 0 : \mathscr{L}_{\hat{A}_k}^{\text{lbd}}\left[\hat{\rho}_T^{\text{th}}\right] \neq 0. \tag{27}$$

The proof of inequality (27) is given in the appendix. This result can be intuitively understood in the simplest case $N_{\text{ext}} = 1$ as follows: The most general form of the operator $\hat{f}_k$ in Eq. (3d) corresponding to a single translational degree of freedom is

$$\hat{f}_k = \sum_{i,j=1}^{N_{\text{ext}}}\sum_k |\widetilde{i}\rangle\langle\widetilde{j}|c_{i,j,k}\hat{p}^k, \tag{28}$$

where $c_{i,j,k}$ are complex coefficients to be determined. Now, imagine that we truncated the translational basis to K states. It is obviously impossible to satisfy the exact thermalization condition in this approximation. Indeed, in order to turn the inequality (27) into the equality while satisfying condition (7), $(\widetilde{N}_{\text{int}}K)^2 - 1$ constraints must be satisfied with only $\widetilde{N}_{\text{int}}^2 K - 1$ unknowns $c_{i,j,k}$ (here we excluded the complex scaling factor).

As discussed in Ref. [14], the terms $\mathscr{L}_{\hat{A}_k}^{\text{lbd}}$ can be regarded as Markovian approximations for relaxation processes similar to those involved in the Doppler cooling. Importantly, each term $\mathscr{L}_{\hat{A}_k}^{\text{lbd}}$ represents an independent frictional process in such an interpretation. At the same time, inequality (27) shows that these processes cannot be independent since each of them drives the system out of thermal equilibrium. This contradiction shows that, if the friction-like Markovian dissipator $\mathscr{L}_{\text{rel}}$ exists for finite temperatures, it must consist of several interdependent terms of the form $\mathscr{L}^{\mathrm{lbd}}_{\hat{A}_k}$, and hence has a nontrivial physical interpretation, as in non-translation-invariant case [27]. Alternatively, the contradiction may signify that no friction-like quantum process exists at nonzero temperatures. Nevertheless, if the latter conjecture is correct, the conventional interpretation of friction in the classical limit would require revisiting.

At the same time, the RT condition

$$\forall\, T' : \mathrm{Tr}\left[\hat{\rho}^{\mathrm{th}}_{T'} \mathscr{L}^{\mathrm{lbd}}_{\hat{A}_k}\left[\hat{\rho}^{\mathrm{th}}_{T}\right]\right] = 0 \tag{29}$$

can be seamlessly satisfied. Indeed, Eq. (29) sets only $\widetilde{N}_{\mathrm{int}} K - 1$ constraints (which is less than the previously mentioned number of $\widetilde{N}^2_{\mathrm{int}} K - 1$ parameters) and can be obeyed together with the TI condition (3c). For instance, the dissipation superoperator $\mathscr{L}_{\mathrm{rel}}$ for the harmonic oscillator example of Sec. IV satisfying criteria i–iii and RT condition (29) at a finite temperature is given by Eqs. (3) with

$$\begin{aligned}\hat{A}_k &\propto \exp\left\{-i\kappa_k \frac{[\hat{x}'_2 \sin(\varphi) + \hat{x}'_1 \cos(\varphi)]}{\sqrt{m_1}}\right\}\\ &\quad\times \exp\left\{\kappa_k \frac{[\beta'_2 \lambda_2 \hat{p}'_2 \sin(\varphi) + \beta'_1 \lambda_1 \hat{p}'_1 \cos(\varphi)]}{\sqrt{m_1}}\right\}\\ &= e^{-i\kappa_k \hat{x}_1} \exp\left\{\kappa_k \frac{1}{\sqrt{m_1}} [\beta'_2 \lambda_2 \hat{p}'_2 \sin(\varphi) + \beta'_1 \lambda_1 \hat{p}'_1 \cos(\varphi)]\right\},\end{aligned} \tag{30}$$

where $\lambda_l = \tanh\left(\frac{\hbar\omega_l}{4k_{\mathrm{B}}T}\right)$.

VI. CONCLUSION

The concept of friction (defined as the phenomenological dissipative model satisfying criteria i–iv) can be consistently extended into quantum mechanics for systems with internal degrees of freedom in the case of a zero-temperature environment. This finding complements the previous no-thermalization-without-correlations result [14], implying that such dissipators are absent for structureless particles. We proved and illustrated on the analytically tractable example that the internal degrees of freedom enable the quantum friction by serving as an ancilla subsystem to harvest the required correlations and mimic system-bath quantum proximity effects. Informally, this implies that, to be thermodynamically consistent, quantum friction must dissipate heat both into an environment and inside the system itself. For this to be true, external and ancilla degrees of freedom need to be nonadiabatically coupled.

Quantum friction can be used as a simple phenomenological relaxation model to simulate the nonequilibrium dynamics of complex molecular systems strongly coupled to an homogeneous environment (e.g., a molecule in a solvent). Such a model is guaranteed to be consistent in the thermodynamic limit and may allow for substantial memory and time savings in numerical studies of fundamental photoinduced processes, such as photoisomerization, light-induced charge and energy transfer in organic materials.

The existence of friction-like quantum dissipators at finite temperatures remains an intriguing open question. The affirmative or negative answers would challenge the microscopic or semiclassical theories of friction. For computational applications permitting approximate thermalization, the relaxed thermalization work-around (8) may be used in place of taxing microscopic models [28,29], if system-bath couplings are weak.

ACKNOWLEDGMENTS

D.V.Zh. thanks Madonna and Sameer Patwardhan for helpful discussions. T.S. and D.V.Zh. thank the National Science Foundation (Award No. CHEM-1012207 to T.S.) for support. D.I.B. is supported by the Air Force Office of Scientific Research Young Investigator Research Program (FA9550-16-1-0254).

APPENDIX: PROOF OF INEQUALITY (27)

The proof is by contradiction. Suppose that the inequality (27) can be turned into equality. This assumption implies that $\langle n|\mathscr{L}^{\mathrm{lbd}}_{\hat{A}_k}[\hat{\rho}^{\mathrm{th}}_{\theta}]\,|l\rangle = 0$ for all n an l or, more explicitly, that

$$\forall\, n, l : R_{n,l} - S_{n,l} = 0, \tag{A1}$$

where

$$R_{n,l} = \sum_m \gamma_m(\theta)\langle n|\varphi_{k,m}\rangle\langle\varphi_{k,m}|l\rangle,$$

$$S_{n,l} = \langle\varphi_{k,n}|\varphi_{k,l}\rangle \frac{\gamma_l(\theta) + \gamma_n(\theta)}{2}.$$

Here $\gamma_i(\theta) = \langle i|\hat{\rho}^{\mathrm{th}}_{\theta}\,|i\rangle = \frac{e^{-E_i/\theta}}{\sum_n e^{-E_n/\theta}}$ is a positive statistical weight of the ith eigenstate.

The equalities (A1) imply that $\sum_{n,l}|R_{n,l}|^2 - \sum_{n,l}|S_{n,l}|^2 = 0$. After some algebra, this relation reduces to

$$\sum_{m,n} |\langle\varphi_{k,m}|\varphi_{k,n}\rangle|^2 \left[\frac{\gamma_m(\theta) - \gamma_n(\theta)}{2}\right]^2 = 0. \tag{A2}$$

Since the term in square brackets is positive for all $m \neq n$, we can conclude that the necessary condition for thermalization is that $\langle\varphi_{k,m}|\varphi_{k,n}\rangle = 0$, or $\langle m|\hat{A}^\dagger_k\hat{A}_k\,|n\rangle = 0$ for all $m \neq n$. The latter implies that

$$\forall\, m : \hat{A}^\dagger_k\hat{A}_k\,|m\rangle = \hat{f}^\dagger_k\hat{f}_k\,|m\rangle = c_{k,m}\,|m\rangle, \tag{A3}$$

where $c_{k,m}$ are certain non-negative constants. The non-negative Hermitian operator $\hat{A}^\dagger_k\hat{A}_k$ can be expanded as

$$\hat{A}^\dagger_k\hat{A}_k = \sum_{i,j=0}^{N-1} |\widetilde{i}\rangle\langle\widetilde{j}|F_{i,j}(\hat{\boldsymbol{p}}), \tag{A4}$$

where $F_{i,j}(p)$ are some complex-valued functions, such that $F_{i,j}(p) = F^*_{j,i}(p)$. Using Eq. (A4), the equality (A3) can be rewritten in the matrix form

$$\sum_j F_{i,j}(\boldsymbol{p})\Psi_{m,j}(\boldsymbol{p}) = c_m\Psi_{m,i}(\boldsymbol{p}). \tag{A5}$$

Note that here we can treat $\boldsymbol{p}$ as c numbers. The $\widetilde{N}_{\mathrm{int}} \times \widetilde{N}_{\mathrm{int}}$ matrix F has at most $\widetilde{N}_{\mathrm{int}}$ distinct eigenvalues λ_k. Each eigenstate $|n\rangle$ is associated with one of these eigenvalues $\lambda(n)$. Let us choose the set of $\widetilde{N}_{\mathrm{int}}$ indices r_k, such that $|r_k\rangle$ is associated with λ_k. Then, each of remaining eigenstates should be representable as a linear combination of $|r_k\rangle$,

$$\Psi_{m,i}(p) = \sum_{k:\lambda(r_k)=\lambda(m)} c_{m,r_k}(\boldsymbol{p})\Psi_{r_k,i}(\boldsymbol{p}), \tag{A6}$$

with $\boldsymbol{p}$-dependent coefficients $c_{r_k,m}(\boldsymbol{p})$. Furthermore,

$$\lambda(n) \neq \lambda(m) \Rightarrow \sum_i \Psi^*_{n,i}(\boldsymbol{p})\Psi_{m,i}(\boldsymbol{p}) = 0 \text{ for all } \boldsymbol{p}. \qquad \text{(A7)}$$

The basis states $|n\rangle$ can generally satisfy constraints (A6) and (A7) only in two cases: (1) some of the internal states are decoupled from the rest (i.e., the dynamic space splits into isolated subspaces) and (2) all λ_k are equal. Here we are not interested in case (1) and assume that the dynamics of all the external and internal degrees of freedom is mixed by couplings. Case (2) implies that

$$\hat{A}_k^\dagger \hat{A}_k = \lambda \geqslant 0, \qquad \text{(A8)}$$

where λ is some non-negative constant. Without loss of generality, it is sufficient to consider two cases: $\lambda = 0$ and $\lambda = 1$.

The case $\lambda = 0$ implies that $\forall\ m : \hat{A}_k\,|m\rangle = 0$, which can be satisfied only if $\hat{A}_k = 0$. Hence, we can exclude the case $\lambda = 0$ from consideration.

Consider now $\lambda = 1$. In this case, the equality $\mathcal{L}^{\text{lbd}}_{\hat{A}_k}[\hat{\rho}^{\text{th}}_T] = 0$ takes the form

$$\hat{A}_k \hat{\rho}^{\text{th}}_T \hat{A}_k^\dagger - \hat{\rho}^{\text{th}}_T = 0. \qquad \text{(A9)}$$

It is easy to show that, in the case of nondegenerate $\gamma_k(\theta)$, the above equality can be satisfied if and only if $\hat{A}_k = 1$, i.e., when $\mathcal{L}^{\text{lbd}}_{\hat{A}_k} = 0$. This completes the proof.

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