No Thermalization without Correlations

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The proof of the long-standing conjecture is presented that Markovian quantum master equations are at odds with quantum thermodynamics under conventional assumptions of fluctuation-dissipation theorems (implying a translation invariant dissipation). Specifically, except for identified systems, persistent system-bath correlations of at least one kind, spatial or temporal, are obligatory for thermalization. A systematic procedure is proposed to construct translation invariant bath models producing steady states that well approximate thermal states. A quantum optical scheme for the laboratory assessment of the developed procedure is outlined.

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Introduction.—A stochastic interaction of a quantum system with a bath brings up the term $\hat{\boldsymbol{F}}^{\rm fr}$ in the relations for time-dependent expectation values of system momenta $\hat{\boldsymbol{p}} = \{\hat{p}_1, \ldots, \hat{p}_N\}$ and positions $\hat{\boldsymbol{x}} = \{\hat{x}_1, \ldots, \hat{x}_N\}$:

$$\frac{d}{dt}\langle \hat{p}_n \rangle = -\left\langle \frac{\partial}{\partial \hat{x}_n} U(\hat{x}) \right\rangle + \langle \hat{F}_n^{\rm fr} \rangle, \tag{1a}$$

$$\frac{d}{dt}\langle \hat{x}_n \rangle = \frac{1}{m_n}\langle \hat{p}_n \rangle, \tag{1b}$$

where $U(\hat{x})$ is a potential energy operator and m_k are effective masses. In this Letter, we study the case where $\hat{\boldsymbol{F}}^{\rm fr} = \hat{\boldsymbol{F}}^{\rm fr}(\hat{\boldsymbol{p}})$ is position independent. In this form, Eqs. (1) apply to many quantum phenomena including the translational motion of an excited atom in vacuum [1], Brownian motion in a dilute background gas [2], light-driven processes in semiconductor, nanoplasmonic, and optomechanical systems [3–5], superconducting currents [6], quantum ratchets [7], energy transport in low-dimensional systems [8], dynamics of chemical reactions [9], two-dimensional vibrational spectroscopy and NMR signals [10,11], as well as more exotic entirely quantum dissipative effects [12,13].

The term $\hat{\boldsymbol{F}}^{\rm fr}(\hat{\boldsymbol{p}})$ in Eqs. (1) admits a simple classical interpretation as friction acting on effective particles moving in a potential $U(\boldsymbol{x})$. Such classical dynamics are described by the familiar Langevin, Drude, and Fokker-Plank models when the system-bath interactions are treated as (i) memoryless (Markovian) and (ii) translation invariant (position-independent). However, we will show that these two assumptions are at odds with quantum thermodynamics. Specifically, we will prove a long-standing no-go conjecture that completely positive [14] Markovian translation-invariant quantum dynamics obeying Eqs. (1) cannot thermalize.

The no-go conjecture was demonstrated by Lindblad as early as in 1976 [16] for a quantum harmonic oscillator with a Gaussian damping [17]. Subsequently, his particular result was extended to a general quantum system under the weight of mounting numerical evidence, however, without proof. The no-go conjecture is de facto incorporated in all popular models such as the Redfield theory [21], the Gaussian phase space ansatz of Yan and Mukamel [22], the master equations of Agarwal [23], Caldeira-Leggett [24], Hu-Paz-Zhang [25], and Louisell-Lax [26], and the semigroup theory of Lindblad [27] along with specialized extensions in different areas of physics and chemistry. These models break either one of assumptions (i) and (ii) or the complete positivity of quantum evolution (see Refs. [15,28,29] for detailed reviews; note Errata [30]). This circumstance is a persistent source of controversies (see, e.g., the discussions [31–33] of original works [34,35]). The matters were further complicated by the discovery that the free Brownian motion $U(\hat{\boldsymbol{x}}) = 0$ circumvents the conjecture [36] (we will identify the full scope of possible exceptions below).

The no-go result challenges studies of the long-time dynamics of open systems. On the one hand, the model's thermodynamic consistency is undermined by assumptions (i) and (ii). On other hand, the same assumptions open opportunities to simulate large systems that are otherwise beyond the reach. Specifically, the abandonment of Markovianity entails a substantial overhead to store and process the evolution history. The value of assumption (ii) can be clarified by the following example. Consider the rethermalization of a harmonic oscillator coupled to a bath (represented by a collection of harmonic oscillators) after displacement from equilibrium by, e.g., an added external field, a varied system-bath coupling, or interactions between parts of a compound system. To account for such a displacement without assumption (ii), one needs to self-consistently identify the equilibrium position for each bath oscillator, rethermalize the bath, and modify the system-bath couplings accordingly. In practice, this procedure is intractable without gross approximations that lead

to either numerical instabilities or physical inaccuracies. Choosing among a polaron-transformation-based method, Redfield, and Förster (hopping) models of quantum transfer epitomizes this dilemma [37].

Remarkably, assumption (ii) enables us to model the displaced state equilibrium by simply adjusting the potential energy $\hat{U}$. Figure 1(a) shows that without this assumption the potential adjustment yields steady state $\hat{\rho}_{\rm st}$ significantly different from the canonical equilibrium $\hat{\rho}_\theta^{\rm th} \propto e^{-(\hat{H}/\theta)}$, where $\theta = k_B T$ and $\hat{H}$ is the system Hamiltonian.

Motivated by these arguments, we propose in this Letter a general recipe to construct approximately thermalizable bath models under assumptions (i) and (ii). Figure 1 illustrates this recipe in application to the above example. The resulting mismatch between $\hat{\rho}_{\rm st}$ and $\hat{\rho}_\theta^{\rm th}$ is small, especially at high temperatures and in the weak system-bath coupling limit. (The calculations details will be explained below.)

It will be shown elsewhere that the proposed recipe is capable of accurately accounting for electronic and spin degrees of freedom. We found it helpful in reservoir engineering and optimal control problems. Moreover, the resulting bath models are realizable in the laboratory and can be used for coupling atoms and molecules nonreciprocally [38]. However, the scope of our recipe is limited by the applicability of assumptions (i) and (ii) and, therefore, cannot encompass strongly correlated systems (as in the case of Anderson localization [39]).

The key results.—Starting by formalizing the problem, we write the general master equation that accounts for memoryless system-bath interactions and ensures positivity of the system density matrix $\hat{\rho}$ at all times [27]:

$$\frac{\partial}{\partial t}\hat{\rho} = \mathcal{L}[\hat{\rho}], \qquad \mathcal{L} = \mathcal{L}_0 + \mathcal{L}_{\rm rel}, \tag{2a}$$

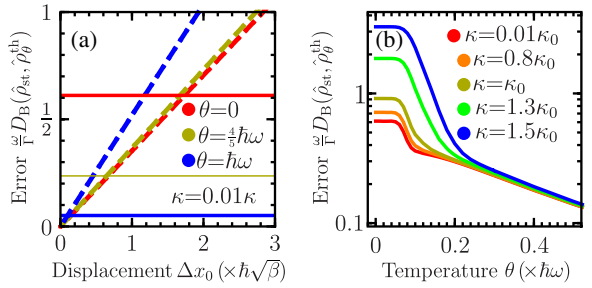

FIG. 1. The errors (expressed in the terms of Bures distance D_B between the thermal state $\hat{\rho}_\theta^{\rm th}$ and its approximation $\hat{\rho}_{\rm st}$) in modeling thermal states of a 1D quantum harmonic oscillator in the displaced equilibrium configurations [due to a change $U(\hat{x}) \to U(\hat{x} - \Delta x_0)$ in the potential energy] using the conventional quantum optical master equation (dashed lines) and the proposed translation-invariant dissipation model defined by Eqs. (2), (3), and (11) (solid lines). (a) The error dependence on displacement Δx_0 for several temperatures θ. (b) The error dependence on temperature θ for different values of κ (in units of $\kappa_0 = \hbar^{-1}\beta^{-\frac{1}{2}}$).

$$\mathcal{L}_0[\odot] = \frac{i}{\hbar}[\odot, \hat{H}], \quad \hat{H} = H(\hat{\boldsymbol{p}}, \hat{\boldsymbol{x}}) = \sum_{n=1}^{N} \frac{\hat{p}_n^2}{2m_n} + U(\hat{\boldsymbol{x}}), \tag{2b}$$

$$\mathcal{L}_{\rm rel} = \sum_{k=1}^{K} \mathcal{L}_{\hat{L}_k}^{\rm lbd}, \quad \mathcal{L}_{\hat{L}}^{\rm lbd}[\hat{\rho}] \stackrel{\rm def}{=} \hat{L}\hat{\rho}\hat{L}^\dagger - \frac{1}{2}(\hat{L}^\dagger\hat{L}\hat{\rho} + \hat{\rho}L^\dagger\hat{L}), \tag{2c}$$

where $\odot$ is the substitution symbol defined, e.g., in Ref. [40]. The superoperator $\mathcal{L}_{\rm rel}$ accounts for system-bath couplings responsible for the friction term $\hat{\boldsymbol{F}}^{\rm fr}$ in Eq. (1a) and depends on a set of generally non-Hermitian operators $\hat{L}_k$. Based on theorems by Holevo [41,42], Vacchini [43–45] has identified the following criterion of translational invariance for the $\mathcal{L}_{\rm rel}$:

Lemma 1: (The justification is in Sec. I of the Supplemental Material [18].) Any translationally invariant superoperator $\mathcal{L}_{\rm rel}$ of the Lindblad form (2c) can be represented as

$$\mathcal{L}_{\rm rel} = \sum_k \mathcal{L}_{\hat{A}_k}^{\rm lbd} + \mathcal{L}_{\rm aux} \quad \text{with} \tag{3a}$$

$$\hat{A}_k \stackrel{\rm def}{=} e^{-i\boldsymbol{\kappa}_k\hat{\boldsymbol{x}}}\tilde{f}_k(\hat{\boldsymbol{p}}), \quad \mathcal{L}_{\rm aux} = -i[\boldsymbol{\mu}_{\rm aux}\hat{\boldsymbol{x}} + f_{\rm aux}(\hat{p}), \odot], \tag{3b}$$

where $\boldsymbol{\kappa}_k$ and $\boldsymbol{\mu}_{\rm aux}$ are N-dimensional real vectors, $\tilde{f}_k$ are complex-valued functions, and $f_{\rm aux}$ is real valued. [The Gaussian dissipators $\mathcal{L}_{\boldsymbol{\mu}_k\hat{\boldsymbol{x}}+\tilde{f}_k^G(\hat{\boldsymbol{p}})}^{\rm lbd}$ $(\boldsymbol{\mu}_k \in \mathbb{R}^N)$ can be reduced to the form Eq. (3) as a limiting case $\boldsymbol{\kappa}_k \to 0$, as shown in Sec. I of Ref. [18]. The generalized unitary drift term $\mathcal{L}_{\rm aux}$ accounts for ambiguity of the separation of the quantum Liouvillian $\mathcal{L}$ in Eq. (2a) into Hamiltonian and relaxation parts.] The converse holds as well.

The primary findings of this work are summarized in the following two no-go theorems.

No-go theorem 1: Let $|\Psi_0\rangle$ be the ground state (or any other eigenstate of $\hat{H}$), such that $\langle\Psi_0|\hat{\boldsymbol{p}}|\Psi_0\rangle = 0$, and which momentum-space wave functions $\Psi_0(\boldsymbol{p}) = \langle\boldsymbol{p}|\Psi_0\rangle$ is nonzero almost everywhere, except for some isolated points. Then, no translationally invariant Markovian process of form (2) and (3) can steer the system to $|\Psi_0\rangle$.

The idea of the proof, whose details are given in Sec. II of the Supplemental Material [18], is to show that the state $\hat{\rho}_0 = |\Psi_0\rangle\langle\Psi_0|$ can be the fixed point of superoperator $e^{t\mathcal{L}}$ only if $\mathcal{L}_{\rm rel} \equiv 0$. First, note that the linearity and translation invariance of the dissipator (3) imply that $\mathcal{L}_{\rm rel}[\int g(\boldsymbol{x}')e^{-(i/\hbar)\boldsymbol{x}'\hat{\boldsymbol{p}}}\hat{\rho}_0 e^{(i/\hbar)\boldsymbol{x}'\hat{\boldsymbol{p}}} d^N\boldsymbol{x}'] = 0$ for any function $g(\boldsymbol{x}')$. This equation can be equivalently rewritten as

$$\mathcal{L}_{\rm rel}[\Psi_0(\hat{\boldsymbol{p}})g(\hat{\boldsymbol{x}})\Psi_0(\hat{\boldsymbol{p}})^\dagger] = 0, \tag{4}$$

using the identities $e^{-(i/\hbar)\boldsymbol{x}'\hat{\boldsymbol{p}}}|\Psi_0\rangle = \sqrt{2\pi\hbar}\Psi_0(\hat{\boldsymbol{p}})|\boldsymbol{x}'\rangle$ and $\int g(\boldsymbol{x}')|\boldsymbol{x}'\rangle\langle\boldsymbol{x}'|d^N\boldsymbol{x}' = g(\hat{\boldsymbol{x}})$, where $|\boldsymbol{x}'\rangle$ is the eigenstate of position operator $\hat{x}_k|\boldsymbol{x}'\rangle = x_k'|\boldsymbol{x}'\rangle$. Let us choose $g(\boldsymbol{x}) = e^{-i\boldsymbol{\lambda}\boldsymbol{x}}$, where $\boldsymbol{\lambda}$ is an arbitrary real vector, and move to the right the $\hat{\boldsymbol{x}}$-dependent terms in the left-hand side of Eq. (4) using the commutation relations $e^{-i\tilde{\boldsymbol{\lambda}}\hat{\boldsymbol{x}}}\hat{\boldsymbol{p}} = (\hat{\boldsymbol{p}} + \hbar\tilde{\lambda})e^{-i\tilde{\boldsymbol{\lambda}}\hat{\boldsymbol{x}}}$

with $\tilde{\boldsymbol{\lambda}} = \boldsymbol{\lambda}, \pm\boldsymbol{\kappa}_k$. This rearrangement brings Eq. (4) to the form $\tilde{G}_{\boldsymbol{\lambda}}(\hat{\boldsymbol{p}})e^{-i\boldsymbol{\lambda}\hat{\boldsymbol{x}}} = 0$ (note that all the operators of form $e^{\pm i\boldsymbol{\kappa}_k\hat{\boldsymbol{x}}}$ expectedly cancel out owing to translation invariance of $\mathcal{L}_{\rm rel}$). The last equality can be satisfied only if the function $\tilde{G}_{\boldsymbol{\lambda}}(\boldsymbol{p})$ vanishes identically for all $\boldsymbol{p}$ and $\boldsymbol{\lambda}$. However, careful inspection of Sec. II of Ref. [18] shows that the latter happens only if $\mathcal{L}_{\rm rel} = 0$.

The statement of the first no-go theorem can be strengthened for a special class of quantum systems. Let $B(\boldsymbol{p}, \boldsymbol{\lambda})$ be the Blokhintsev function [46], which is related to Wigner quasiprobability distribution $W(\boldsymbol{p}, \boldsymbol{x})$ as

$$B(\boldsymbol{p}, \boldsymbol{\lambda}) = \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} e^{i\boldsymbol{\lambda}\boldsymbol{x}} W(\boldsymbol{p}, \boldsymbol{x}) d^N\boldsymbol{x}. \tag{5}$$

No-go theorem 2: Suppose that the Blokhintsev function $B_\theta(\boldsymbol{p}, \boldsymbol{\lambda})$ of the thermal state $\hat{\rho}_\theta^{\rm th} \propto e^{-(\hat{H}/\theta)}$ characterized by temperature $k_B T = \theta$ is such that

$$\forall\ \boldsymbol{p}, \boldsymbol{\lambda}\colon\ B_\theta(\boldsymbol{p}, \boldsymbol{\lambda}) > 0, \qquad B_\theta(\boldsymbol{p}, -\boldsymbol{\lambda}) = B_\theta(\boldsymbol{p}, \boldsymbol{\lambda}), \tag{6a}$$

$$\forall\ \boldsymbol{p} \neq \boldsymbol{0}, \boldsymbol{\lambda} \neq \boldsymbol{0}\colon\ B_\theta(\boldsymbol{p}, \boldsymbol{\lambda}) < B_\theta(\boldsymbol{0}, \boldsymbol{0}). \tag{6b}$$

Then, no translationally invariant Markovian process (2) and (3) can asymptotically steer the system to $\hat{\rho}_\theta^{\rm th}$.

The proof of this theorem is given in Sec. III of the Supplemental Material [18] and generally follows the same logic as the outlined proof of the first no-go theorem. Using Eq. (5) and the familiar formula for the thermal state Wigner function [47], it is easy to check that the criteria (6) are satisfied for any θ in the case of a quadratic potential U. This means that the Lindblad's original conclusion on inability to thermalize the damped harmonic oscillator using the Gaussian friction term $\mathcal{L}_{\rm rel} = \mathcal{L}^{\rm lbd}_{\boldsymbol{\mu}\hat{\boldsymbol{x}}+\boldsymbol{\eta}\hat{\boldsymbol{p}}}$ is equally valid for all Markovian translationally invariant dissipators.

Corollary 2.1: No translationally invariant Markovian process of form (2) and (3) can steer the quantum harmonic oscillator into a thermal state of form $\hat{\rho}_\theta^{\rm th} \propto e^{-(\hat{H}/\theta)}$.

Practical implications of the no-go theorems.—In classical thermodynamics, the bath is understood as a constant-temperature heat tank "unaware" of a system of interest. However, the no-go theorems indicate that system-bath correlations of at least one kind—spatial or temporal—become obligatory for thermalization once quantum mechanical effects are taken into account. These correlations break the bath translation invariance or Markovianity assumptions, respectively.

Nevertheless, in the view of computational advantages outlined above, it is desirable to incorporate these assumptions into the master equations (2) and (3). Now we are going to introduce the recipe to construct such models with a minimal error in the thermal state. In order to proceed, note that in the limit $(\hbar\boldsymbol{\kappa}_k)^2 \ll \langle\hat{\boldsymbol{p}}^2\rangle$, Eqs. (2) and (3) reduce to the familiar Fokker-Planck equation

$$\frac{\partial}{\partial t}\varpi(\boldsymbol{p}) \simeq \mathrm{Tr}(\delta(\boldsymbol{p} - \hat{\boldsymbol{p}})\mathcal{L}_0[\hat{\rho}]) + \sum_{n,l}\frac{\partial^2 D_{n,l}(\boldsymbol{p})\varpi(\boldsymbol{p})}{\partial p_n \partial p_l} - \sum_n \frac{\partial F_n^{\rm fr}(\boldsymbol{p})\varpi(\boldsymbol{p})}{\partial p_n} \tag{7}$$

for the momentum probability distribution $\varpi(\boldsymbol{p}) = \mathrm{Tr}[\delta(\boldsymbol{p} - \hat{\boldsymbol{p}})\hat{\rho}]$. The friction forces $\boldsymbol{F}^{\rm fr}$ in Eq. (7) as well as Eq. (1a) have the form

$$\boldsymbol{F}^{\rm fr}(\hat{\boldsymbol{p}}) = -\sum_k \hbar\boldsymbol{\kappa}_k |\tilde{f}_k(\hat{\boldsymbol{p}})|^2, \tag{8}$$

whereas the momentum-dependent diffusion operator is

$$D_{n,l}(\hat{\boldsymbol{p}}) = \frac{\hbar^2}{2}\sum_k |\tilde{f}_k(\hat{\boldsymbol{p}})|^2 \kappa_{k,n}\kappa_{k,l}. \tag{9}$$

Equations (8) and (9) can be satisfied by different sets of $\boldsymbol{\kappa}_k$ and $\tilde{f}_k(p)$. We will exploit this nonuniqueness to reduce the system-bath correlation errors. Our strategy is reminiscent of the familiar way of making density functional calculations practical via error cancellation in approximated exchange-correlation functionals. We shall demonstrate the generic procedure by considering a one-dimensional oscillator with the Hamiltonian $\hat{H} = (m/2)\hat{p}^2 + (m\omega^2/2)\hat{x}^2$ (here the dimension subscript n is omitted for brevity). Corollary implies that $\mathcal{L}_{\rm rel}[\hat{\rho}_\theta^{\rm th}] \neq 0$ and $\hat{\rho}_{\rm st} \neq \hat{\rho}_\theta^{\rm th}$ for any θ, where $\hat{\rho}_{\rm st} = \hat{\rho}|_{t\to\infty}$ is the actual fixed point of the evolution operator $e^{t\mathcal{L}}$. However, the net discrepancies can be reduced by imposing the following thermal population conserving constraint:

$$\frac{d}{dt}\langle e^{-\alpha\hat{H}}\rangle_\theta\Big|_{t=0} = 0; \qquad \left|\frac{d^2}{dt^2}\langle e^{-\alpha\hat{H}}\rangle_\theta\right|_{t=0} \to \min \text{ for all } \alpha, \tag{10}$$

where $\langle\odot\rangle_\theta(t) = \mathrm{Tr}(\odot e^{t\mathcal{L}}[\hat{\rho}_\theta^{\rm th}])$. This constraint can be intuitively justified when the characteristic decay rates are much smaller than the typical transition frequencies, such that the dissipation can be treated perturbatively. Since the term $\mathcal{L}_{\rm rel}[\hat{\rho}_\theta^{\rm th}]$ generates only rapidly oscillating off-diagonal elements in the basis of $\hat{H}$, Eq. (10) ensures that the first-order perturbation vanishes on average for the exact thermal state: $\lim_{t\to\infty}(1/t)\int_0^t e^{\tau\mathcal{L}_0}\mathcal{L}_{\rm rel}e^{(t-\tau)\mathcal{L}_0}[\hat{\rho}_\theta^{\rm th}]\mathrm{d}\tau = 0$.

In the case of the driftless dissipation $\mathcal{L}_{\rm aux} = 0$, Eq. (10) is satisfied by the following functions $\tilde{f}_k(p)$ in Eq. (3):

$$\tilde{f}_k(p) = c_k e^{p\beta\hbar\lambda_k}, \qquad \lambda_k = \kappa_k \tanh\left(\frac{\hbar\omega}{4\theta}\right), \tag{11}$$

where $\beta = (m\hbar\omega)^{-1}$ and the constants c_k should be chosen to satisfy Eq. (8). The corresponding dissipator (3) reproduces the familiar microphysical model of quantum Brownian motion [see, e.g., Eq. (16) in Ref. [36]] in the limit $\boldsymbol{\kappa} \to 0$, $\omega \to 0$. Furthermore, the resulting dynamics

tends to decrease (increase) the average system energy $\langle\hat{H}\rangle_\theta$ if its initial temperature θ' is higher (lower) than θ:

$$\frac{d}{dt}\langle\hat{H}\rangle_{\theta'}|_{t=0} = \frac{c_k^2}{\omega}\tilde{\gamma}_k^{\rm en}(\theta',\theta)(\langle\hat{H}\rangle_\theta - \langle\hat{H}\rangle_{\theta'})|_{t=0}, \quad (12)$$

where $\tilde{\gamma}_k^{\rm en}(\theta',\theta) = 2\omega\beta\hbar^2\kappa_k\lambda_k\exp(\beta\hbar^2\lambda_k^2\coth(\hbar\omega/2\theta')) > 0$.

Equation (12) suggests that $\hat{\rho}_{\rm st}$ is close to $\hat{\rho}_\theta^{\rm th}$. This conclusion is supported by the simulations presented in Fig. 2(a) for the isotropic dissipator $\mathcal{L}_{\rm rel} = \mathcal{B}_{\kappa,\tilde{f}^{\rm iso}}$,

$$\mathcal{B}_{\kappa,\tilde{f}^{\rm iso}} \overset{\rm def}{=} \mathcal{L}_{\hat{A}^+}^{\rm lbd} + \mathcal{L}_{\hat{A}^-}^{\rm lbd}, \qquad \hat{A}^\pm = e^{\mp i\kappa\hat{x}}\tilde{f}^{\rm iso}(\pm\hat{p}). \quad (13)$$

One can see that the high-quality thermalization is readily achieved by tuning the free parameters c_k and κ_k even in the strong dissipation regime.

To understand the result (11), note that the terms $\mathcal{L}_{\hat{A}_k}^{\rm lbd}$ in Eq. (3) represent independent statistical forces $\langle -\hbar\boldsymbol{\kappa}_k|\tilde{f}_k(\hat{\boldsymbol{p}})|^2\rangle$ contributing to the net friction $\langle\hat{\boldsymbol{F}}^{\rm fr}\rangle$. In classical mechanics, such forces at $\theta = 0$ steer the system to the state of rest by acting against the particles' momenta, hence,

$$\tilde{f}_k(\hat{\boldsymbol{p}}) = 0 \quad \text{when } \boldsymbol{p}\boldsymbol{\kappa}_k < 0 \quad \text{(classical mechanics)}. \quad (14)$$

However, clipping the functions (11) according to Eq. (14) introduces significant errors, as displayed by dotted curves in Fig. 2(a). Thus, the "endothermic" tails of $\tilde{f}_k(\hat{\boldsymbol{p}})$ at $\boldsymbol{p}\boldsymbol{\kappa}_k > 0$ break the thermalization in the classical case, but reduce errors in the quantum mechanical treatment. To clarify this counterintuitive observation, note that the physical requirement $(d/dt)\langle\hat{O}\rangle_\theta = 0$ for any observable $\hat{O}$ in the thermodynamic equilibrium $\hat{\rho}_{\rm st} = \hat{\rho}_\theta^{\rm th}$ is violated by the master equations (2) and (3) due to the no-go theorems, i.e.,

$$\frac{d}{dt}\langle\hat{x}_n^2\rangle_\theta\Big|_{t=0} = \hbar^2\sum_k\left\langle\left|\frac{\partial}{\partial\hat{p}_n}\tilde{f}_k(\hat{\boldsymbol{p}})\right|^2\right\rangle_\theta\Big|_{t=0} > 0, \quad (15)$$

in the driftless case $\mathcal{L}_{\rm aux} = 0$. The inequality (15) provides further evidence for the no-go theorems and is the hallmark of the "position diffusion," a known artifact in the quantum theory of Brownian motion [45].

According to Eq. (15), $(d/dt)\langle\hat{x}^2\rangle_\theta|_{t=0}$ is sensitive to smoothness of $\tilde{f}_k(\boldsymbol{p})$. Specifically, the right-hand side of Eq. (15) is exploded by any highly oscillatory components of $\tilde{f}_k(\boldsymbol{p})$ and diverges if $\tilde{f}_k(\boldsymbol{p})$ is discontinuous. This entirely quantum effect is the origin of poor performance of the clipped solutions (14) seen in Fig. 2(a). Equation (15) uncovers unavoidable errors in the potential energy. The optimal solutions (11) enforce error cancellation $(d/dt)\langle\hat{p}^2/2m\rangle_\theta|_{t=0} = -(d/dt)\langle U(\hat{x})\rangle_\theta|_{t=0}$ between kinetic and potential energies leaving the total energy intact $(d/dt)\langle\hat{H}\rangle_\theta|_{t=0} = 0$. In fact, the error cancellation is achieved with a large class of physically feasible functions $\tilde{f}_k(\boldsymbol{p})$ that may substantially differ from the solutions (11) everywhere but the region of high probability density $\varpi(p) = {\rm Tr}[\delta(\hat{p}-p)\hat{\rho}_\theta^{\rm th}]$ (however, note the remark in Sec. IV of the Supplemental Material [18]). This is illustrated in Fig. 2(a) by dashed curves overlapping with solid curves.

The master equations (2) and (3) provide accurate nonperturbative description of collisions with a background gas of atoms or photons [5,44,48–50]. Hence, the above theoretical conclusions can be directly tested in the laboratory using well-developed techniques, e.g., the setup shown in Fig. 2(b). Here a two-level atom is subject to two orthogonally polarized counterpropagating monochromatic nonsaturating laser fields of the same amplitude $\mathcal{E}$ and frequency $\omega_{\rm l}$. We show in Sec. IV of Ref. [18] that the translational motion of the atom can be modeled using Eq. (2) with an isotropic friction term of form $\mathcal{L}_{\rm rel} = \mathcal{B}_{\kappa,\tilde{g}^{\rm iso}}$. Here,

$$\kappa = \frac{\omega_{\rm l}}{c}, \quad \tilde{g}^{\rm iso}(p) = \tilde{c}_1[\tilde{c}_2^2 + (p-\tilde{c}_3)^2]^{-\frac{1}{2}}, \quad \tilde{c}_k \in \mathbb{R}, \quad (16)$$

and the parameters $\tilde{c}_k$ can be tuned by $\mathcal{E}$ and $\omega_{\rm l}$.

Now we are ready to clarify why the deviations from canonical equilibrium increase with $|\kappa|$ in Fig. 2(a). The parameters $\hbar|\kappa|$ and $\tilde{g}^{\rm iso}(p)^2$ in Eq. (16) can be regarded as the change of atomic momentum after absorption of a photon and the absorption rate. The case of small $\hbar|\kappa| \ll \sqrt{\langle\hat{p}^2\rangle}$ and large $\tilde{g}^{\rm iso}(p)^2$ implies tiny and frequent momentum exchanges subject to the central limit theorem. The net result is a velocity-dependent radiation pressure with vanishing fluctuations. The opposite case of large $\hbar|\kappa| \gg \sqrt{\langle\hat{p}^2\rangle}$ and small $\tilde{g}^{\rm iso}(p)^2$ is the strong shot noise limit, where the stochastic character of light absorption is

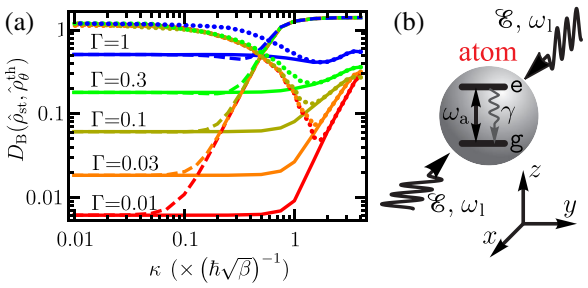

FIG. 2. (a) The accuracy of thermalization of the harmonic oscillator at $\theta = 0$ by the dissipator $\mathcal{L}_{\rm rel} = \Gamma\mathcal{B}_{\kappa,\tilde{f}^{\rm iso}}$ as a function of κ and Γ. The solid curves show the Bures distance D_B between the thermal state $\hat{\rho}_\theta^{\rm th}$ and its approximation $\hat{\rho}_{\rm st}$ for the case $\tilde{f}^{\rm iso}(p)$ defined by Eq. (11) with $c = \omega/\sqrt{\tilde{\gamma}^{\rm en}(0,0)}$. The dotted curves represent the clipped versions (14) of $\tilde{f}^{\rm iso}(p)$. The dashed curves correspond to the case of functions $\tilde{f}^{\rm iso}(p)$ approximated by Eq. (16) with parameters $\tilde{c}_i$ chosen such that $(d^l/dp^l)[\tilde{f}^{\rm iso}(p) - \tilde{g}^{\rm iso}(p)]|_{p=0} = 0$ for $l = 0,\ 1,\ 2$. (b) The Doppler cooling setup to test the model (2), (3) in the laboratory.

no longer averaged out, notably perturbing the thermal state. Note that a similar interpretation applies to quantum statistical forces in Ref. [51].

The dissipative model (2) and (3) with optimized parameters (11) is further analyzed in Fig. 1 using the same parameters as in Fig. 2(a). Both Figs. 1 and 2(a) indicate that thermalization can be modeled for a wide range of recoil momenta $\hbar\kappa \in (-(\hbar\sqrt{\beta})^{-1}, (\hbar\sqrt{\beta})^{-1})$ and the higher the temperature, the better the accuracy. Thus, Eqs. (8) and (9) enable us to simulate a variety of velocity dependences of friction and diffusion.

Finally, Fig. 1(a) benchmarks such simulations against the commonly used quantum optical master equation (QOME) [52] defined by Eq. (2c) with $K = 2$, $\hat{L}_1 = \sqrt{2\Gamma\omega}(1 - e^{-(\hbar\omega/\theta)})^{-\frac{1}{2}}\hat{a}$, $\hat{L}_2 = \sqrt{2\Gamma\omega}(e^{(\hbar\omega/\theta)} - 1)^{-\frac{1}{2}}\hat{a}^\dagger$, where $\hat{a}$ is the harmonic oscillator annihilation operator. For a correct comparison, the parameters of both models are adjusted to ensure identical decay rates in Eq. (12). Systematic errors in our model and QOME are comparable for the equilibrium displacements $\Delta x_0 \sim \hbar\beta^{-\frac{1}{2}}$ at zero temperature and $\Delta x_0 \sim 0.1\hbar\beta^{-\frac{1}{2}}$ for $\theta \sim \hbar\omega$. For low-frequency molecular vibrational modes ($m \sim 10^4$ atomic units, $\omega \sim 200$ cm^{-1}), these shifts are of order 0.4 and 0.04 Å, respectively, which are in the range of typical molecular geometry changes due to optical excitations or liquid environments. We found the displacement-independent errors in the models (2), (3) to be very important for quantum control via reservoir engineering. Furthermore, the same feature can also be exploited for engineering the mechanical analogs of nonreciprocal optical couplings [53] and energy-efficient molecular quantum heat machines [38]. These subjects will be explored in a forthcoming publication.

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