Vibrational relaxation in the Kubo oscillator: Stochastic pumping of heat

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We present a model for a molecular level heat pump that operates when a stochastic time dependent force modulates the molecular vibrational energies. The model consists a molecular unit, represented by a Kubo oscillator, coupled to two solids characterized by distinct spectral properties and kept at unequal temperatures. In the fast modulation limit we derive expressions for the vibrational energy transition rates in the Kubo oscillator, and show that they do not trivially correspond to the population transition rates, unlike the field-free (or adiabatic) limit. We discuss the operation principle of the pump and manifest, analytically and numerically, directing of heat against a temperature gradient for a broad range of system and bath parameters. The present formalism could also describe a unidirectional exciton energy flow in a metal-molecule-metal junction under random noise. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3109899]

I. INTRODUCTION

Heat flows spontaneously from objects at high temperature to objects of low temperature. Directing heat against a temperature gradient requires the application of an external perturbation. While macroscopic heat engines, pumps, and refrigerators mark the beginning of the "Industrial Revolution," mesoscopic and molecular analogs of these devices are a new topic of interest with applications in molecular electronics,[1] reaction dynamics,[2] thermal machinery,[3] and thermometry.[4]

The generic nanopump model includes a molecular element bridging two solids at different temperatures. A spatial asymmetry should be built into the model in order to define a preferential directionality. This can be achieved by using solids with distinct spectral properties. An external force modulates the subsystem (molecular) energetics, leading to a net exchange of heat between the baths against, or in the absence, of a temperature gradient. This process is closely related to the ratchet effect where a particle current is catalyzed in the absence of a dc voltage drop due to the asymmetry in the spatial potential and the influence of time dependent forces.[5]

Recent studies have carefully analyzed the operation principles of prototype classical[6–11] and quantum[12–18] thermal machines, seeking to optimize performance. In particular, we have recently proposed a molecular level heat pump where an external force *periodically* modulates the vibrational levels of the molecule.[19] This modulation affects periodic oscillations of the internal molecular temperature and its coupling to the solids, resulting in a unidirectional heat flow against temperature gradient. We have analyzed the device efficiency for various modulation wave forms, and discussed optimization techniques. Specifically, Ref. 19 examined the adiabatic and quasiadiabatic modulation limits, i.e., the vibrational energies were oscillating at a frequency that was of the order or smaller than the inverse of the system relaxation time.

In this paper we focus on the *fast modulation* limit, demonstrating pumping of heat in response to *random noise*. This idea was first suggested in Ref. 20, and here we give a detailed account of our formulation and results. Our objective is rather than to elaborate on the device efficiency, to manifest a facile pumping of heat for a broad range of subsystem and bath parameters. In our simplified picture we consider heat exchange between distinct macroscopic solids connected by a Kubo oscillator,[21] representing a molecular element suffering stochastic modulations of its energy levels. Considering a dichotomous noise, we achieve pumping of heat relaying on the asymmetry $\omega_R \sim B_0 \ll \omega_L$, where B_0 is the frequency of the Kubo oscillator and ω_ν is the characteristic cutoff frequency of the $\nu=L,R$ bath. Numerical simulations demonstrate the pumping operation using a Lorentzian spectral line shape, applicable in the fast modulation limit. Thus, while noise is typically considered as an obstacle, here it is utilized for gaining functionality, similarly to the mechanism of Brownian motors.[5]

Formulating a theory for vibrational energy relaxation, allowing for fluctuations of the vibrational states, is important for understanding the relaxation dynamics of a solute strongly interacting with its solvent. Recent studies have developed a Landau–Teller expression for the *state to state* vibrational relaxation rate incorporating energy changes.[22,23] Here we further develop microscopic expressions for the vibrational energy transition rates in a specific model, a Kubo oscillator coupled to a harmonic bath. We show that the energy transition rates are not proportional to the population (state to state) relaxation rates, unlike the static and adiabatic limits. Thus, this paper essentially presents a generalization of the field-free vibrational relaxation rate studies to time dependent (stochastic) situations.

In a recent study Pekola *et al.*[24] proposed a Brownian refrigerator which conveys electronic energy unidirectionally in response to random noise. Although our formalism de-

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scribes vibrational energy flow, it can be standardly generalized to describe pumping of heat between distinct metals.[25] Other works explored electron cooling in a double-well heterostructure by an ac modulation of the well potential,[26] and described mechanisms of heat pumping in electronic systems, driven by ac fields.[27]

The structure of this paper is as follows. The vibrational relaxation of a Kubo oscillator coupled to a *single* thermal bath is analyzed in Sec. II. Generalization to multiple reservoirs is described in Sec. III, where an analytical model and numerical simulations manifest pumping of heat against a temperature gradient. Section IV briefly discusses the electronic analog, pumping of heat between distinct metals, then concludes.

II. ENERGY RELAXATION IN THE KUBO OSCILLATOR: A SINGLE BATH CASE

A. Model

We consider a Kubo oscillator[21] bilinearly coupled to a *single* reservoir including a collection of harmonic oscillators, and investigate the transfer of energy between the subsystem (Kubo mode) and bath. The model could be realized by adsorbing a molecule on a dielectric surface, blocking particle transfer, while allowing for heat exchange between the modules. The total Hamiltonian includes three contributions,

$$H = H_0(t) + H_B + V. \tag{1}$$

H_0 includes the isolated subsystem, a Kubo oscillator,

$$H_0(t) = \sum_n E_n(t)|n\rangle\langle n|; \quad E_n(t) = [E_n^{(0)} + \epsilon_n(t)]. \tag{2}$$

$E_n^{(0)} = nB_0$ is the static energy of level $|n\rangle$, $\epsilon_n(t)$ is a time dependent stochastic contribution. We assume that the average over stationary fluctuations vanishes, $\langle \epsilon(t)\rangle_\epsilon = 0$, while higher moments survive. The oscillator is coupled to a thermal bath of temperature $T = 1/\beta$, $(k_B \equiv 1)$ represented by a set of independent harmonic oscillators $(\hbar \equiv 1)$

$$H_B = \sum_k \omega_k b_k^\dagger b_k. \tag{3}$$

$b_k^\dagger$ and b_k are the bosonic creation and annihilation operators, respectively. The interaction between the subsystem and the bath is taken to be bilinear (displacement-displacement),

$$V = F\sum_n c_n|n\rangle\langle n-1|; \quad F = \sum_k \lambda_k(b_k^\dagger + b_k), \tag{4}$$

where $c_n = \sqrt{n}$, and the system-bath interaction is characterized by the spectral function

$$g(\omega) = 2\pi\sum_k \lambda_k^2 \delta(\omega - \omega_k). \tag{5}$$

We typically use a simple power-law model, e.g., $g(\omega) = \xi\omega e^{-\omega/\omega_c}$, where ξ is a dimensionless damping constant and ω_c is the cutoff (characteristic) frequency of the bath. Models (1)–(4) can be easily generalized to include multiple thermal baths, assuming the reservoirs do not directly interact, only through their interaction with the local oscillator, see Sec. III.

In what follows we simplify the discussion and consider a two-level system (TLS) $(n=0,1)$ for the local Hamiltonian. In this case system and interaction terms are given by

$$H_0^{\mathrm{TLS}}(t) = \frac{B(t)}{2}\sigma_z; \quad B(t) = [B_0 + \epsilon(t)],$$
$$V^{\mathrm{TLS}} = F\sigma_x. \tag{6}$$

Here $\sigma_x = |1\rangle\langle 0| + |0\rangle\langle 1|$ and $\sigma_z = |1\rangle\langle 1| - |0\rangle\langle 0|$. $B_0 = E_1^{(0)} - E_0^{(0)}$ is the static level spacing, and $\epsilon(t)$ is the stochastic modulation of this energy gap. We sometimes refer to the truncated harmonic mode as a "spin." For this model we calculate next the state to state transition rate $k_{n\to n'}$ and the energy transition rate $f_{n'\to n}(n,n'=0,1)$. In the presence of random noise we show that these rates are not linearly related. In the weak coupling limit the TLS dynamics can be trivially carried back to the harmonic limit $(n=0,1,\ldots,\infty)$, as we discuss below.

B. Formalism: Stochastically averaged master equation

Closed kinetic equations for the $|n\rangle$ state population can be easily obtained in the weak system-bath coupling limit.[28,29] Briefly, this involves (i) studying the dynamics within second order perturbation theory, (ii) going into the Markovian limit, assuming short correlation time of bath fluctuations in comparison to the system relaxation time, and (ii) averaging over the stochastic process under the decoupling approximation,

$$\left\langle e^{i\int_0^x \epsilon(t')dt'} P_n(x)\right\rangle_\epsilon \sim \left\langle e^{i\int_0^x \epsilon(t')dt'}\right\rangle_\epsilon \langle P_n(x)\rangle_\epsilon. \tag{7}$$

Here $P_n(n=0,1)$ denotes the TLS population, and the average is performed over energy fluctuations. Decomposition (7) relays on the separation of time scales: Energy fluctuations are assumed to be fast in comparison to the characteristic system relaxation time. The three assumptions (i)–(iii) result in the following rate equation[28]

$$\langle \dot{P}_1(t)\rangle_\epsilon = -k_{1\to 0}\langle P_1(t)\rangle_\epsilon + k_{0\to 1}\langle P_0(t)\rangle_\epsilon,$$
$$\langle P_1(t)\rangle_\epsilon + \langle P_0(t)\rangle_\epsilon = 1, \tag{8}$$

with the activation $k_{0\to 1}$ and relaxation $k_{1\to 0}$ rates

$$k_{0\to 1} = \int_{-\infty}^{\infty} d\omega g(\omega)N(\omega)I(B_0 - \omega),$$
$$k_{1\to 0} = \int_{-\infty}^{\infty} d\omega g(\omega)[N(\omega)+1]I(B_0 - \omega). \tag{9}$$

The elements here are the phonon spectral function $g(\omega)$ defined in Eq. (5), extended to negative values $g(\omega) = -g(-\omega)$, the Bose–Einstein occupation factor

$$N(\omega) = [e^{\beta\omega} - 1]^{-1}, \tag{10}$$

and the spectral line shape of the Kubo oscillator,

$$I(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt e^{i\omega t}\left\langle e^{i\int_0^t\epsilon(t')dt'}\right\rangle_{\epsilon}. \tag{11}$$

For a detailed derivation of Eqs. (8) and (9) see Appendix A. The relaxation rate (9) could be also derived from the general formulation of Ref. 22, where distinct operators act on the diagonal and nondiagonal elements of the subsystem.

In the absence of fluctuations, $I(\omega)=\delta(\omega)$, the field-free vibrational relaxation rates[30] can be retrieved from Eq. (9): The rates are evaluated at the bare TLS frequency, $k_{0\to1}=g(B_0)N(B_0)$, $k_{1\to0}=g(B_0)[N(B_0)+1]$, and the equilibrium population obeys the detailed balance condition $P_1/P_0=e^{-\beta B_0}$. In contrast, for a general driving this condition is violated, as the time dependent field drives the subsystem out of the thermal equilibrium with the bath. This effect is the origin of interesting nonequilibrium effects, e.g., stochastic cooling of a spin.[29] Furthermore, as we show below, for a two-bath model the stochastic perturbation may generate a unidirectional energy current against a temperature gradient.

While the derivation of the master Eq. (8) assumes a fluctuating spin impurity (6), it can be trivially generalized in the weak coupling regime to describe a harmonic local mode $(n=0,1\ldots,\infty)$ under a stochastic field. In this case only transitions between nearest states survive,

$$\begin{aligned}\langle\dot{P}_n\rangle_{\epsilon}=&-[(n+1)k_{n\to n+1}+nk_{n\to n-1}]\langle P_n\rangle_{\epsilon}\\&+(n+1)k_{n+1\to n}\langle P_{n+1}\rangle_{\epsilon}+nk_{n-1\to n}\langle P_{n-1}\rangle_{\epsilon},\end{aligned} \tag{12}$$

with the activation and relaxation rates (9). Note that for harmonic systems the rates are independent of the index n.

C. Heat current

The internal energy of the subsystem is modified both by the external modulation of the spacing (work), and due to thermally activated population transfer processes (heat). The goal of this subsection is to derive an analytical expression for the heat flux exchanged between the system and bath in the presence of stochastic energy modulations. We again focus on the TLS model (6), then extend the results to the harmonic case (2)–(4). In the absence of time dependent forces the heat flux J is given by[31]

$$J(t)=B_0[k_{1\to0}P_1(t)-k_{0\to1}P_0(t)], \tag{13}$$

and energy transition rates (units of 1/time) are thus given by $k_{n\to n'}$, the state to state transition rates. We analyze next the heat flux incorporating energy fluctuations. We use the general definition of the energy flux operator between neighboring sites,[32] applicable for both stationary and time dependent situations, $\hat{J}_{s\to s+1}=i/2[h_s^0-h_{s+1}^0,V(s,s+1)]$, where h_s^0 is the local Hamiltonian at site s, and $V(s,s+1)$ is the nearest neighbors interaction. In the present case this reduces to

$$\hat{J}=\frac{i}{2}[(H_0^{\mathrm{TLS}}-H_B),V^{\mathrm{TLS}}]. \tag{14}$$

The current is defined positive when flowing from the TLS to the bath. We substitute Eqs. (3) and (6) into Eq. (14) and obtain the current operator

$$\hat{J}(t)=-\frac{1}{2}\left[i\sigma_x\sum_k\lambda_k\omega_k(b_k^{\dagger}-b_k)+B(t)\sigma_y\sum_k\lambda_k(b_k^{\dagger}+b_k)\right], \tag{15}$$

with $\sigma_y=-i|1\rangle\langle0|+i|0\rangle\langle1|$. Using the short notation $F=\Sigma_k\lambda_k(b_k^{\dagger}+b_k)$, $G=i\Sigma_k\lambda_k\omega_k(b_k^{\dagger}-b_k)$, we rewrite this expression as

$$\hat{J}(t)=-\tfrac{1}{2}[\sigma_xG+B(t)\sigma_yF]. \tag{16}$$

The expectation value of the heat current is given by $J=\mathrm{Tr}\{\rho\hat{J}\}$, where ρ is the total density matrix, and the trace is performed over the thermal bath and the subsystem degrees of freedom. A further averaging over the TLS energy fluctuations is necessary. Since in steady state the condition $\langle\mathrm{Tr}\{\rho\partial V/\partial t\}\rangle_{\epsilon}=0$ translates to $\langle\mathrm{Tr}\{\rho G\sigma_x\}\rangle_{\epsilon}=\langle\mathrm{Tr}\{\rho B(t)\sigma_yF\}\rangle_{\epsilon}$, the steady-state noise-averaged current can be calculated by studying only one of the terms in Eq. (16), e.g.,

$$\langle J\rangle_{\epsilon}=-\langle\mathrm{Tr}\{\rho G\sigma_x\}\rangle_{\epsilon}=-\langle\mathrm{Tr}_B\{\rho_{1,0}G+\rho_{0,1}G\}\rangle_{\epsilon}. \tag{17}$$

Here $\rho_{i,j}$ are the matrix elements of the density matrix, and Tr_B denotes a partial trace, over the bath states only.

Under the same set of approximations employed above for deriving Eq. (8), one can acquire the *steady-state* heat current, i.e., the net heat transferred to the bath from the TLS per unit time,

$$\langle J\rangle_{\epsilon}=B_0[\langle P_1\rangle_{\epsilon}f_{1\to0}-\langle P_0\rangle_{\epsilon}f_{0\to1}], \tag{18}$$

see Appendix A for details. The noise-averaged population is obtained by solving Eq. (8) in steady state, taking $\langle\dot{P}_n\rangle_{\epsilon}=0$.[33] The energy transition rates (units time^{-1}) are given by

$$\begin{aligned}f_{0\to1}&=\frac{1}{B_0}\int_{-\infty}^{\infty}d\omega\omega g(\omega)I(B_0-\omega)N(\omega),\\f_{1\to0}&=\frac{1}{B_0}\int_{-\infty}^{\infty}d\omega\omega g(\omega)I(B_0-\omega)[N(\omega)+1].\end{aligned} \tag{19}$$

We can interpret these expressions as follows. The energy excitation rate $f_{0\to1}$ is given by the energy ω which the thermal bath transfers to the subsystem, multiplied by the reservoir density of states and the thermal occupation factor. We integrate it over different TLS energy spacing, weight by the noise spectral function, and scale it by the bare gap B_0. Similar reasoning applies for the energy decay rate $f_{1\to0}$.

In the static limit our model satisfies $f_{n\to n'}=k_{n\to n'}$,[30] thus when population is transferred between levels $n\to n'$, the energy $E_{n'}-E_n$ is exchanged between the system and bath. In contrast, in the presence of stochastic force we cannot trivially connect the energy transfer rates (19) to the population transition rates (9). Note that if the time modulation has been

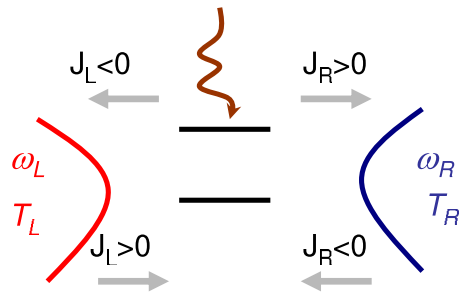

FIG. 1. (Color online) Scheme of the TLS stochastic pump. A molecular element (TLS) under an external perturbation (curly line) is coupled to two solids of different spectral properties. The arrows display the sign notation.

a deterministic-periodic function as in Ref. 19, denoted here by $\epsilon_d(t)=\Sigma_{n=-\infty}^{\infty}[Q_n\cos(n\Omega t)+R_n\sin(n\Omega t)]$, the excitation rates would have reduced to

$$k_{0\to 1}=\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega g(\omega)N(\omega)\int_{-\infty}^{\infty}dt e^{i(B_0-\omega)t}e^{i\int_0^t\epsilon_d(t')dt'},$$

$$f_{0\to 1}=\frac{1}{2\pi B_0}\int_{-\infty}^{\infty}d\omega\omega g(\omega)N(\omega)\int_{-\infty}^{\infty}dt e^{i(B_0-\omega)t}e^{i\int_0^t\epsilon_d(t')dt'}. \quad (20)$$

Using the Fourier decomposition $e^{i\int_0^t\epsilon_d(t')dt'}=\Sigma_{n=-\infty}^{\infty}J_n e^{in\Omega t}$, one gets $k_{0\to 1}=\Sigma_n k_{0\to 1}^{(n)}$; $f_{0\to 1}=\Sigma_n f_{0\to 1}^{(n)}$, and $f_{0\to 1}^{(n)}=((B_0+n\Omega)/B_0)k_{0\to 1}^{(n)}$, where $k_{0\to 1}^{(n)}=J_n g(B_0+n\Omega)N(B_0+n\Omega)$, i.e., the Fourier components of the state to state transition rates and the energy transition rates are proportional.

In the weak coupling limit Eq. (18) can be easily generalized to the harmonic (Kubo) case,[31]

$$\langle J\rangle_\epsilon=B_0\sum_{n=1}^{\infty}n[\langle P_n\rangle_\epsilon f_{n\to n-1}-\langle P_{n-1}\rangle_\epsilon f_{n-1\to n}], \quad (21)$$

where the transition rates $f_{n\to n'}$ are defined in Eq. (19), and the population is calculated by solving Eq. (12) in steady state. Finally, note that in the present model work cannot be extracted from the thermal bath since coherences are not retained.[13,14]

III. TWO-BATH MODEL: STOCHASTIC PUMPING OF HEAT

We generalize the formalism of Sec. II to the multiple-bath case, where the subsystem (Kubo mode) is bilinearly coupled to two reservoirs. For a schematic representation see Fig. 1. We show that when the reservoirs are distinct, i.e., are characterized by different spectral functions, one can direct heat between reservoirs at the same temperature, or pump heat against a temperature bias, due to the application of random noise.

A. Model

We consider a two-bath generalization of the TLS-boson Hamiltonian (6), $H=H_0^{\rm TLS}(t)+H_B+V^{\rm TLS}$,

$$H_0^{\rm TLS}(t)=\frac{B_0+\epsilon(t)}{2}\sigma_z,$$

$$H_B=\sum_{\nu,k}\omega_k b_{\nu,k}^\dagger b_{\nu,k}, \quad (22)$$

$$V^{\rm TLS}=F\sigma_x;\quad F=\sum_{\nu,k}\lambda_{\nu,k}(b_{\nu,k}^\dagger+b_{\nu,k}).$$

The index $\nu=L,R$ runs over the different reservoirs, temperature β_ν^{-1}. Due to the additive nature of the interaction, it can be easily shown that in the weak coupling limit the dynamics follows the quantum master Eqs. (8) and (9) with rates given by the sum of L and R-induced relaxations $k_{n\to n'}=\Sigma_\nu k_{n\to n'}^\nu$,[31] e.g.,

$$k_{0\to 1}^\nu=\int_{-\infty}^{\infty}d\omega g_\nu(\omega)N_\nu(\omega)I(B_0-\omega). \quad (23)$$

The Bose–Einstein factors are calculated at the respective temperature β_ν^{-1}, $N_\nu(\omega)=[e^{\beta_\nu\omega}-1]^{-1}$. In what follows the phonon spectral function takes the form

$$g_\nu(\omega)=A_\nu\omega e^{-\omega/\omega_\nu}, \quad (24)$$

where ω_ν is the characteristic cutoff frequency and A_ν is a constant. Assuming a Gaussian process, going to the fast modulation limit $\langle\epsilon(t_1)\epsilon(t_2)\rangle=2\gamma\delta(t_1-t_2)$, one finds that the noise spectral line shape can be approximated by a Lorentzian function

$$I(\omega)=\frac{\gamma/\pi}{\omega^2+\gamma^2} \quad (25)$$

of width γ. The limit $\gamma\to 0$ corresponds to the static limit with the spectral function approaching a delta function. We will also consider a symmetric dichotomous Markovian noise, where the noise has two realizations, $\epsilon(t)=\pm\Omega$ with a jump frequency μ. If $\Omega>\mu$ the line shape function consists of two sharply shaped peaks located at $\omega=\pm\Omega$,[28]

$$I(\omega)\sim\tfrac{1}{2}[\delta(\omega-\Omega)+\delta(\omega+\Omega)]. \quad (26)$$

Finally, the heat current in the multibath case should be separately calculated at each interface using Eq. (18),[31]

$$\langle J_R\rangle_\epsilon=B_0[\langle P_1\rangle_\epsilon f_{1\to 0}^R-\langle P_0\rangle_\epsilon f_{0\to 1}^R], \quad (27)$$

with the R-bath induced transition rates (19). A similar expression holds at the L contact. The current is defined positive when flowing L to R, see Fig. 1.

B. Pumping mechanism

The pumping mechanism relays on the inherent asymmetry in the phonon baths spectral properties: We assume that $\omega_R\lesssim B_0\ll\omega_L$ and take $T_L\geq T_R$. Due to the fast stochastic modulation, the spacing $B(t)$ can be suddenly reduced to values below ω_R. Since these modulations are faster that the subsystem relaxation time, the TLS effective temperature becomes significantly low, even lower than T_R. The TLS then

absorbs energy from both thermal baths. In contrast, fluctuations that largely increase the gap lead to a high effective internal temperature, while practically disconnecting the R bath from the system for $B(t) \gg \omega_R$. If the internal temperature is higher than T_L, energy will dissipate from the Kubo mode to the left bath. It is thus clear that depending on the system parameters, we may inject energy from the R bath to the L bath, even when $T_L > T_R$, due to the built-in spatial asymmetry of the contacts. Note that this principle is general, independent of the specific form assumed for the noise spectral function and the details of the bath spectral properties.

This mechanism was proposed in Ref. 19, and it is adopted here with two important distinctions: (i) Here we consider a random noise, while in Ref. 19 we carefully shaped a periodic pulse in order to achieve pumping. (ii) The present pump is operating in the fast modulation regime, while in Ref. 19 we examined adiabatic/quasiadiabatic systems, where the modulation frequency was assumed smaller, or the same order, of the system inverse time scale.

C. An exactly solvable model

We utilize next the dichotomous noise line shape (26) and analytically manifest directing of heat in the absence of temperature gradient, exclusively based on the solids' distinct spectral properties. We design the system as follows: The L solid has a high cutoff frequency, $\omega_L \gg B_0$, while the phonon cutoff frequency of the R bath is of the order of the static gap, $\omega_R \sim B_0$. This results in $g_R(B_0+\Omega) \ll g_R(B_0-\Omega)$, where practically we take $g_R(B_0+\Omega)$ to zero, assuming a sharp cutoff. Under this assumption the energy transition rates induced by the R bath are given by Eq. (19)

$$f^R_{0\to 1} = \frac{1}{2B_0}(B_0-\Omega)g_R(B_0-\Omega)N_E(B_0-\Omega),$$
$$f^R_{1\to 0} = \frac{1}{2B_0}(B_0-\Omega)g_R(B_0-\Omega)[N_E(B_0-\Omega)+1]. \tag{28}$$

Here $N_E(\omega)=[e^{\beta_E\omega}-1]^{-1}$, with $\beta_E=1/T_L=1/T_R$. In deriving this equation we have also assumed that $B_0 > \Omega$, i.e., the noise does not invert the levels. The heat current at the R contact is given by Eq. (27). This current becomes negative, i.e., the R surface is cooled down, when the condition

$$\frac{\langle P_1\rangle_\epsilon}{\langle P_0\rangle_\epsilon} < e^{-\beta_E(B_0-\Omega)} \tag{29}$$

is satisfied. We calculate next this ratio. The steady-state population is given by generalizing Eq. (8) to the two-bath case yielding

$$\frac{\langle P_1\rangle_\epsilon}{\langle P_0\rangle_\epsilon} = \frac{k^L_{0\to 1}+k^R_{0\to 1}}{k^L_{1\to 0}+k^R_{1\to 0}}, \tag{30}$$

with

$$k^R_{0\to 1} = g_R(B_0-\Omega)N_E(B_0-\Omega)/2,$$
$$k^L_{0\to 1} = g_L(B_0-\Omega)N_E(B_0-\Omega)/2 + g_L(B_0+\Omega)N_E(B_0+\Omega)/2,$$
$$k^R_{1\to 0} = g_R(B_0-\Omega)[N_E(B_0-\Omega)+1]/2,$$
$$k^L_{1\to 0} = g_L(B_0-\Omega)][N_E(B_0-\Omega)+1]/2 + g_L(B_0+\Omega)[N_E(B_0+\Omega)+1]/2. \tag{31}$$

Using the short notations $N_\pm \equiv N_E(B_0\pm\Omega)$, $g^\pm_L \equiv g_L(B_0\pm\Omega)$, $g^\pm_R \equiv g_R(B_0\pm\Omega)$, we question the inequality (29),

$$\frac{\langle P_1\rangle_\epsilon}{\langle P_0\rangle_\epsilon} = \frac{(g^-_L+g^-_R)N_- + g^+_L N_+}{(g^-_L+g^-_R)(N_-+1)+g^+_L(N_++1)} < \frac{N_-}{1+N_-}. \tag{32}$$

It can be easily shown that this relation is always satisfied, since $N_+ < N-$. Thus, we have proven that heat is directed between two baths at the same temperature, given that the spectral function of one reservoir strongly varies around the static molecular frequency $g^+_R \ll g^-_R$. Similar analysis yields pumping of heat against a temperature gradient ($T_L > T_R, N_L(B_0-\Omega) \gg N_L(B_0+\Omega)$) if the ratio of the bosonic occupation factors fulfills $(N_L(B_0-\Omega)/N_R(B_0-\Omega)) < 1 + (g_L(B_0+\Omega)/g_L(B_0-\Omega))$. Since $N_L(\omega) > N_R(\omega)$ for $T_L > T_R$, it is clear that the spectral energy should strongly vary with frequency in order to enable pumping against a large temperature gradient. We have also analyzed the pump operation assuming Einstein solids, characterizing each reservoir by a single frequency. The Carnot limit can be reached when the device is working reversibly.[20]

D. Numerical results

We exemplify directing of heat against, or in the absence of, a temperature gradient, simulating Eq. (27) with the stationary population determined by solving Eq. (8) in steady state. In the calculations below we adopt the Lorentzian line shape (25), and typically assume that both solids are characterized by the Ohmic spectral function with $\omega_L \sim 100$ and $\omega_R \sim B_0$, $A_\nu = 1$ [see Eq. (24)]. The calculations are performed in dimensionless units. If the energy parameters are given in meV, the current should be divided by the factor $\hbar = 4.14$ meV ps to yield fluxes in units of meV/ps.

Note that the parameters should be chosen so as to consistently obey the condition $(k^\nu_{1\to 0}+k^\nu_{0\to 1}) \ll \omega_\nu$, i.e., the bath correlation time ω_ν^{-1} should be short in comparison to the subsystem characteristic time scale. Since the relaxation rates depend on the system-bath coupling strength, incorporated into A_ν, [see Eqs. (5), (23), and (24)], this condition could be satisfied by reducing the system-bath coupling, or A_ν, as required. Note that lowering this value equally at both ends, $A = A_\nu < 1$, does not affect the levels population, while the L and R currents simply scale down, since $\langle J_\nu\rangle_\epsilon \propto A_\nu$, following Eqs. (19) and (27). One should thus interpret the heat currents plotted in Figs. 2, 4, and 5 as the scaled quantity $\langle J_\nu\rangle_\epsilon / A_\nu$.

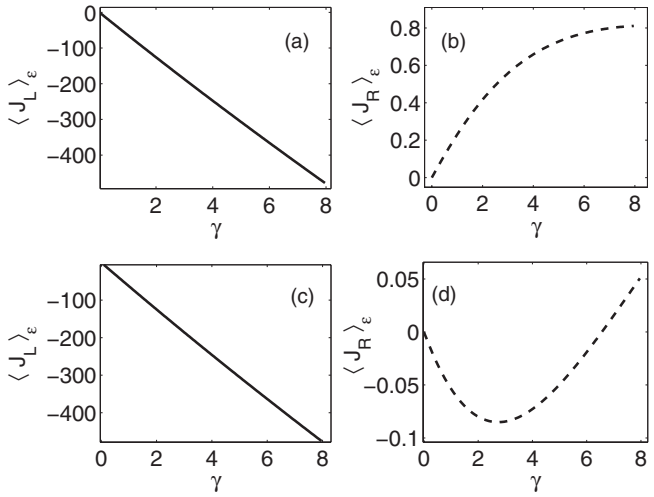

FIG. 2. Energy exchange between reservoirs at the same temperature as a function of noise width. $T_L=T_R=25$; $\omega_L=200$, $\omega_R=3$. [(a) and (b)] For $B_0=5$ both reservoirs are heated up by the external force. [(c) and (d)] For a higher gap, $B_0=15$, energy is pumped from the R bath and absorbed in the L side for $0<\gamma<6$.

First we assume that both reservoirs are held at the same temperature, and demonstrate that we can direct heat from the R interface to the L contact due to the onset of random noise. Figure 2 reveals that depending on the TLS energy gap, heat can be pumped out of the R reservoir for a range of γ [Eq. (25)]. For small gap $\langle J_L \rangle_\epsilon$ is negative (a) and $\langle J_R \rangle_\epsilon$ is positive (b), i.e., both reservoirs are heated up due to the external force (see Fig. 1 for clarifying the sign convention). In contrast, for large energy spacing, $B_0 \sim 15$, while the L bath is still absorbing heat (c), the current at the R interface is negative, and the contact is being cooled down (d). Note that in the presence of external perturbations $\langle J_L \rangle_\epsilon \neq \langle J_R \rangle_\epsilon$.

Figure 3 presents a color map of the heat current at the R side. The flux at the central oval ($\gamma>2; 12<B_0<20$) is negative, i.e., the right bath is cooled down in this regime. We can explain this behavior as follows. For the Ohmic function (24) with $\omega_R=3$ the right bath is practically disconnected from the TLS at energies of the order $\omega \gtrsim 15$. Therefore, the effect of the noise is mostly influential when the subsystem energy spacing is chosen close to this value. For $B_0 \sim 15$ fluctuations that reduce the gap lead to an overlap with the R phonon spectral function, thus the (effectively cold) TLS can accept energy from this contact. Fluctuations

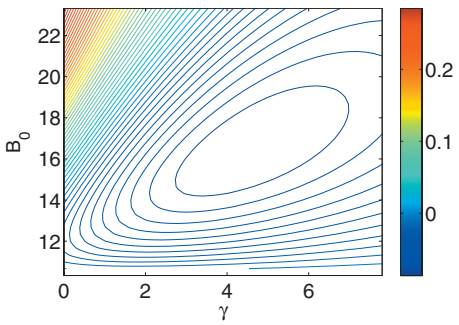

FIG. 3. (Color) Color-map of the heat flux at the R contact, revealing a pumping regime (central oval). $\omega_L=200$, $\omega_R=3$, and $T_L=T_R=25$. For these parameters J_L (not plotted) is negative.

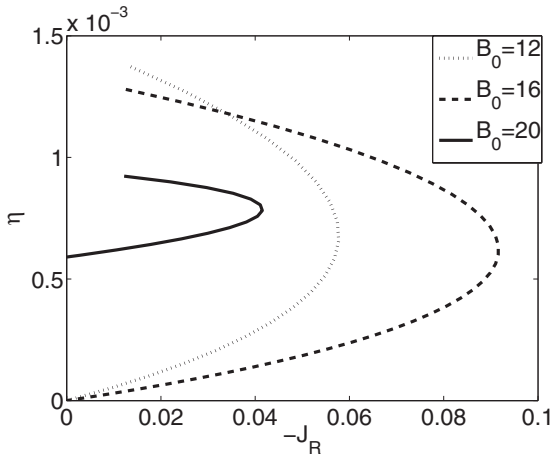

FIG. 4. Chiller plot of the heat pump with parameters as in Fig. 3, $B_0=12$ (dotted), $B_0=16$ (dashed), and $B_0=20$ (full). The control parameters is the noise width $\gamma=0-8$, $T_L=T_R=25$.

that significantly increase the gap ($\omega>15$) imply a complete isolating of the R contact, as its spectral function now does not overlap with the molecular vibrational frequency. Energy is then solely exchanged between the (hot) TLS and the L solid.

In order to understand the device performance we further define the temporal cooling efficiency

$$\eta = \frac{-\langle J_R \rangle_\epsilon}{\langle J_R \rangle_\epsilon - \langle J_L \rangle_\epsilon}, \tag{33}$$

where the denominator is the work (per unit time) done by the stochastic perturbation, and the numerator is the heat extracted from the R bath. The performance of the device can be understood by plotting the chiller curve, efficiency as a function of heat pumped. Using the control parameter γ we obtain a typical behavior, similarly to that observed in other models of quantum refrigerators,[19,34] see Fig. 4.

We further demonstrate pumping of heat against a temperature gradient in Fig. 5. When $\gamma \ll 1$ the currents at the L and R contacts are equal (a). In accordance with the sign notation the flux is positive since the current flows from L to R. As we begin to increase γ we find that the L and R currents deviate due to the application of the external work, $\langle J_L \rangle_\epsilon<0$ and $\langle J_R \rangle_\epsilon>0$, where energy is dissipated into both contacts (b) and (c). For high enough γ (d) the current at the R contact becomes negative (inset), i.e., heat is pumped from this reservoir.

A color map of the pumping regime for various temperatures and noise amplitudes is shown in Fig. 6. Here $\langle J_R \rangle_\epsilon$ is negative for $\gamma<8$ and $T_L-T_R \lesssim 4$. We have verified that the total entropy of the system $-\langle J_L \rangle_\epsilon / T_L + \langle J_R \rangle_\epsilon / T_R$ always increases, in agreement with the second law of thermodynamics. Note that the pumped current is rather low, yet the purpose of this work is to demonstrate that the pumping effect is ubiquitous, rather than to develop optimization schemes.

IV. SUMMARY

We have presented here the operation principle of a stochastic heat pump: A molecular level device that pumps heat

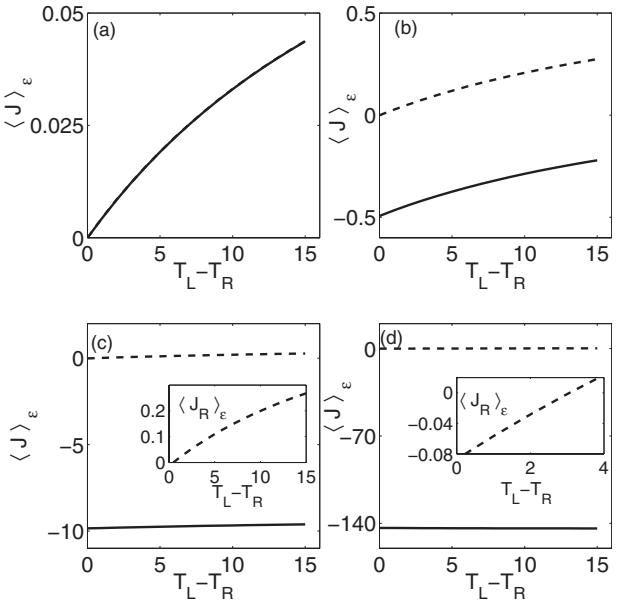

FIG. 5. Pumping heat against a temperature gradient $T_L > T_R$, $\omega_L = 200$, $\omega_R = 3$, $B_0 = 15$, and $T_R = 25$. Current at the left (right) contact is plotted as a full (dashed) line. (a) No noise, $I(\omega) = \delta(\omega)$; J_L and J_R (same line) are both positive as heat flows from L to R in the absence of time dependent noise. (b) $\gamma = 0.01$; heat flows from the TLS into both contacts, $J_L < 0$ and $J_R > 0$. (c) $\gamma = 0.2$; heat flows from the TLS into both contacts, $J_L < 0$ and $J_R > 0$ (inset). (d) $\gamma = 3$; heat is extracted from R (inset) and absorbed at the L side, $J_L < 0$ and $J_R < 0$.

against a temperature gradient when the molecular vibrational states are stochastically modulated. Using a simple dichotomous noise model we have analytically demonstrated directing of heat in the absence of a temperature bias. Our numerical results have further manifested the facile pumping of heat for a broad range of parameters. From the fundamental aspect, in this study we have derived both the state to state vibrational excitation-relaxation rates of the Kubo model, and the energy excitation-relaxation rates, and have shown that they are not trivially connected in the fast modulation limit, in contrast to the field-free and adiabatic cases.[19]

The proposed pumping mechanism could also explain unidirectional exciton energy flow in the absence (or against) temperature gradient. The exciton pump could be built by considering a fluctuating molecular group bridging two metals with different properties, e.g., distinct densities of state. For example, the left metal is characterized by a wide band

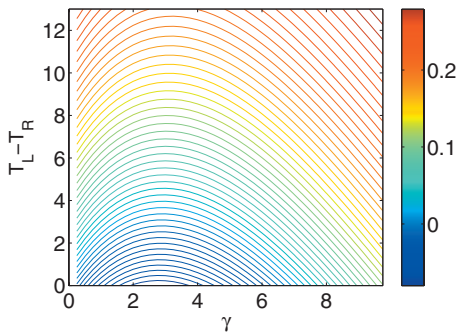

FIG. 6. (Color) Pumping of heat against a temperature gradient. A colormap of the heat flux at the R contact where $\langle J_R \rangle_\epsilon$ is negative for $\gamma < 8$ and $T_L - T_R \lesssim 4$; $\omega_L = 200$, $\omega_R = 3$, $B_0 = 15$, and $T_R = 25$.

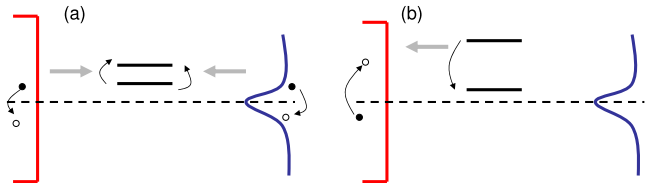

FIG. 7. (Color online) Scheme of an exciton stochastic pump. A local mode under time dependent perturbations is coupled to metals with different DOS: wide band solid (L), and a narrow band contact (R). The dashed lime represents the Fermi energy in the system. (a) When the TLS gap shrinks, its effective local temperature goes down and the subsystem absorbs energy from both metals. (b) At large spacing the (hot) TLS emits energy only to the L side, generating electron-hole pairs. The curved arrows represent electron-hole scattering processes in the metals and population transfer in the local mode.

with a constant density of states (DOS), while the right metal has a narrow band structure, $B_0 \gtrsim E_B - \epsilon_F$, where E_B is the width of the R conduction band, ϵ_F is the Fermi energy, and B_0 is the static TLS spacing, see Fig. 7. In analogy with the phonon pump, fluctuations that reduce the TLS energy spacing imply an effective low local temperature, and the subsystem absorbs energy from both metals (a). Fluctuations that largely enhance the molecular spacing lead to a high effective temperature, while practically disconnecting the TLS from the R metal (b), resulting in a net flow of energy from the R side toward the L contact. Utilizing materials with more complicated band structures can further lead to the reversal of the effect as a function of noise amplitude. Note that our formal derivation (Appendix A) is valid for a general-statistics bath. Equations (8) and (18) are thus applicable assuming fermionic reservoirs, upon substituting the appropriate bath correlation functions into the rate constants.

The pumping mechanism discussed here inherently depends on the asymmetry in the phonon spectral properties. Specifically, in order to design an efficient pump,[20] the solids should be characterized by narrow bands, $g_\nu(\omega) = C$, for $\omega_\nu^1 < \omega < \omega_\nu^2$; and 0 otherwise, where C is a constant and $\omega_\nu^1(\omega_\nu^2)$ is the lower (upper) cutoff frequency. In this case, irrespective of the stochastic noise properties, ergodicity is broken,[35] and the ensemble average of the heat pumped in an array of junctions will differ from the time-averaged heat pumped in an individual junction. It is also of interest to note that while, in principle, the breakdown of ergodicity in our model is not related to the onset of a nonequilibrium noise, interestingly, since our derivation assumes weak system-bath coupling, it is the stochastic noise that reveals the nonergodicity. The reason is that in the absence of stochastic fluctuations the rates are calculated at the bare gap B_0, see discussion after Eq. (11), thus the dynamics is not sensitive to the spectral properties of the reservoirs. However, when we turn on the noise, the system explores other spectral regimes, thus the non-Markovian properties of the thermal baths reflect themselves, and the dynamics becomes nonergodic.

Temperature reduction in nanolevel objects is important in various applications, e.g., for cooling molecular electronics devices,[1] for controlling chemical reactions and molecular dynamics,[2] and for realizing nanomechanical devices.[3] We expect that the general pumping mechanism described here might be observed in various systems suffering random

noise, for example, in nanomechanical resonators.[36] Considering a double clamped nanobeam, the natural frequency could be mechanically modulated due to the beam's mass variation resulting from adsorption-desorption processes.[37] The resonator frequency could be also electrostatically tuned by (stochastically) varying the bias applied to a gate electrode.[38]

ACKNOWLEDGMENTS

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APPENDIX A: DERIVATION OF THE NOISE-AVERAGED QUANTUM MASTER EQUATION AND AN EXPRESSION FOR THE HEAT CURRENT

We derive here the quantum master equation for the TLS population (8) and an expression for the heat current (18). The model includes a truncated Kubo model ($n=0,1$) with a time dependent energy spacing, interacting with a thermal reservoir,

$$H=\tfrac{1}{2}[B_0+\epsilon(t)](|1\rangle\langle 1|-|0\rangle\langle 0|)+F[|0\rangle\langle 1|+|1\rangle\langle 0|]+H_B. \tag{A1}$$

We assume that the thermal bath includes a set of independent harmonic oscillators, creation operator $b_k^\dagger$, and take $F=\Sigma_k\lambda_k(b_k^\dagger+b_k)$; λ_k are real numbers. The evolution of the total density matrix obeys the Liouville equation ($\hbar\equiv 1$)

$$\frac{\partial\rho}{\partial t}=-i[H,\rho]. \tag{A2}$$

Using the transformation $\tilde{\rho}=e^{iH_Bt}\rho(t)e^{-iH_Bt}$, the equations of motion for the density matrix elements $\tilde{\rho}_{i,j}$ can be written explicitly in terms of the bath operators (we omit the tilde from now on)

$$\begin{aligned}
\dot{\rho}_{1,1}&=-iF(t)\rho_{0,1}+i\rho_{1,0}F(t),\\
\dot{\rho}_{0,0}&=-iF(t)\rho_{1,0}+i\rho_{0,1}F(t),\\
\dot{\rho}_{0,1}&=i[B_0+\epsilon(t)]\rho_{0,1}-iF(t)\rho_{1,1}+i\rho_{0,0}F(t),\\
\dot{\rho}_{1,0}&=-i[B_0+\epsilon(t)]\rho_{1,0}-iF(t)\rho_{0,0}+i\rho_{1,1}F(t).
\end{aligned} \tag{A3}$$

Here $F(t)=e^{iH_Bt}Fe^{-iH_Bt}$. Next we formally integrate the nondiagonal terms $\dot{\rho}_{0,1}$ and $\dot{\rho}_{1,0}$ using the Leibnitz integral rule

$$\frac{d}{dt}\int_{u(t)}^{v(t)}f(t,\tau)d\tau=v'(t)f(t,v(t))-u'(t)f(t,u(t))+\int_{u(t)}^{v(t)}\frac{\partial}{\partial t}f(t,\tau)d\tau, \tag{A4}$$

and obtain the integrodifferential equations

$$\begin{aligned}
\rho_{0,1}(t)&=\int_0^t e^{iB_0(t-\tau)}e^{i\int_\tau^t\epsilon(t')dt'}\\
&\quad\times[-iF(\tau)\rho_{1,1}(\tau)+i\rho_{0,0}(\tau)F(\tau)]d\tau,\\
\rho_{1,0}(t)&=\rho_{0,1}^*(t).
\end{aligned} \tag{A5}$$

We substitute these expressions into the equations of motion of the diagonal elements $\dot{\rho}_{0,0}$ and $\dot{\rho}_{1,1}$, and trace over the thermal bath, assuming the density matrix can be decomposed at all times as $\rho(t)=\rho_B\sigma(t)$. Here $\sigma(t)$ is the reduced (subsystem) density matrix and $\rho_B=e^{-\beta H_B}/\mathrm{Tr}_B(e^{-\beta H_B})$. Following the standard Redfield–Bloch derivation,[39] i.e., using second order perturbation theory combined with the assumption that bath correlation functions decay rapidly on the time scale of the change of $\sigma(t)$, we obtain the quantum master equation for the diagonal reduced density matrix elements $P_n(t)\equiv\sigma_{n,n}(t)$, $n=0,1$

$$\begin{aligned}
\dot{P}_1&=P_0(t)\int_0^t e^{iB_0(t-\tau)}e^{i\int_\tau^t\epsilon(t')dt'}\langle F(\tau)F(t)\rangle_B d\tau\\
&\quad+P_0(t)\int_0^t e^{-iB_0(t-\tau)}e^{-i\int_\tau^t\epsilon(t')dt'}\langle F(t)F(\tau)\rangle_B d\tau\\
&\quad-P_1(t)\int_0^t e^{iB_0(t-\tau)}e^{i\int_\tau^t\epsilon(t')dt'}\langle F(t)F(\tau)\rangle_B d\tau\\
&\quad-P_1(t)\int_0^t e^{-iB_0(t-\tau)}e^{-i\int_\tau^t\epsilon(t')dt'}\langle F(\tau)F(t)\rangle_B d\tau,\\
P_0(t)&=1-P_1(t).
\end{aligned} \tag{A6}$$

Here $\langle O\rangle_B\equiv\mathrm{Tr}_B\{\rho_B O\}$. We average next over energy fluctuations. When the characteristic timescale for the states fluctuations is very short in comparison with the characteristic subsystem relaxation time, one can use the decoupling approximation

$$\left\langle e^{i\int_\tau^t\epsilon(t')dt'}P_1(t)\right\rangle_\epsilon\sim\left\langle e^{i\int_\tau^t\epsilon(t')dt'}\right\rangle_\epsilon\langle P_1(t)\rangle_\epsilon. \tag{A7}$$

In the Markovian limit we further extend the upper limit in the (noise-averaged) integrals (A6) to infinity. Using $\langle F(t)F(\tau)\rangle_B=\langle F(t-\tau)F(0)\rangle_B$, and the fact that the noise is stationary, we obtain

$$\begin{aligned}
\langle\dot{P}_1(t)\rangle_\epsilon&=\langle P_0(t)\rangle_\epsilon\int_{-\infty}^{\infty}e^{iB_0x}\left\langle e^{i\int_0^x\epsilon(t')dt'}\right\rangle_\epsilon\langle F(0)F(x)\rangle_B dx\\
&\quad-\langle P_1(t)\rangle_\epsilon\int_{-\infty}^{\infty}e^{iB_0x}\left\langle e^{i\int_0^x\epsilon(t')dt'}\right\rangle_\epsilon\langle F(x)F(0)\rangle_B dx,\\
\langle P_0(t)\rangle_\epsilon&=1-\langle P_1(t)\rangle_\epsilon.
\end{aligned} \tag{A8}$$

For the simple model employed here, $F=\Sigma_k\lambda_k(b_k^\dagger+b_k)$, the bath correlation functions can be exactly calculated, e.g.,

$$\langle F(x)F(0)\rangle = \sum_k \lambda_k^2[N(\omega_k)e^{i\omega_k x} + (N(\omega_k)+1)e^{-i\omega_k x}], \tag{A9}$$

with $N(\omega)=[e^{\beta\omega}-1]^{-1}$. We substitute Eq. (A9) in Eq. (A8) and obtain the Markovian master equation

$$\begin{aligned}\langle \dot{P}_1(t)\rangle_\epsilon &= \langle P_0(t)\rangle_\epsilon k_{0\to 1} - \langle P_1(t)\rangle_\epsilon k_{1\to 0},\\ \langle P_0(t)\rangle_\epsilon &= 1 - \langle P_1(t)\rangle_\epsilon,\end{aligned} \tag{A10}$$

with the rates

$$k_{0\to 1} = \int_0^\infty g(\omega)[N(\omega)I(B_0-\omega) + (N(\omega)+1)I(B_0+\omega)]d\omega, \tag{A11}$$

$$k_{1\to 0} = \int_0^\infty g(\omega)[(N(\omega)+1)I(B_0-\omega) + N(\omega)I(B_0+\omega)]d\omega.$$

Here $g(\omega)=2\pi\Sigma_k\lambda_k^2\delta(\omega-\omega_k)$ is the bath spectral function and $I(\omega)$ is the noise line shape

$$I(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt e^{i\omega t}\left\langle e^{i\int_0^t \epsilon(t')dt'}\right\rangle_\epsilon. \tag{A12}$$

Note that if we extend the function $g(\omega)$ to negative values, $g(\omega)=-g(-\omega)$, integrals (A11) can be compactly rewritten as

$$\begin{aligned}k_{0\to 1} &= \int_{-\infty}^{\infty} g(\omega)N(\omega)I(B_0-\omega)d\omega,\\ k_{1\to 0} &= \int_{-\infty}^{\infty} g(\omega)[N(\omega)+1]I(B_0-\omega)d\omega.\end{aligned} \tag{A13}$$

The detailed balance condition $k_{1\to 0}=k_{0\to 1}e^{\beta\omega}$ is not satisfied in the presence of the noise, while it is still obeyed at each frequency separately.

We evaluate next the heat current flowing from the subsystem into the thermal reservoir. We begin with the general definition of the heat current operator as discussed in Ref. 32, applied to a TLS coupled to a bosonic bath

$$\hat{J} = \frac{i}{2}[H_0^{\mathrm{TLS}} - H_B, V^{\mathrm{TLS}}]. \tag{A14}$$

In the present case this translates to

$$\hat{J} = -\tfrac{1}{2}[G\sigma_x + B(t)\sigma_y F], \tag{A15}$$

with the operators $F=\Sigma_k\lambda_k(b_k^\dagger+b_k)$, $G=i\Sigma_k\lambda_k\omega_k(b_k^\dagger-b_k)$. In steady state the expectation values of the two terms in Eq. (A15) are equal, thus we can calculate the expectation value of the current using

$$\langle J\rangle_\epsilon = -\langle \mathrm{Tr}\{\rho G\sigma_x\}\rangle_\epsilon = -\langle \mathrm{Tr}_B\{\rho_{1,0}G + \rho_{0,1}G\}\rangle_\epsilon. \tag{A16}$$

Here $\rho_{i,j}$ are the matrix elements of the total density matrix and Tr_B denotes a partial trace over the bath states only. Assuming weak system-bath interactions, using the decoupling approximation, further going the Markovian limit, we find that the noise-averaged thermal current is given by

$$\begin{aligned}\langle J\rangle_\epsilon &= i\langle P_0\rangle_\epsilon\int_{-\infty}^{\infty} e^{iB_0x}\left\langle e^{i\int_0^x \epsilon(t')dt'}\right\rangle_\epsilon \langle G(0)F(x)\rangle_B dx\\ &\quad - i\langle P_1\rangle_\epsilon\int_{-\infty}^{\infty} e^{iB_0x}\left\langle e^{i\int_0^x \epsilon(t')dt'}\right\rangle_\epsilon \langle F(x)G(0)\rangle_B dx.\end{aligned} \tag{A17}$$

The relations $\langle G(0)F(x)\rangle_B=-\langle F(0)G(x)\rangle_B$ and $\langle F(x)G(0)\rangle_B=-\langle G(x)F(0)\rangle_B$ were utilized here. Explicitly, the bath correlation functions are given by

$$\begin{aligned}\langle F(x)G(0)\rangle_B &= i\sum_k \lambda_k^2\omega_k[(N(\omega_k)+1)e^{-i\omega_k x} - N(\omega_k)e^{i\omega_k x}],\\ \langle F(0)G(x)\rangle_B &= i\sum_k \lambda_k^2\omega_k[(N(\omega_k)+1)e^{i\omega_k x} - N(\omega_k)e^{-i\omega_k x}].\end{aligned} \tag{A18}$$

We substitute these expressions into Eq. (A17) and obtain

$$\begin{aligned}\langle J\rangle_\epsilon &= \langle P_1\rangle_\epsilon\int_0^\infty d\omega\omega g(\omega)[N(\omega)+1]I(B_0-\omega)\\ &\quad - \langle P_1\rangle_\epsilon\int_0^\infty d\omega\omega g(\omega)N(\omega)I(B_0+\omega)\\ &\quad - \langle P_0\rangle_\epsilon\int_0^\infty d\omega\omega g(\omega)N(\omega)I(B_0-\omega)\\ &\quad + \langle P_0\rangle_\epsilon\int_0^\infty d\omega\omega g(\omega)[N(\omega)+1]I(B_0+\omega).\end{aligned} \tag{A19}$$

Extending $g(\omega)$ to negative values, $g(\omega)=-g(-\omega)$, leads to the compact result

$$\begin{aligned}\langle J\rangle_\epsilon &= \langle P_1\rangle_\epsilon\int_{-\infty}^{\infty} d\omega\omega g(\omega)[N(\omega)+1]I(B_0-\omega)\\ &\quad - \langle P_0\rangle_\epsilon\int_{-\infty}^{\infty} d\omega\omega g(\omega)N(\omega)I(B_0-\omega).\end{aligned} \tag{A20}$$

Note that the population should be calculated in steady-state, solving Eq. (A10) in the long time limit.

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