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Nature of heat in strongly coupled open quantum systems

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We show that any heat definition expressed as an energy change in the reservoir energy plus any fraction of the system-reservoir interaction is not an exact differential when evaluated along reversible isothermal transformations, except when that fraction is zero. Even in that latter case the reversible heat divided by temperature, namely entropy, does not satisfy the third law of thermodynamics and diverges in the low temperature limit. These results are found within the framework of nonequilibrium Green functions (NEGF) using a single level quantum dot strongly coupled to fermionic reservoirs and subjected to a time-dependent protocol modulating the dot energy as well as the dot-reservoir coupling strength.

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I. INTRODUCTION

The nature of heat is one of the most fundamental questions which has been driving research in thermodynamics since its origins. Nowadays, establishing a thermodynamically consistent notion of heat for open quantum system is of crucial importance for mesoscopic physics and for the study of energy conversion in small devices. This issue has direct implications on defining meaningful notions of efficiency in thermoelectricity or photoelectricity for instance.

For systems weakly interacting with their reservoirs the situation is rather clear [1–7]. The heat flux is defined as minus the energy change in the reservoir and can be directly related to the system energy changes since the system-reservoir coupling energy is negligible. This definition has been extensively used to study the performance of a broad range of nanodevices (see, e.g., [8–20]).

The situation is also clear in the strong coupling regime, as long as the system operates in a steady state [21–23] (see also, e.g., [24,25]). Indeed attributing the coupling energy to the system or to the reservoirs is equivalent in this case since net changes in the coupling energy are zero. The first law reduces to Kirchhoff's law for heat fluxes crossing the system and the second law reduces to the nonnegativity of $-\sum_\nu \dot{Q}_\nu / T_\nu \geqslant 0$, where $\dot{Q}_\nu$ is the heat entering the system from reservoir ν and T_ν is the temperature of that reservoir. This result can easily be shown using scattering theory or nonequilibrium Green functions (NEGF) approaches. Many performance studies have thus considered steady state setups (see, e.g., [26–32]).

However, the situation is very different when considering strong coupling setups where the system is driven by a time-dependent process since in this case changes in the coupling energy must be accounted for. Few studies have considered them because the dynamics typically becomes difficult to solve. These setups are important for instance to study any kind of stroke engine or the thermodynamic cost for turning on or off the interaction between a system and its reservoirs. They are also indispensable to consider reversible transformations which play a central role in thermodynamics. Indeed, thermodynamics predicts that the heat produced along a reversible transformation, when divided by the reservoir temperature, is the change of a state function called entropy.

In this paper we use the framework of NEGF to show that any attempt to define heat as the energy change in the reservoir energy plus any nonzero fraction of the system-reservoir interaction is not an exact differential when evaluated along reversible isothermal transformations. We also find that the state function entropy obtained for zero fraction does not satisfy the third law of thermodynamics and diverges in the low temperature limit.

The plan of the paper is as follows. Heat notions including different fractions $0 \leqslant \alpha \leqslant 1$ of the system-reservoir interaction energy are defined in Sec. II. The model system used for their explicit evaluation is presented in Sec. III. Their reversible expressions and their thermodynamic consistency is discussed in Sec. IV. Their first irreversible correction is given in Sec. V. The special case of no driving in the coupling and wide band approximation is discussed in Sec. VI. Conclusions are drawn in Sec. VII.

To highlight the physical content of our paper, the technical parts have been relegated to Appendixes. Expressions for the energy and matter current in terms of NEGF are given in Appendix A. The gradient expansion technique needed to consider slow transformations is described in Appendix B. It is used for our model system in Appendix C to calculate the reversible heat (C 1), its first correction (C 2), and to show that in absence of driving in the coupling and in the wide band limit our NEGF treatment becomes equivalent to that of Ref. [33] (C 3).

II. HEAT DEFINITIONS

The typical Hamiltonian of an open quantum system S coupled to multiple reservoirs ν at temperatures T_ν and chemical potentials μ_ν is

$$\hat{H}(t) = \hat{H}_S(t) + \sum_\nu [\hat{H}_\nu + \hat{V}_\nu(t)], \qquad (1)$$

where $\hat{H}_S$ ($\hat{H}_\nu$) denotes the system (reservoir ν) Hamiltonian and $\hat{V}_\nu$ is the system-reservoir interaction.

We start by introducing the class of all possible heat definitions expressed as the change in the quantum expectation value of the reservoir Hamiltonian plus a fraction $0 \leqslant \alpha \leqslant 1$ of the system-reservoir coupling energy (we set $\hbar = e = k_B = 1$ throughout the paper)

$$\dot{Q}_{\nu,\alpha} = J_{\nu,\alpha} - \mu_\nu I_\nu, \tag{2}$$

where the matter and heat currents entering the system from reservoir ν are given by

$$I_\nu = -\,\mathrm{Tr}\{\hat{N}_\nu\, d_t\hat{\rho}\} = -d_t\langle\hat{N}_\nu\rangle, \tag{3}$$

$$J_{\nu,\alpha} = -\,\mathrm{Tr}\{\big(\hat{H}_\nu + \alpha\hat{V}_\nu\big)d_t\hat{\rho}\}, \tag{4}$$

and $\hat{\rho}(t)$ is the density matrix of the total system. The heat flux definition most commonly used in the literature corresponds to the choice $\alpha = 0$ and can be expressed in terms of the rate of change in the number operator $\hat{N}_\nu$ and in the Hamiltonian $\hat{H}_\nu$ of the reservoir ν, since $J_{\nu,0} = -d_t\langle\hat{H}_\nu\rangle$ [25,34–39]. The choice $\alpha = 1$ was considered for instance in Ref. [40] and the choice $\alpha = 1/2$ in Ref. [33].

III. THE MODEL

The specific model that we consider consists of an externally driven level $\varepsilon(t)$ bilinearly coupled to a single fermionic reservoir R at equilibrium. Its Hamiltonian is given by (1), where the level, the reservoir, and their coupling, respectively, read

$$\hat{H}_S(t) = \varepsilon(t)\hat{d}^\dagger\hat{d}, \quad \hat{H}_R = \sum_k \varepsilon_k \hat{c}_k^\dagger\hat{c}_k, \tag{5}$$

$$\hat{V}(t) = \sum_k [V_k(t)\hat{d}^\dagger\hat{c}_k + \mathrm{H.c.}]. \tag{6}$$

Here $\hat{d}^\dagger$ ($\hat{d}$) and $\hat{c}_k^\dagger$ ($\hat{c}_k$) create (annihilate) an electron in the level of the system and in state k of the reservoir, respectively. ε_k is the energy of the latter. We emphasize that the external driving can modify the position of the level $\varepsilon(t)$ as well as the strength of the system-reservoir coupling $V_k(t)$. Following Ref. [41], we assume that this latter is of the form

$$V_k(t) = u(t)\,V_k, \quad u(t) \in \mathbb{R}. \tag{7}$$

For the simulations presented in this paper, we will consider the driving protocols

$$\varepsilon(t) = \varepsilon_0 + \frac{\Delta_\varepsilon}{2}(1 - \cos\omega_0 t), \tag{8}$$

$$u^2(t) = 1 + \frac{\Delta_\Gamma}{2\Gamma_0}(1 - \cos\omega_0 t). \tag{9}$$

IV. REVERSIBLE HEAT

We now use the framework of NEGF to evaluate the heat flux (2) along a reversible (very slow driving protocols) isothermal transformation for our model. Details are provided in Appendix A. The explicit expression of the heat flux in terms of NEGF is given by (2) with the particle and energy currents (A1) and (A2). In general a NEGF depends on two times t_1 and t_2, but only depends on their difference $\tau = t_1 - t_2$ at steady state. If the driving acting on the system is slow compared to the system relaxation time scale, after a Fourier transform in $\tau \to E$, one can make use of the slow time dependence of the resulting NEGF in $t = (t_1 + t_2)/2$ to evaluate its equation of motion. This procedure is known as the gradient expansion and is detailed in Appendix B. When using it to evaluate the heat flux for our model (5)–(7) as shown in Appendix C, we obtain to the lowest order which corresponds to the reversible limit

$$\dot{Q}_\alpha^{(1)} = \frac{d}{dt}\left\{\int \frac{dE}{2\pi} f\,A^{(0)}[(E-\mu) + (1-2\alpha)(E-\varepsilon)]\right\} - \int \frac{dE}{2\pi} f\{A^{(0)}\,d_t\varepsilon + (1-\alpha)[\mathrm{Re}\,G^{r(0)}\,\partial_t\Gamma + A^{(0)}\,\partial_t\Lambda]\}, \tag{10}$$

where $f(E) = [e^{(E-\mu)/T} + 1]^{-1}$ is the Fermi-Dirac distribution in the reservoir, the zero order retarded Green function is given by

$$G^{r(0)}(t,E) = [E - \varepsilon(t) - \Lambda(t,E) + i\Gamma(t,E)/2]^{-1} \tag{11}$$

and $A^{(0)}(t,E) = -2\,\mathrm{Im}\,G^{r(0)}(t,E)$ is the system spectral function. The Lamb shift and broadening caused by the coupling to the reservoir are taken as [34,42]

$$\Lambda(t,E) = u^2(t)\,\Gamma_0\,\frac{1}{2}\frac{(E-E_B)W_B}{(E-E_B)^2 + W_B^2}, \tag{12}$$

$$\Gamma(t,E) = u^2(t)\,\Gamma_0\,\frac{W_B^2}{(E-E_B)^2 + W_B^2}, \tag{13}$$

where E_B and W_B are the center and width of the band, respectively. To our knowledge (10) is the first explicit expression for a reversible heat of the kind (2). We also emphasize that this result is exact since the gradient expansion is exact for reversible transformations. Two major results ensue.

A. State function

A central requirement in thermodynamics is that the reversible heat change is an exact differential. This implies that mixed derivatives of the heat rate with respect to the driving parameters $\varepsilon(t)$ and $u(t)$ should be equal to each other:

$$\frac{\partial^2 Q_\alpha^{(1)}}{\partial\varepsilon\,\partial u} = \frac{\partial^2 Q_\alpha^{(1)}}{\partial u\,\partial\varepsilon}. \tag{14}$$

Our first important result is that this property is only satisfied for $\alpha = 0$. For any other choice of α, the reversible heat is not an exact differential and thus cannot be considered as a thermodynamically consistent definition. This result can be explicitly seen in Fig. 1 where two different reversible driving protocols connecting the same initial and final point give rise to different reversible heat except for $\alpha = 0$.

B. Third law

Our second important result is that since the equilibrium entropy is the state function whose differential is the reversible

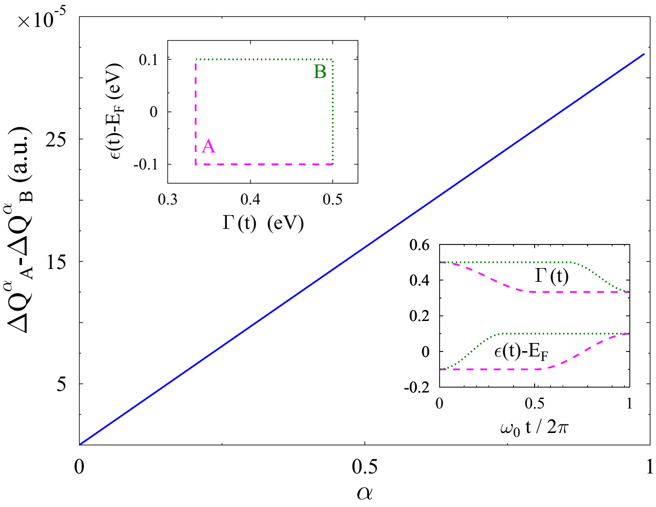

FIG. 1. (Color online) Difference between the reversible heat produced along two different driving protocols denoted by A and B and corresponding to (8) and (9) with parameters $T = 10$ K, $\varepsilon_0 = -0.1$ eV, $\Delta_\varepsilon = 0.2$ eV, $\Delta_\Gamma = -1/6$ eV, $\Gamma_0 = 0.5$ eV, $\omega_0 = 10^{13}$ s^{-1}. The band parameters are $E_B = 0$ and $W_B = 5$ eV and the Fermi energy is $E_F = 0$. The two protocols are shown in the left top inset and the time dependence of the level position and coupling strength corresponding to the protocols are given in the bottom right inset.

heat divided by temperature

$$d_t S^{\rm eq} = \dot{Q}_0^{(1)}/T, \tag{15}$$

by integrating the reversible heat rate (10) we are able to find the equilibrium entropy up to a constant (see Appendix C 1 for details)

$$\begin{aligned} S^{\rm eq} = & \int \frac{dE}{2\pi} A^{(0)} \big(-f \ln f - [1-f] \ln[1-f] \big) \\ & + \int \frac{dE}{2\pi} A^{(0)} f \frac{(E-\varepsilon)}{T} \\ & + \int \frac{dE}{2\pi} A^{(0)} \ln[1-f] \bigg(\partial_E \Lambda + \frac{E-\varepsilon-\Lambda}{\Gamma} \partial_E \Gamma \bigg). \end{aligned} \tag{16}$$

The first contribution has the appealing form of an energy resolved equilibrium entropy. The second one is exactly half of the equilibrium expectation value of the coupling energy divided by temperature, namely $\langle \hat{V}_\nu(t) \rangle^{\rm eq}/(2T)$. The third one is due to the energy resolution of the Lamb shift and broadening and thus vanishes in the wide-band limit when $\Lambda \to 0$ and Γ does not depend on energy. In the low temperature limit $T \to 0$, the first terms goes to zero as expected by the third law of thermodynamics, but the other two terms diverge, casting doubts on the thermodynamic relevance of the heat definition $\dot{Q}_0$. The weak coupling limit resolves the divergence problem and thus satisfies the third law because the coupling strength is taken to zero before taking the low temperature limit. Indeed, in this case the first term becomes the weak coupling Shannon entropy and the last two vanish. While one may have expected that the finite coupling can create a finite entropy in the system at low temperature, justifying a divergent entropy is more difficult and seems pathological. Figure 2 shows the temperature dependence of the reversible heat $Q_0^{(1)}$ given by (10). At low temperature the reversible heat tends to a constant, thus leading to a $1/T$ divergence of the equilibrium entropy $S^{\rm eq}$ with temperature.

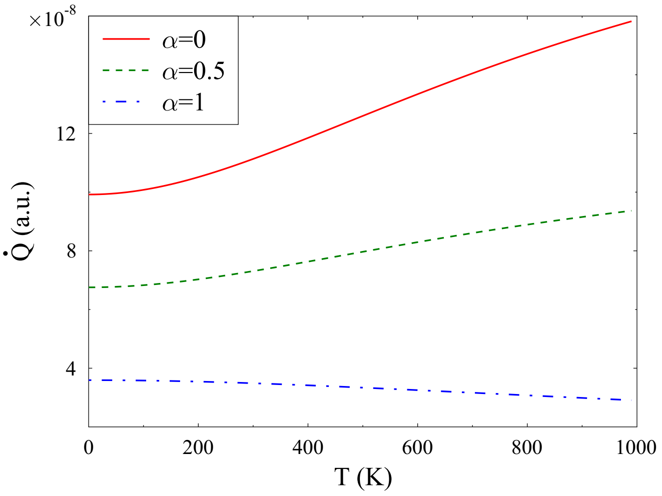

FIG. 2. (Color online) Reversible heat, Eq. (10), as function of temperature for simultaneous driving (8) and (9) at $t = 0.4\,\pi/\omega_0$. The parameters are the same as in Fig. 1.

V. BEYOND REVERSIBLE HEAT

The general expression for the heat obtained using gradient expansion to first order beyond the reversible contribution $Q_\alpha^{(1)} + Q_\alpha^{(2)}$ is derived in Appendix C 2. If one considers the heat $\alpha = 0$ generated along the cycle of a periodic driving of duration τ when the system reaches a stationary regime (i.e., when initial transients are gone), the reversible heat is a state function and vanishes along the cycle $Q_0^{(1)} = 0$, and the remaining heat contribution is given by

$$\begin{aligned} Q_0^{(2)} = & \int_0^\tau dt \int \frac{dE}{2\pi} \partial_E f \frac{[A^{(0)}]^2}{2} \\ & \times \left(d_t\varepsilon + \partial_t \Lambda + \partial_t \Gamma \frac{E-\varepsilon-\Lambda}{\Gamma} \right)^2. \end{aligned} \tag{17}$$

Since $\partial_E f$ is always negative, this heat is always negative as expected from the second law of thermodynamics.

VI. WIDE BAND AND CONSTANT COUPLING

We demonstrated that the heat $\alpha = 1/2$ is in general inconsistent with equilibrium thermodynamics. In this section we consider the special case where the couplings to the reservoirs are time independent (u constant) and where the wide band approximation is used. We show that in this case the reversible heat $\alpha = 1/2$ may misleadingly appear thermodynamically consistent.

Under these assumptions, the heat definition $Q_{1/2}$ was proposed in Ref. [33] when considering a strongly coupled *ac*-driven resonant level coupled to a single reservoir treated by scattering and Floquet theories. We made sure in Appendix C 3 that in this case our treatment reproduces the expression for the heat $Q_{1/2}$ (the reversible contribution $Q^{(1)}_{1/2}$ as well as its first correction $Q^{(2)}_{1/2}$) found in Ref. [33].

Turning to the thermodynamic analysis of these results, we find that by integrating the reversible heat

$$\dot{Q}^{(1)}_{1/2} = T\, d_t S^{\mathrm{eq}}_{1/2}, \tag{18}$$

the resulting equilibrium entropy is given by

$$S^{\mathrm{eq}}_{1/2} = \int \frac{dE}{2\pi} A^{(0)}(-f \ln f - [1-f]\ln[1-f]). \tag{19}$$

This is the first contribution to the entropy found in (16) which we have seen satisfies the third law of thermodynamics. Also, due to the absence of driving in the coupling, the equilibrium entropy is necessarily a state function. While appealing the results crucially depend on the two assumptions made (time-independent coupling and wide band approximation).

VII. CONCLUSION

We contributed to the fundamental question of the nature of heat in an open quantum system strongly interacting with a reservoir and driven by a time-dependent force in the system and in the system-reservoir energy, within the framework of NEGF.

Our central finding is that any heat definition expressed as the change in the quantum expectation value of the reservoir energy plus any fraction α of the coupling energy displays thermodynamic inconsistencies. Any α different from zero leads to a reversible heat which is not a state function. The choice $\alpha = 0$ is more appealing since the reversible heat is a state function and the second law is satisfied for our model, but it leads to an entropy which diverges in the low temperature limit in contradiction with the third law of thermodynamics. Our considerations were made possible by using the gradient expansion of NEGF which provides, to our knowledge, the first explicit reversible expression for the various heat definitions that we considered. The only assumption made in our approach is intrinsic to NEGF techniques and somehow necessary to guarantee a proper thermalization of the system (zeroth law). It consist of treating the reservoirs as ideal equilibrated objects by assuming that the reservoir Green functions are always thermal.

Our conclusion reinforces our proposal in Ref. [43] to abandon heat definitions (and other thermodynamic quantities) expressed as quantum expectation values of operators in order to derive a consistent thermodynamics within the framework of NEGF for open quantum system beyond the weak coupling limit.

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APPENDIX A: PARTICLE AND ENERGY FLUXES

We consider the standard definition for the particle and energy fluxes at the interface with reservoir ν, Eqs. (3) and (4), respectively. In terms of Green functions, these definitions yield [35,41]

$$\begin{aligned} I_\nu(t) = 2\,\mathrm{Re}\,\mathrm{Tr}\int dt_1\{&G^<(t,t_1)\,\Sigma^a_\nu(t_1,t)\\ &+ G^r(t,t_1)\,\Sigma^<_\nu(t_1,t)\}, \end{aligned} \tag{A1}$$

$$\begin{aligned} J_{\nu,\alpha}(t) = {}&(\alpha-1)\,\partial_t\langle\hat{V}_\nu(t)\rangle - \alpha\, d_t\langle\hat{V}_\nu(t)\rangle\\ &+ 2\,\mathrm{Im}\,\mathrm{Tr}\int dt_1\{G^<(t,t_1)\,\partial_t\Sigma^a_\nu(t_1,t)\\ &+ G^r(t,t_1)\,\partial_t\Sigma^<_\nu(t_1,t)\}, \end{aligned} \tag{A2}$$

where

$$\begin{aligned} \langle\hat{V}_\nu(t)\rangle = 2\,\mathrm{Im}\,\mathrm{Tr}\int dt_1\{&G^<(t,t_1)\,\Sigma^a_\nu(t_1,t)\\ &+ G^r(t,t_1)\,\Sigma^<_\nu(t_1,t)\}. \end{aligned} \tag{A3}$$

The partial derivatives in the first and third terms on the right side of Eq. (A2) indicate a time derivative of the system-reservoir coupling only in the external driving. $\mathrm{Tr}\{\cdots\}$ denotes a trace over the system subspace. $G^< = G^{-+}$ and $G^r = G^{--} - G^{-+}$ are matrices in the system subspace and are the lesser and retarded projections of the single-particle Green function

$$G_{mm'}(\tau,\tau') = -i\langle T_c\, \hat{d}_m(\tau)\, \hat{d}^\dagger_{m'}(\tau')\rangle, \tag{A4}$$

where T_c denotes the contour ordering operator, τ and τ' are the contour variables, and the contour branches are labeled as time ordered $s=-$, and antitime ordered $s=+$. $\Sigma^<_\nu = \Sigma^{-+}_\nu$ and $\Sigma^a_\nu = \Sigma^{-+}_\nu - \Sigma^{++}_\nu$ are also matrices in the system space and are the lesser and advanced projections of the self-energy due to the coupling to reservoir ν,

$$[\Sigma_\nu(\tau,\tau')]_{mm'} = \sum_{k\in\nu} V_{mk}(t)\, g_k(\tau,\tau')\, V_{km'}(t'), \tag{A5}$$

where

$$g_k(\tau,\tau') \equiv -i\langle T_c\, \hat{c}_k(\tau)\, \hat{c}^\dagger_k(\tau')\rangle \tag{A6}$$

is the equilibrium Green function for the free electrons in the reservoir ν. The equations of motion for the projection s_1s_2 of the GF (A4) are given by

$$\begin{aligned} &\left(i\frac{\overrightarrow{\partial}}{\partial t_1} - H_S(t_1)\right) G^{s_1s_2}(t_1,t_2)\\ &\quad = \sigma^z_{s_1s_2}\delta(t_1-t_2) + \sum_{s_3}\int dt_3\, \Sigma^{s_1s_3}(t_1,t_3)\, s_3\, G^{s_3s_2}(t_3,t_2), \end{aligned} \tag{A7}$$

$$G^{s_1s_2}(t_1,t_2)\left(-i\frac{\overleftarrow{\partial}}{\partial t_2}-H_S(t_2)\right)$$
$$=\sigma^z_{s_1s_2}\delta(t_1-t_2)+\sum_{s_3}\int dt_3\, G^{s_1s_3}(t_1,t_3)\, s_3\, \Sigma^{s_3s_2}(t_3,t_2), \tag{A8}$$

where σ^z is the Pauli matrix, and $\Sigma^{s_1s_2}(t_1,t_2)$ is the total self-energy, i.e., the self-energy due to the system-reservoirs couplings and the intrasystem interactions.

APPENDIX B: GRADIENT EXPANSION

Green functions and self-energies are two-time functions $F(t_1,t_2)$. Introducing via a change of variable the classical time scale $t=(t_1+t_2)/2$, and the quantum time scale $s=t_1-t_2$, and performing a Fourier transform in the quantum time leads to the time-dependent energy resolved function $F(t,E)=\int ds e^{iEs}F(t,s)$, which is the Wigner transform of $F(t,s)$. Naturally

$$F(t_1,t_2)=F(t,s)=\int\frac{dE}{2\pi}\,e^{-iEs}F(t,E). \tag{B1}$$

Below we will consider partial derivatives of the form $\partial_{t_2}F(t_1,t_2)$ [see Eq. (A2)]. Their Wigner transforms read $[\partial_t/2+iE]F(t,E)$. We will also consider integral expression such as

$$F(t_1,t_2)=\int dt_3\, F_1(t_1,t_3)\,F_2(t_3,t_2), \tag{B2}$$

whose Wigner transform reads [44]

$$F(t,E)=F_1(t,E)\,\hat{\mathcal{G}}(t,E)\,F_2(t,E), \tag{B3}$$

where

$$\hat{\mathcal{G}}(t,E)=\exp\left(\frac{1}{2i}[\overleftarrow{\partial}_t\,\overrightarrow{\partial}_E-\overleftarrow{\partial}_E\,\overrightarrow{\partial}_t]\right) \tag{B4}$$

is the gradient operator. At steady state the dependence on t vanishes and only the energy resolution E survives. This means that when the driving is slow relative to the characteristic relaxation time scales of the system, we can expand (B4) in Taylor series and truncate the series to the suited level. Traditionally the gradient expansion goes to the first order, but we will need the second order below:

$$F(t,E)\approx F_1(t,E)\,F_2(t,E)$$
$$+\frac{i}{2}\{F_1(t,E);F_2(t,E)\}-\frac{1}{8}[F_1(t,E);F_2(t,E)], \tag{B5}$$

where

$$\{F_1(t,E);F_2(t,E)\}$$
$$=\partial_E F_1(t,E)\,\partial_t F_2(t,E)-\partial_t F_1(t,E)\,\partial_E F_2(t,E), \tag{B6}$$

$$[F_1(t,E);F_2(t,E)]$$
$$=\partial_E^2 F_1(t,E)\,\partial_t^2 F_2(t,E)$$
$$+\partial_t^2 F_1(t,E)\,\partial_E^2 F_2(t,E)-\partial_{tE}^2 F_1(t,E)\,\partial_{tE}^2 F_2(t,E). \tag{B7}$$

Below we will also need to consider the dependence of the full self-energy $\Sigma(t_1,t_2)$ on the system-reservoir coupling $u(t)$. Since

$$\Sigma(t_1,t_2)=u(t_1)\,S(t_1,t_2)\,u(t_2), \tag{B8}$$

it is easy to show that up to second order gradient expansion, the functions Σ and S are related by

$$\Sigma(t,E)\approx u^2(t)\,S(t,E)-\tfrac{1}{4}\big(\partial_t^2u(t)-[\partial_t u(t)]^2\big)\partial_E^2 S(t,E). \tag{B9}$$

Similarly their time derivatives are related by

$$\partial_t\Sigma(t,E)\approx u^2(t)\,\partial_t S(t,E)+u(t)\,\partial_t u(t)\,S(t,E). \tag{B10}$$

APPENDIX C: SLOW DRIVING OF A SINGLE LEVEL COUPLED TO A RESERVOIR

We now restrict our consideration to a single level, Eqs. (5)–(7). The position of the level $\varepsilon(t)$ as well as its coupling to the reservoir $u(t)$ are driven by a slowly changing external field, Eqs. (8) and (9).

After gradient expansion,

$$G^r(t_1,t_2)\to G^r(t,E), \tag{C1}$$

$$G^<(t_1,t_2)\to G^<(t,E)=i\,A(t,E)\,\phi(t,E), \tag{C2}$$

where the system spectral function is given by

$$A(t,E)\equiv -2\,\mathrm{Im}\,G^r(t,E) \tag{C3}$$

and $\phi(t,E)$ is the nonequilibrium population of the level. Also

$$\Sigma^r(t_1,t_2)\to\Sigma^r(t,E)=\Lambda(t,E)-i\Gamma(t,E)/2, \tag{C4}$$

$$\Sigma^<(t_1,t_2)\to\Sigma^<(t,E)=i\,\Gamma(t,E)\,f(E), \tag{C5}$$

where Λ and Γ are the Lamb shift and the broadening caused by the coupling to the reservoir and $f(E)$ is the Fermi-Dirac thermal distribution.

We now apply the second order gradient expansion (B5) to expressions for the fluxes, Eqs. (A1) and (A2). This leads to

$$I(t)=\int\frac{dE}{2\pi}\,I(t,E)=\frac{d}{dt}\int\frac{dE}{2\pi}A(t,E)\,\phi(t,E), \tag{C6}$$

$$J_\alpha(t)=(\alpha-1)\,\partial_t\langle\hat{V}(t)\rangle+\left(\frac{1}{2}-\alpha\right)d_t\langle\hat{V}(t)\rangle$$
$$+\int\frac{dE}{2\pi}\,E\,I(t,E), \tag{C7}$$

where

$$I(t,E) = \{E - \varepsilon(t); A\phi\}, \tag{C8}$$

$$\langle\hat{V}(t)\rangle = 2\int\frac{dE}{2\pi}(A\phi\,\Lambda + \mathrm{Re}\,G^r\,\Gamma f) + \frac{1}{2}\int\frac{dE}{2\pi}(\{\Gamma; A\phi\} - \{\Gamma\phi; A\}), \tag{C9}$$

$$\partial_t\langle\hat{V}(t)\rangle = \int\frac{dE}{2\pi}(A\phi\,\partial_t\Lambda + \mathrm{Re}\,G^r\,\partial_t\Gamma\,\phi) + \frac{1}{4}\int\frac{dE}{2\pi}(\{\partial_t\Gamma; A\phi\} - \{\partial_t\Gamma\,\phi; A\}). \tag{C10}$$

Note that evaluation of expressions (C6) and (C7) up to second order in gradient expansion requires the knowledge of the G^r, A, and ϕ only up to first order [see Eqs. (C14)–(C18) below]. Note also that in the spirit of the Botermans and Malfliet (BM) approximation [45], we substituted $f(E)$ by $\phi(t,E)$ in all the expressions involving derivatives of the lesser projection of the self-energy.

The retarded projection of the Green function $G^r(t,E)$, the spectral function $A(t,E)$, and the nonequilibrium distribution $\phi(t,E)$ can be expanded as

$$G^r(t,E) = G^{r(0)}(t,E) + G^{r(1)}(t,E) + G^{r(2)}(t,E) + \cdots, \tag{C11}$$

$$A(t,E) = A^{(0)}(t,E) + A^{(1)}(t,E) + A^{(2)}(t,E) + \cdots, \tag{C12}$$

$$\phi(t,E) = \phi^{(0)}(t,E) + \phi^{(1)}(t,E) + \phi^{(2)}(t,E) + \cdots, \tag{C13}$$

where the orders coincide with the orders of the gradient expansion. Inserting this expansion in the gradient expansion expression for the Green function equations-of-motion (A7) and (A8), and identifying terms order by order, one finds that [46,47]

$$G^{r(0)}(t,E) = [E - \varepsilon(t) - \Sigma^r(t,E)]^{-1}, \tag{C14}$$

$$A^{(0)}(t,E) = \frac{\Gamma(t,E)}{[E - \varepsilon(t) - \Lambda(t,E)]^2 + [\Gamma(t,E)/2]^2}, \tag{C15}$$

$$\phi^{(0)}(t,E) = f(E), \tag{C16}$$

and

$$G^{r(1)}(t,E) = A^{(1)}(t,E) = 0, \tag{C17}$$

$$\phi^{(1)} = -d_E f\,\frac{A^{(0)}}{2}\left(d_t\varepsilon + \partial_t\Lambda + \partial_t\Gamma\,\frac{E - \varepsilon - \Lambda}{\Gamma}\right). \tag{C18}$$

1. Reversible driving

The reversible transformation in the system is performed by a reversible driving, which corresponds to expanding the fluxes to first order in Eqs. (C6) and (C7). To do so we only need the zero order correction of the retarded Green function $G^{r\,(0)}(t,E)$, its corresponding $A^{(0)}(t,E)$, and of the population $\phi^{(0)}(t,E)$. We find

$$I^{(1)}(t) = \int\frac{dE}{2\pi}\partial_t A^{(0)}\,f, \tag{C19}$$

$$J_\alpha^{(1)}(t) = (\alpha - 1)[\partial_t\langle\hat{V}(t)\rangle]^{(1)} + \left(\frac{1}{2} - \alpha\right)d_t\langle\hat{V}(t)\rangle^{(0)} + \int\frac{dE}{2\pi}E[\partial_t A^{(0)}\,f + d_t\varepsilon\,\partial_E(A\,f)], \tag{C20}$$

where

$$\langle\hat{V}(t)\rangle^{(0)} = 2\int\frac{dE}{2\pi}(A^{(0)}f\,\Lambda + \mathrm{Re}\,G^{r(0)}\,\Gamma f), \tag{C21}$$

$$[\partial_t\langle\hat{V}(t)\rangle]^{(1)} = \int\frac{dE}{2\pi}(A^{(0)}f\,\partial_t\Lambda + \mathrm{Re}\,G^{r(0)}\,\partial_t\Gamma). \tag{C22}$$

Using (C19)–(C22) in the definition (2) yields Eq. (10).

Since both the Lamb shift $\Lambda(t,E)$ and broadening $\Gamma(t,E)$ are proportional to $u^2(t)$ [see Eqs. (12) and (13)], and taking into account (10), the condition (14) means that the derivative of $\int dE\,f\,A^{(0)}\,d_t\varepsilon$ with respect to the driving parameter for the system-reservoir coupling $u(t)$ should be equal to the derivative of $(1-\alpha)\int dEf[\mathrm{Re}G^{r(0)}\,\partial_t\Gamma + A^{(0)}\,\partial_t\Lambda]$ with respect to the driving parameter for the level position $\varepsilon(t)$. It is easy to see that this condition is satisfied only for $\alpha = 0$.

Since the exact differential of the reversible heat defines entropy

$$T\,d_t S(t) = \dot{Q}_0^{(1)}(t), \tag{C23}$$

we find that the entropy is given (up to a constant) by

$$S = \int\frac{dE}{2\pi}f\left(A\left[\frac{E-\mu}{T} + \frac{E-\varepsilon}{T}\right] + \frac{2}{T}\arctan\frac{E - \varepsilon - \Lambda}{\Gamma/2}\right). \tag{C24}$$

Utilizing

$$\frac{E-\mu}{T} = \ln\frac{1 - f(E)}{f(E)}, \tag{C25}$$

$$\frac{f(E)}{T} = \frac{d}{dE}\ln[1 - f(E)], \tag{C26}$$

and performing an integration by parts for the last term in (C24), we get Eq. (16). We stress that the reversible driving results do not rely on the BM approximation.

2. Beyond reversible driving

To calculate the fluxes (C6) and (C7) to second order, we therefore need corrections up to first order of the retarded Green function $G^{r\,(0,1)}(t,E)$, its corresponding $A^{(0,1)}(t,E)$, and of the nonequilibrium population $\phi^{(0,1)}(t,E)$. This leads to

$$I^{(2)}(t) = \int\frac{dE}{2\pi}[\partial_t(A^{(0)}\,\phi^{(1)}) + d_t\varepsilon\,\partial_E(A^{(0)}\,\phi^{(1)})], \tag{C27}$$

$$J_\alpha^{(2)}(t) = (\alpha - 1)[\partial_t\langle\hat{V}(t)\rangle]^{(2)} + \left(\frac{1}{2} - \alpha\right)d_t\langle\hat{V}(t)\rangle^{(1)} + \int\frac{dE}{2\pi}E[\partial_t(A^{(0)}\,\phi^{(1)}) + d_t\varepsilon\,\partial_E(A^{(0)}\,\phi^{(1)})], \tag{C28}$$

where

$$\langle \hat{V}(t)\rangle^{(1)} = 2\int \frac{dE}{2\pi}\, A^{(0)}\phi^{(1)}\,\Lambda + \frac{1}{2}\int \frac{dE}{2\pi}(\{\Gamma; A^{(0)} f\} - \{\Gamma f; A^{(0)}\}), \tag{C29}$$

$$[\partial_t\langle \hat{V}(t)\rangle]^{(2)} = \int \frac{dE}{2\pi}(A^{(0)}\phi^{(1)}\,\partial_t\Lambda + \mathrm{Re}\, G^{r(0)}\,\partial_t\Gamma\,\phi^{(1)}) + \frac{1}{4}\int \frac{dE}{2\pi}(\{\partial_t\Gamma; A^{(0)} f\} - \{\partial_t\Gamma\, f; A\}). \tag{C30}$$

Using (C27)–(C30) in the definition (2) yields

$$\dot{Q}^{(2)}_{\alpha} = \left(\frac{1}{2} - \alpha\right) d_t\langle \hat{V}(t)\rangle^{(1)} + \frac{d}{dt}\left\{\int \frac{dE}{2\pi} A^{(0)}\left[(E-\mu)\phi^{(1)} + \frac{1-\alpha}{4}\partial_t\Gamma\partial_E f\right]\right\} + \int \frac{dE}{2\pi}\partial_E f\,\frac{[A^{(0)}]^2}{2}\left(d_t\varepsilon + \partial_t\Lambda + \partial_t\Gamma\frac{E-\varepsilon-\Lambda}{\Gamma}\right) \times \left[d_t\varepsilon + (1-\alpha)\left(\partial_t\Lambda + \partial_t\Gamma\frac{E-\varepsilon-\Lambda}{\Gamma}\right)\right]. \tag{C31}$$

When considering periodic transformations where the system has reached a stationary regime, the second law of thermodynamics states that

$$Q_0 = Q_0^{(2)} \leqslant 0, \tag{C32}$$

where we used the fact that $\Delta S^{\mathrm{eq}} = Q_0^{(1)}/T = 0$. We verify that this relation is satisfied since along such cyclic transformation only the last two lines of Eq. (C31) survive and one finds that for $\alpha = 0$ they become

$$\int \frac{dE}{2\pi}\partial_E f\,\frac{[A^{(0)}]^2}{2}\left(d_t\varepsilon + \partial_t\Lambda + \partial_t\Gamma\frac{E-\varepsilon-\Lambda}{\Gamma}\right)^2, \tag{C33}$$

which is indeed always negative or zero.

3. Wide band and no driving in the coupling

We now consider the wide band approximation (WBA) [i.e., $\Lambda = 0$ and $\Gamma(E) = \Gamma = \text{const.}$] and driving only in the level position and not in the coupling [$u(t) = 1$] to show that our expressions (10), (C19)–(C22) and (C27)–(C31) reduce in this case to the results derived in Ref. [33] using scattering and Floquet theories.

Under these assumptions we can make use of the identity

$$\partial_t A^{(0)}(t,E) = -d_t\varepsilon(t)\,\partial_E A^{(0)}(t,E). \tag{C34}$$

We start by considering the particle current. Utilizing (C34) in (C19) and integrating by parts in energy leads to

$$I^{(1)}(t) = d_t\varepsilon\int \frac{dE}{2\pi}\, d_E f\, A^{(0)}. \tag{C35}$$

Similarly, utilizing (C34) in (C27) and integrating by parts in energy leads to

$$I^{(2)}(t) = \partial_t\int \frac{dE}{2\pi} A^{(0)}\,\phi^{(1)} \equiv -\frac{1}{2}\partial_t\int \frac{dE}{2\pi} d_E f\,[A^{(0)}]^2\, d_t\varepsilon, \tag{C36}$$

where the second equality is obtained by using the WBA version of (C18). Expressions (C35) and (C36) are the results presented in Eq. (S.33) of the supporting information of Ref. [33]. Note that difference in sign is due to our flux definition (positive when going from the reservoir to the system) which is opposite to the choice in Ref. [33].

We now turn to evaluating the coupling term. Using (C21) within the WBA one gets

$$[d_t\langle \hat{V}(t)\rangle]^{(1)} \equiv d_t\langle \hat{V}(t)\rangle^{(0)} = 2\int \frac{dE}{2\pi}\,\Gamma\, f\,\partial_t \mathrm{Re}\, G^{r(0)}. \tag{C37}$$

Utilizing

$$d_t \mathrm{Re}\, G^{r(0)} = -d_t\varepsilon\,\partial_E \mathrm{Re}\, G^{r(0)} \tag{C38}$$

and integrating in energy by parts leads to

$$[d_t\langle \hat{V}(t)\rangle]^{(1)} = 2\int \frac{dE}{2\pi}\, d_E f\,\Gamma\,\mathrm{Re}\, G^{r(0)}\, d_t\varepsilon \equiv 2\int \frac{dE}{2\pi}\, d_E f\, A^{(0)}\,(E-\varepsilon)\, d_t\varepsilon. \tag{C39}$$

Similarly in the WBA (C29) becomes

$$[d_t\langle \hat{V}(t)\rangle]^{(2)} \equiv d_t\langle \hat{V}(t)\rangle^{(1)} = -\frac{1}{2}d_t\int \frac{dE}{2\pi}\,\Gamma\, d_E f\,\partial_t A^{(0)}. \tag{C40}$$

Since using (C34),

$$\partial_t A^{(0)} = \frac{2\,(E-\varepsilon)\, d_t\varepsilon}{\Gamma}[A^{(0)}]^2, \tag{C41}$$

we get that

$$[d_t\langle \hat{V}(t)\rangle]^{(2)} = -d_t\int \frac{dE}{2\pi}\, d_E f\,[A^{(0)}]^2\,(E-\varepsilon)\, d_t\varepsilon. \tag{C42}$$

Expressions (C39) and (C42) are the results presented in Eq. (S.36) of the supporting information of Ref. [33].

We finally turn to the energy current. Taking the choice $\alpha = 1/2$ and disregarding the driving in the system-reservoir coupling (the first term) in Eq. (C20), after using (C34), we get

$$J^{(1)}_{1/2}(t) = \int \frac{dE}{2\pi}\, d_E f\, E\, A^{(0)}\, d_t\varepsilon. \tag{C43}$$

Similarly Eq. (C28) after employing (C34) yields

$$J^{(2)}_{1/2}(t) = \int \frac{dE}{2\pi}\, E\, A^{(0)}(\partial_t\phi^{(1)} + d_t\varepsilon\,\partial_E\phi^{(1)}). \tag{C44}$$

Substituting the WBA version of Eq. (C18) and performing the derivatives leads to

$$J^{(2)}_{1/2}(t) = -\frac{1}{2}\int \frac{dE}{2\pi}\, d_E f \times \{E\, d_t([A^{(0)}]^2\, d_t\varepsilon) - (A^{(0)}\, d_t\varepsilon)^2\}. \tag{C45}$$

Expressions (C43) and (C45) are the results presented in Eq. (S.32) of the supporting information of Ref. [33]. Once more, the difference in sign is due to our opposite convention for the flux compared to Ref. [33].

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