Entropy and information flow in quantum systems strongly coupled to baths

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Considering von Neumann expression for reduced density matrix as thermodynamic entropy of a system strongly coupled to baths, we use nonequilibrium Green’s function (NEGF) techniques to derive bath and energy resolved expressions for entropy, entropy production, and information flows. The consideration is consistent with dynamic (quantum transport) description and expressions reduce to expected forms in limiting cases of weak coupling or steady-state. Formulation of the flows in terms of only system degrees freedom is convenient for simulation of thermodynamic characteristics of open nonequilibrium quantum systems. We utilize standard NEGF for derivations in noninteracting systems, Hubbard NEGF is used for interacting systems. Theoretical derivations are illustrated with numerical simulations within generic junction models.

I. INTRODUCTION

Rapid development of experimental techniques at the nanoscale in the last decade has led to miniaturization of devices for energy storage and conversion to sizes where quantum mechanics becomes relevant. For example, thermoelectric single atom and single molecule junctions are expected to operate more effectively compared to their bulk analogs due to possible utilization of quantum effects. Proper description of performance of nanoscale devices for energy conversion requires development of corresponding nonequilibrium quantum thermodynamics. Moreover, with molecules chemisorbed on at least one of the contacts, thermodynamic theory should account for strong system-bath couplings.

In recent years there is a surge of research in this field both experimentally and theoretically. One of the guiding principles for theoretical research is consistency of the thermodynamic description with underlying system dynamics. Thermodynamic formulations for systems strongly coupled to their baths can be roughly divided into two groups: 1. supersystem-superbath and 2. system-bath approaches.

The first group complements the physical supersystem (system strongly coupled to its baths) with a set of superbaths (additional baths) weakly coupled to the supersystem. Choosing thermodynamic border at the weak link (i.e. between the supersystem and superbath) and utilizing tools of standard thermodynamics, thermodynamics of the system strongly coupled to its baths is introduced as the difference between thermodynamic formulations for the supersystem and free baths (both weakly coupled to the superbaths). This approach was pioneered in Refs. and extended to nonequilibrium using scattering theory, and nonequilibrium Green’s function formulations. However, this way of building the thermodynamic description is inconsistent with the microscopic dynamical description of the physical system. Thus, it is natural that the approach has difficulties in describing energy fluctuations.

The second group builds the thermodynamic description using physical supersystem only (system strongly coupled to its baths, no additional baths are assumed). This approach postulates von Neumann entropy expression for reduced density matrix of the system as thermodynamic entropy. Then, the second law is formulated in terms of system and baths characteristics. The integral expression for entropy production defined as relative entropy is guaranteed to be positive, although it does not increase monotonically. The approach was originally proposed in Refs. and later used in a number of studies. An attractive feature of the formulation is its consistency with the dynamical (quantum transport) description. Although this approach was recently criticized as being formulated using external to the system (i.e. baths) variables and as being not consistent with expected behavior at thermal equilibrium, it seems, that Green’s function based formulation presented below is capable of satisfying the requirements: below we express all thermodynamic characteristics of the system in terms of system variables only, and reaching thermal equilibrium was shown in Ref. to be consequence of a symmetry of the Schwinger-Keldysh action.

Another active area of research establishes a connection between thermodynamic and information theory. A number of experimental and theoretical studies establish foundations for thermodynamics of quantum information. Recently, discussion of quantum information flows in Markovian open quantum systems was presented in Refs. In particular, the local Clausius inequality relating entropy balance of a subsystem to the information flow was established for system weakly coupled to its baths (Markov dynamics with second order in system-bath couplings).

Here, we utilize the system-bath approach to extend description of quantum information flow to non-Markov dynamics of systems strongly coupled to their baths. We reformulate the system-bath approach in terms of Green’s functions. This leads to local (system variables
only) formulation and allows to introduce separability of baths contributions beyond weak (second order) coupling. Also, strong coupling results in energy-resolved expressions for entropy and information fluxes. The structure of the paper is as follows: in Section II we introduce Green’s function based formulation first for non-interacting and then for interacting systems. The former uses the standard nonequilibrium Green’s function (NEGF) technique \[68–70\], while the latter employs its many-body flavor - the Hubbard NEGF \[71–73\]. Numerical simulations within generic junction models for thermodynamic and information properties of open quantum systems are presented in Section II. Section IV summarizes our findings and indicates directions for future research.

II. THERMODYNAMICS: GREEN’S FUNCTIONS FORMULATION

We consider a junction which consists of system \( S \) strongly coupled to set of baths \( \{ B \} \). The system and the couplings are subjected to time-dependent driving. Hamiltonian of the model is (here and below \( e = k_B = \hbar = 1 \))

\[
\hat{H}(t) = \hat{H}_S(t) + \sum_B \left( \hat{H}_B + \hat{V}_{SB}(t) \right)
\]

(1)

Before system-bath coupling is established at time \( t_0 \), baths are assumed to be in thermal equilibrium characterized by temperature \( \beta_B = 1/T_B \) and chemical potential \( \mu_B \).

System-bath approach to thermodynamics introduced in Ref. \[47\] defines von Neumann expression as the system entropy

\[
S(t) \equiv - \text{Tr}_S \left[ \hat{\rho}_S(t) \log \hat{\rho}_S(t) \right]
\]

(2)

Here, \( \hat{\rho}(t) \) is the density operator of the universe (system plus baths) and \( \hat{\rho}_S(t) \equiv \text{Tr}_B(\hat{\rho}(t)) \). Considering the system and baths initially in the product state \( \hat{\rho}(t_0) = \hat{\rho}_S(t_0) \otimes \hat{\rho}_B^{eq} \), this leads to integral version of the second law in the form \[47\]

\[
\Delta S(t) = \sum_B \beta_B Q_B(t) + \Delta P(t)
\]

(3)

where

\[
Q_B(t) \equiv - \text{Tr}[\hat{H}_B \dot{\hat{\rho}}(t)] + \text{Tr}[\dot{\hat{H}}_B \hat{\rho}(t_0)]
\]

\[
\Delta P(t) \equiv D[\dot{\hat{\rho}}(t)]|\hat{\rho}_S(t) \otimes B \hat{\rho}_B^{eq}|
\]

(4)

are the heat transferred from bath \( B \) into the system and entropy production during time \( t - t_0 \). Here, \( D[\dot{\hat{\rho}}]|\hat{\rho}_2 \] = \( \text{Tr}[\dot{\hat{\rho}}_1 \log \hat{\rho}_1] - \text{Tr}[\dot{\hat{\rho}}_1 \log \hat{\rho}_2] \) is the quantum relative entropy.

Below, starting from \[2\] and using NEGF techniques we introduce expressions for thermodynamic characteristics (entropy, entropy production, heat and information fluxes) in terms of single-particle Green’s functions. These expressions are defined in the system subspace only and are suitable for actual calculations. Note that expression for heat in \[4\] is consistent with definitions of particle and energy fluxes accepted in quantum transport considerations. Also, the system-bath approach \[2–4\] does not introduce artificial additions to the physical system. Thus, thermodynamic formulation is consistent with dynamic (quantum transport) description. Note also that while thermodynamic formulation of Ref. \[47\] strict in assumption of initial product state, Green’s function based analysis in principle allows to relax this restriction by shifting consideration from the Keldysh to Konstantinov-Perel contour \[74, 75\]. First, we utilize standard NEGF \[68, 70\] and consider non-interacting system. After that, we use the Hubbard NEGF \[71, 73\] to generalize the consideration to interacting systems.

Exact formulations of the second law of thermodynamics in the form of energy resolved partial Clausius, Eq. \[5\], and local Clausius, Eq. \[17\], expressions together with equations for the energy resolved entropy, heat, entropy production and information fluxes, Eqs. \[9\], \[18\], \[19\], \[27\], \[28\], and \[30\], are the main results of our consideration.
A. Non-interacting system

First, we consider an open non-interacting Fermi system described by the Hamiltonian \([1]\) with

\[
\hat{H}_S(t) = \sum_{i,j \in S} H^\text{i}_ij(t) \hat{d}_i^\dagger \hat{d}_j, \quad \hat{H}_B = \sum_{k \in B} \varepsilon_k \hat{c}_k^\dagger \hat{c}_k
\]

\[
\hat{V}_B(t) = \sum_{i \in S, k \in B} \left( V_{ik}(t) \hat{d}_i^\dagger \hat{c}_k + V_{ki}(t) \hat{c}_k^\dagger \hat{d}_i \right)
\]

Here, \(\hat{d}_i^\dagger\) (\(\hat{d}_i\)) and \(\hat{c}_k^\dagger\) (\(\hat{c}_k\)) create (annihilate) electron in orbital \(i\) of the system and state \(k\) of the bath \(B\), respectively.

For the non-interacting system \([5]\) entropy \([2]\) is \([6]\)

\[
S(t) = -\text{Tr}_S \left[ -iG^< (t, t) \ln ( -iG^< (t, t) ) \right]
- \text{Tr}_S \left[ iG^> (t, t) \ln ( iG^> (t, t) ) \right]
\]

where \(G^\pm(t, t)\) are matrices in the system subspace representing greater/lesser projections of the single-particle Green’s function defined on the Keldysh contour as \([63-70]\)

\[
G_{ij}(\tau, \tau') \equiv -i \langle T_e \hat{d}_i(\tau) \hat{d}_j^\dagger(\tau') \rangle
\]

Here, \(T_e\) is the contour ordering operator, \(\tau_1, \tau_2\) are the contour variables, operators in the expression are in the Heisenberg picture, and \((\ldots) = \text{Tr}[\ldots \hat{\rho}(t_0)]\).

Using \([6]\) and Dyson equation for \([7]\) leads to differential analog of the second law \([3]\) in the form of energy-resolved partial Clausius relation (see Appendix A for details)

\[
d\frac{d}{dt}S_B(t; E) = \beta_B \hat{Q}_B(t; E) + \hat{P}_B(t; E)
\]

where

\[
\frac{d}{dt}S_B(t; E) = \text{Tr}_S \left[ iB(t; E) \ln \frac{iG^> (t, t)}{-iG^< (t, t)} \right]
\]

\[
\hat{Q}_B(t; E) = (E - \mu_B) \text{Tr}_S \left[ iB(t; E) \right]
\]

\[
\hat{P}_B(t; E) = \text{Tr}_S \left[ iB(t; E) \ln \frac{iG^> (t, t) f_B(E)}{-iG^< (t, t) [1 - f_B(E)]} \right]
\]

are the bath and energy resolved entropy, heat and entropy production fluxes, and where

\[
\gamma_{ij}^B(t; E) = \sum_{n \in S} \int_{t_n}^{t} ds
\]

\[
\left( \sigma_{in}^B(t, s; E) G_{nj}^\geq (s, t) - \sigma_{in}^B(t, s; E) G_{nj}^\leeq (s, t) \right) e^{iE(s-t)}
+ \left( G_{in}^\geq (t, s) \sigma_{nj}^B(t, s; E) - G_{in}^\leeq (t, s) \sigma_{nj}^B(t, s; E) \right) e^{iE(t-s)}
\]

is the matrix of energy-resolved particle flux at interface \(S - B\). Here, \(E\) is resolution in the energy of bath states,

\[
sigma_{in}^B(t_1, t_2; E) = i \gamma_{in}^B(t_1, t_2; E) f_B(E)
\]

\[
\sigma_{nj}^B(t_1, t_2; E) = -i \gamma_{nj}^B(t_1, t_2; E) [1 - f_B(E)]
\]

are the lesser and greater projections of the self-energy due to coupling to bath \(B\), \(f_B(E)\) is the Fermi-Dirac thermal distribution, and \([76]\)

\[
\gamma_{in}^B(t_1, t_2; E) = 2\pi \sum_{k \in B} V_{ik}(t_1) V_{kj}(t_2) \delta(E - \varepsilon_k)
\]

is the energy-resolved dissipation matrix at interface \(S - B\).

Expressions \([9]\) introduce energy resolved fluxes of entropy, heat and entropy production. Corresponding total fluxes are obtained by summing over baths and integrating over energy

\[
\frac{d}{dt}S_B(t; E) = \sum_B \int \frac{dE}{2\pi} \frac{d}{dt}S_B(t; E)
\]

\[
\hat{Q}_B(t; E) = \int \frac{dE}{2\pi} \hat{Q}_B(t; E)
\]

\[
\hat{P}_B(t; E) = \int \frac{dE}{2\pi} \hat{P}_B(t; E)
\]

That is, in noninteracting systems the fluxes are exactly additive in terms of bath contributions (below we show that the same is true in presence of interactions). Thus, non-Markov character of Green’s function formulation alleviates non-adiativity problems of quantum master equation considerations \([77-80]\).

Additive form of fluxes, Eq.\([13]\), also indicates that for system which consists of several coupled parts,

\[
\hat{H}_S(t) = \sum_{p=1}^{N_p} \hat{H}_S^{(p)}(t) + \sum_{p_1 < p_2}^{N_p} \hat{H}_S^{(p_1p_2)}(t),
\]

such that each part \(p\) is connected to its own group of baths \(\{B_p\}\), one can use expressions for entropy of part \(p\),

\[
S_p(t) = -\text{Tr}_p [\dot{\rho}_p(t) \ln \dot{\rho}_p(t)],
\]

and for multipartite mutual information,

\[
I_{1,\ldots,N_p}(t) = \sum_{p=1}^{N_p} S_p(t) - S(t),
\]

to derive energy resolved version of the local Clausius expression (see Appendix A for details)

\[
\frac{d}{dt}S_p(t; E) = \sum_{B_p} \left( \beta_{B_p} \hat{Q}_{B_p}(t; E) + \hat{P}_{B_p}(t; E) \right) + \dot{I}_p(t; E)
\]

(17)
Here,
\[ \frac{d}{dt} S_p(t; E) = \sum_{B_p} Tr_p \left[ i \pi \mathcal{G}_p^\dagger (t; E) \ln \frac{i \pi \mathcal{G}_p^\dagger (t; E)}{-i \pi \mathcal{G}_p^\dagger (t; E)} \right] + 2\pi \delta(E) Tr_p \left[ (\mathbf{G}^\prec(t, t), \mathbf{H}^{(S)}(t))_p \ln \frac{i \pi \mathcal{G}_p^\dagger (t; E)}{-i \pi \mathcal{G}_p^\dagger (t; E)} \right] \]
and
\[ i \pi \delta_p(t; E) \equiv \frac{d}{dt} S_p(t; E) - \sum_{B_p} \frac{d}{dt} S_{B_p}(t; E) \]
\[ i \pi \delta_p(t; E) \equiv \frac{d}{dt} S_p(t; E) \ln \frac{i \pi \mathcal{G}_p^\dagger (t; E)}{-i \pi \mathcal{G}_p^\dagger (t; E)} \]
are the part \( p \) entropy and information fluxes, respectively. Subscript \( p \) in \( (\mathbf{G}^\prec(t, t), \mathbf{H}^{(S)}(t))_p \), \( \mathcal{G}_p^\dagger(t; E) \), and \( i \pi \delta_p(t; E) \) in (18) and (19) indicates matrices in the subspace \( p \) of \( S \).

\section*{B. Interacting system}

We now turn to interacting systems. In the basis \( \{|S\rangle\} \) of many-body states of an isolated system contributions to the Hamiltonian (1) are
\[ \hat{H}_S(t) = \sum_{S_1, S_2 \in S} H_{S_1, S_2}^S \hat{X}_{S_1, S_2} \]
\[ \hat{H}_B = \sum_{k \in B} \varepsilon_k \hat{c}_k^\dagger \hat{c}_k \]
\[ \hat{V}_{SB}(t) = \sum_{S_1, S_2 \in S} \sum_{k \in B} (V_{S_1, S_2} \hat{X}_{S_1, S_2}^\dagger \hat{c}_k + H.c.) \]
Here, \( \hat{X}_{S_1, S_2} \equiv |S_1\rangle \langle S_2| \) is the Hubbard operator. Note that while focus of our consideration is on Fermi baths, generalization to Bose case is straightforward.

Entropy of the system, Eq. (2), is defined by the system density operator. Its representation in the basis of the system many-body states is
\[ \rho_S(t)_{S_1, S_2} = \langle \hat{X}_{S_1, S_2}(t) \rangle \]

Exact equation of motion (EOM) for the system density matrix is (see Appendix E for details)
\[ \frac{d}{dt} \rho_S(t)_{S_1, S_2} = -i[H^{(S)}(t), \rho_S(t)]_{S_1, S_2} \]
\[ + \sum B \int \frac{dE}{2\pi} i \pi \mathcal{G}_S^\dagger (t; E) \ln \frac{i \pi \mathcal{G}_S^\dagger (t; E)}{-i \pi \mathcal{G}_S^\dagger (t; E)} \]
where
\[ i \pi \mathcal{G}_S(t; E) \equiv \sum_{S_3, S_4 \in S} \int_{-\infty}^t ds \left( \Sigma^\leq_{S_3, S_4}(S_3 S_4)(t, s; E) e^{i(E_{S_3, S_4}(t, s; E) f_B(E)} \right) \]
is the matrix of energy resolved probability flux at interface \( S - B \),
\[ \Sigma^\leq_{S_3, S_4}(S_3 S_4)(t_1, t_2; E) \equiv i \Gamma^B_{S_3, S_4}(t_1, t_2; E) f_B(E) \]
\[ \Gamma^B_{S_3, S_4}(t_1, t_2; E) \equiv 2\pi \sum_{k \in B} V_{S_1, S_2}^k(t_1) V_{k, S_4}(t_2) \delta(E - \varepsilon_k) \]
is the energy-resolved dissipation matrix. \( \mathcal{G}_S(t_1, t_2) \) are greater/lesser projections of the Hubbard Green’s function defined on the Keldysh contour as (1) and (3)
\[ \mathcal{G}_{S_1, S_2}(t_1, t_2) \equiv -i\langle \hat{T}_c \hat{X}_{S_1, S_2}(t_1) \hat{X}^\dagger_{S_2, S_1}(t_2) \rangle \]

EOM (22) leads to expression for second law in the form of energy resolved version of the partial Clausius relation (8) with entropy, heat and entropy production fluxes given by (see Appendix C for derivation)
\[ \frac{d}{dt} S_B(t; E) = -Tr_S \left[ \mathbf{I}^B(t; E) \ln \rho_S(t) \right] \]
\[ Q_B(t; E) = (E - \mu_B) Tr_S [\mathbf{N} \mathbf{I}^B(t; E)] \]
\[ \dot{P}_B(t; E) = -Tr_S \left[ \mathbf{I}^B(t; E) \left( \ln \rho_S(t) - \mathbf{N} \ln \frac{f_B(E)}{1 - f_B(E)} \right) \right] \]
Here, \( \mathbf{N} \) is matrix representing the system number operator in the basis of many-body states \( \{|S\rangle\} \), its elements \( N_{S_1, S_2} \equiv \langle S_1| N |S_2\rangle = \delta_{N_{S_1}, S_2} N_{S_1} \) yield information on
number of electrons $N_S$ in state $|S\rangle$. As previously, total fluxes are given by integrating over energy and summing over baths, Eq. (13).

Finally, for the multipartite system [14] one can derive energy-resolved local Clausius expression [17]. Derivation follows the same steps as in the noninteracting case considered in Appendix [A]. The only new feature is connection between probability and particle/energy fluxes as discussed in Appendix [C]. Similar to noninteracting case, Eq. (18), consideration of part of the system results in non-zero contribution from the first term in the right of (22) to the entropy flow

$$\frac{d}{dt}S_p(t; E) = -\sum_{B_p} [\text{Tr}_{p}[I_{p}^{B_p}(t; E) \ln \rho_p(t)]] + 2\pi i \delta(E) \text{Tr}_{p}[\left[H^{(S)}(t), \rho_S(t)\right]_p \ln \rho_p(t)]$$

(28)

Here,

$$\dot{\rho}_p(t) \equiv \text{Tr}_{S\setminus p}[\dot{\rho}_S(t)], \quad I_{p}^{B_p}(t; E) \equiv \text{Tr}_{S\setminus p}[I_{B_p}(t; E)], \quad \left[H^{(S)}(t), \rho_S(t)\right]_p \equiv \text{Tr}_{S\setminus p}[\left[H^{(S)}(t), \rho_S(t)\right]]_p.$$

(29)

Using [5], [27], and [28] in energy resolved analog of (16) (see Eq. (A16) in Appendix [A]), leads to the energy resolved local Clausius expression (17) with information flux given by

$$\dot{I}_p(t; E) = \dot{I}_{p}^{\text{reg}}(t; E) + \dot{I}_p^{\delta}(t; E)$$

$$\dot{I}_{p}^{\text{reg}}(t; E) \equiv \sum_{B_p} \left[\text{Tr}_{S}[I_{p}^{B_p}(t; E) \ln \rho_S(t)] - \text{Tr}_{p}[I_{B_p}(t; E) \ln \rho_p(t)]\right]$$

(30)

$$\dot{I}_p^{\delta}(t; E) \equiv 2\pi i \delta(E) \times \text{Tr}_{p}[\left[H^{(S)}(t), \rho_S(t)\right]_p \ln \rho_p(t)].$$

(31)

III. NUMERICAL ILLUSTRATIONS

Here we illustrate our derivations with simulations performed in generic junction model sketched in Fig. 1. Fermi energy $E_F$ in each bath is taken as zero, and bias $V_i$ between left and right sides is applied symmetrically, $\mu_L = E_F + V_i/2$ and $\mu_R = E_F - V_i/2 (i = 1, 2)$. Simulations are performed at steady state.

First, we consider two-level system as an example for noninteracting $S$. Hamiltonian of the system is given in Eq. (14) with

$$\hat{H}_S^{(i)} = \varepsilon_i \hat{d}_i^\dagger \hat{d}_i \quad (i = 1, 2)$$

$$\hat{H}_S^{(12)} = t_{12} (\hat{d}_1^\dagger \hat{d}_2 + \hat{d}_2^\dagger \hat{d}_1)$$

(31)

FIG. 2: Junction of Fig. 1 with $S$ represented by two-level system. Shown are steady state energy resolved (a) information flow $\dot{I}$, Eq. (19), and (b) entropy production $\dot{P}$, Eq. (9). Characteristics of parts $S_1$ and $S_2$ are shown with solid (blue) and dashed (red) lines, respectively. Triangles (blue) and circles (red) present information flow and entropy production evaluated using formulation for interacting systems, Eqs. (30) and (27). See text for parameters.

Here, $\hat{d}_i$ ($\hat{d}_i^\dagger$) creates (annihilates) electron in level $\varepsilon_i$ of subsystem $S_i$.

Figure 2 shows results of the simulation. Parameters are $T = 300$ K, $\varepsilon_1 = \varepsilon_2 = 0$, $t_{12} = 0.1$ eV, $\gamma_i^B = \delta_{ij} 0.05$ eV, $V_1 = 0.4$ eV and $V_2 = -0.2$ eV. Simulation was performed on energy grid spanning range from $-10$ to $10$ eV with step $0.001$ eV. Panel (a) shows information flow from $S_1$ and into $S_2$, which is natural consequence of $V_1 > |V_2|$. Because of steady-state $\dot{I}_1 = -\dot{I}_2$. Entropy production is presented in panel (b). The simulations were performed utilizing non-interacting (lines) and interacting (markers) methodology. Fig. 2 shows close correspondence between NEGF and Hubbard NEGF results.

We now turn to consider interacting system. As a toy model we take quantum dot junction in the regime of strong Coulomb repulsion. Subsystems $S_1$ and $S_2$ represent spin up and spin down levels of the system. The dot is subjected coupling to external spin degree of free-
IV. CONCLUSION

Starting from von Neumann expression with reduced (system) density matrix as definition of thermodynamic entropy for a system strongly coupled to its baths, we formulate the second law of thermodynamics in the form of bath and energy resolved partial and local Clausius relations. The derivation yields expressions for entropy, heat, and information flows and for entropy production rate formulated in terms of system variables only. This makes the expressions suitable for actual calculations of the thermodynamic characteristics of open nanoscale molecular devices.

The expressions are derived using the standard NEGF for noninteracting and Hubbard NEGF for interacting systems. Utilization of Green’s function techniques allows to generalize Markov weak coupling (second order in system-baths) consideration of Ref. [67] to strongly coupled case of non-Markov system dynamics. In particular, we utilize exact equation of motion for the reduced (system) density matrix in terms of Green’s functions, introduce energy resolution of the thermodynamic flows, and show that Green’s function analysis allows to alleviate non-separability problems of density matrix considerations and thus to introduce exact general form of information flow. Expressions for thermodynamic characteristics reduce to known expected limiting forms in weak coupling or steady-state situations. We stress that while theoretical consideration in the manuscript focuses on Fermi baths and charge flux between the system and baths, generalization to incorporate Bose degrees of freedom and energy flux is straightforward within the interacting (Hubbard NEGF) formulation.

Theoretical derivations are illustrated with numerical results for a junction which consists of two sub-systems each coupled its own pair of baths (Fig. [1]). Generic models of the two-level system and quantum dot with spin-flip processes are used as illustrations for noninteracting and interacting system, respectively. Energy resolved thermodynamic characteristics of the interacting...
system are shown to demonstrate strongly correlated features (Kondo), which in principle can be detected in corresponding flows similar to conductance measurements.

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Appendix A: Derivation of energy resolved partial and local Clausius expression for noninteracting system

For noninteracting systems (i.e. systems described by quadratic Hamiltonian), the Wick’s theorem holds for any part of the universe (system plus baths). This means that corresponding many-body density operator for any part of the system has Gaussian form. Thus, path integral formulation yields for the local density matrix

\[ \rho_A(t) = \det \left[ iG^<_A(t,t) \right] \ln \left( \frac{iG^<_A(t,t)}{G^>_{-A}(t,t)} \right) \]  

(A1)

Here, \( A \) can be any part of the universe. Below we consider system \( (A = S) \) or its part \( (A = p) \), and assume that each part \( p \) of the system is coupled to its own set of baths \( \{B_p\} \).

Assuming von Neumann expression for entropy of the part \( A \), Eq. (A1) leads to

\[ S_A(t) = -\text{Tr}_A \left[ \rho_A(t) \ln \rho_A(t) \right] = -\text{Tr}_A \left[ -iG^<_A(t,t) \ln \left( -iG^<_A(t,t) \right) \right] \]

(A2)

Here, \( G^<_A(t,t) \) is the lesser/lesser or retarded/advanced projection of the single-particle Green’s function for the system, \( G^<_A(t,t) \) \((A = S)\), or its part, \( G^<_p(t,t) \) \((A = p)\). Taking time derivative of (A2) leads to expression for entropy flux

\[ \frac{d}{dt}S_A(t) = \text{Tr}_A \left[ \left( -i \frac{d}{dt} G^<_A(t,t) \right) \ln \left( \frac{iG^<_A(t,t)}{G^>_{-A}(t,t)} \right) \right] \]

(A3)

Dyson equation for the lesser projection of the single particle Green’s function is

\[ -\frac{i}{dt}(G^<_A(t,t))_{ij} = [G^<(t,t), \mathbf{H}^{(S)}(t)]_{ij} + \sum_{n \in S} \int_{t_0}^{t} ds \left( G^<_{in}(t,s) \sigma^<_n(s,t) \sigma^>_n(s,t) - \sigma^<_n(s,t) \sigma^>_n(s,t) \right) \]

(A4)

and similar expressions for \( \sigma \) leads to

\[ -\frac{i}{dt}(G^<_A(t,t))_{ij} = [G^<(t,t), \mathbf{H}^{(S)}(t)]_{ij} + \sum_{n \in B} \int_{t_0}^{t} ds \left( G^<_{in}(t,s) \sigma^<_n(s,t) \sigma^>_n(s,t) - \sigma^<_n(s,t) \sigma^>_n(s,t) \right) \]

(A5)

with

\[ g^<_k(t,t') = i \kappa e^{-i\kappa(t-t')} \quad \text{and} \quad g^>_k(t,t') = -i[1 - \kappa] e^{-i\kappa(t-t')} \]

(A6)

and

\[ \sum_{k \in B} \ldots = \int \frac{dE}{2\pi} \sum_{k \in B} \delta(E - \varepsilon_k) \ldots \]

(A7)

leads to

\[ -\frac{i}{dt}(G^<_A(t,t))_{ij} = [G^<(t,t), \mathbf{H}^{(S)}(t)]_{ij} \]

(A8)

Substituting (A11) into (A3) yields

\[ \frac{d}{dt}S_A(t) = \text{Tr}_A \left[ [G^<(t,t), \mathbf{H}^{(S)}(t)]_{ij} \ln \left( \frac{iG^>_A(t,t)}{iG^<_A(t,t)} \right) \right] + \sum_{B_A} \int \frac{dE}{2\pi} \text{Tr}_A \left[ i^{B_A} \ln \left( \frac{iG^>_A(t,t)}{iG^<_A(t,t)} \right) \right] \]

(A9)

where the matrix of energy-resolved particle flux \( \mathbf{i}^B(t;E) \) is defined in (10).

Substituting (A11) into (A3) yields

\[ \frac{d}{dt}S_A(t) = \text{Tr}_A \left[ [G^<(t,t), \mathbf{H}^{(S)}(t)]_{ij} \ln \left( \frac{iG^>_A(t,t)}{iG^<_A(t,t)} \right) \right] + \sum_{B_A} \int \frac{dE}{2\pi} \text{Tr}_A \left[ i^{B_A} \ln \left( \frac{iG^>_A(t,t)}{iG^<_A(t,t)} \right) \right] \]

(A10)

where subscript \( A \) in \([G^<(t,t), \mathbf{H}^{(S)}(t)]_{ij} \) indicates sub-matrix with indices in subspace \( A \).
Partial Clausius expression, Eq. (8)

We now restrict our consideration to the system ($A = S$). In this case first term in the right side of (A12) is identically zero, and we can introduce energy-resolved version of the entropy flux as defined in [9] and [13]. Energy resolved version of the partial Clausius inequality (8) follows from

$$
\ln \frac{f_B(E)}{1 - f_B(E)} = -\beta_B(E - \mu_B)
$$

and definitions of energy resolved heat and entropy production fluxes given in [7]. Note that definition of the heat flux $\dot{Q}_B(t)$ is consistent with the standard quantum transport definitions of particle $I_B(t)$ and energy $J_B(t)$ fluxes

$$
\dot{Q}_B(t) \equiv J_B(t) - \mu_B I_B(t)
$$

$$
J_B(t) \equiv -\frac{d}{dt} \langle \hat{H}_B(t) \rangle
$$

$$
I_B(t) \equiv -\frac{d}{dt} \sum_{k \in B} \langle \hat{c}_k^{\dagger}(t) \hat{c}_k(t) \rangle
$$

Local Clausius expression, Eq. (17)

This is the current expression in the second term of (A12).

Main difference (when compared with $A = S$) is nonzero contribution from the first term in the right in (A12). Thus, energy resolution for both specific entopy flux of the system, Eq. (9), is substituted with part specific expression, Eq. (18), with additional delta-term in it.

Using (9), (10) and (18) in energy resolved analog of (10),

$$
I_{1,\ldots,N_p} = \int \frac{dE}{2\pi} I_{1,\ldots,N_p}(t; E),
$$

leads to separability of the multipartite mutual information into part-specific contributions

$$
\dot{I}_{1,\ldots,N_p}(t; E) = \sum_p \frac{d}{dt} S_p(t; E)
$$

$$
- \sum_p \sum_{B_p} \left( \beta_{B_p} \dot{Q}_{B_p}(t; E) + \dot{P}_{B_p}(t; E) \right)
$$

$$
\equiv \sum_p \dot{I}_p(t; E)
$$

Rearranging terms in the latter expression yields (17) with information flux consisting of regular and delta-type contributions as defined in Eq. (19).

Appendix B: Derivation of exact EOM for system density matrix, Eq. (22)

We start with writing Heisenberg EOM for $\hat{X}_{SS'}(t)$ under dynamics governed by the Hamiltonian [1] and [20]. Averaging result over an initial density operator leads to

$$
\frac{d}{dt} \langle \hat{X}_{SS'}(t) \rangle =
$$

$$\int_S \sum_{S'} \langle \hat{H}^{(S)}_{SS'}(t) \hat{X}_{SS'}(t) - H^{(S)}_{SS'}(t) \hat{X}_{SS'}(t) \rangle
$$

$$\int_S \sum_{S'} \langle \hat{H}^{(S)}_{SS'}(t) \hat{X}_{SS'}(t) - H^{(S)}_{SS'}(t) \hat{X}_{SS'}(t) \rangle
$$

where $\hat{G}_{SS'}^\xi(t, t)$ and $\hat{G}_{SS'}^{\xi}(t, t)$ are the equal time greater/lesser projections of the Hubbard Green’s functions defined on the contour as

$$
\hat{G}_{SS'}^\xi(t, t') \equiv -i \langle T_e \hat{X}_{SS'}^\xi(t) \hat{c}_k^\dagger(t') \rangle
$$

$$
\hat{G}_{SS'}^{\xi}(t, t') \equiv -i \langle T_e \hat{c}_k(t) \hat{X}_{SS'}^\xi(t) \rangle
$$

Integral forms of the right and left Dyson equations for (22) are

$$
\hat{G}_{SS'}^\xi(t, t') =
$$

$$\sum_{S_4, S_5 \in S} \int d\sigma \hat{G}_{SS'}^\xi(S_4, S_5) \langle \sigma, \sigma' \rangle V_{S_4 S_5}(s) g_k(\sigma, \sigma')
$$

$$\hat{G}_{SS'}^{\xi}(t, \tau') =
$$

$$\sum_{S_4, S_5 \in S} \int d\sigma g_k(\tau, \sigma') V_{S_4 S_5}(s) \hat{G}_{SS'}^\xi(S_4, S_5) \langle \sigma, \tau' \rangle
$$

where

$$
g_k(\tau, \tau') \equiv -i \langle T_e \hat{c}_k(\tau) \hat{c}_k^\dagger(\tau') \rangle
is the single-particle Green’s function of free electron in state $k$ of contact $B$.

Substituting lesser projections of (B3) into (B1) leads to

$$\frac{d}{dt} \langle \hat{X}_{S_2 S_1}(t) \rangle = -i [\hat{H}^{(S)}(t), \rho_S(t)]_{S_1 S_2} \quad \text{(B5)}$$

$$+ \sum_B \sum_{S_1 S_2 S_4 \in S} \int_0^t ds \left( \sum_{(S_1 S_2)}^{B <}(t, s) \varrho_{(S_1 S_2)}^{S}(s, t) \right) \quad \text{(a)}$$

$$- \sum_{(S_1 S_2)}^{B >}(t, s) \varrho_{(S_1 S_2)}^{S}(s, t) \quad \text{(b)}$$

$$- \sum_{(S_1 S_2)}^{B >}(t, s) \varrho_{(S_1 S_2)}^{S}(s, t) \quad \text{(c)}$$

$$+ \sum_{(S_1 S_2)}^{B >}(t, s) \varrho_{(S_1 S_2)}^{S}(s, t) \quad \text{(d)}$$

$$+ \sum_{(S_1 S_2)}^{B >}(t, s) \varrho_{(S_1 S_2)}^{S}(s, t) \quad \text{(e)}$$

$$- \sum_{(S_1 S_2)}^{B >}(t, s) \varrho_{(S_1 S_2)}^{S}(s, t) \quad \text{(f)}$$

$$- \sum_{(S_1 S_2)}^{B >}(t, s) \varrho_{(S_1 S_2)}^{S}(s, t) \quad \text{(g)}$$

$$+ \sum_{(S_1 S_2)}^{B >}(t, s) \varrho_{(S_1 S_2)}^{S}(s, t) \quad \text{(h)}$$

where $\Sigma_{(S_1 S_2)}^{B >}(t, s)$ are the greater/lesser projections of the self-energy due to coupling to contact $B$

$$\Sigma_{(S_1 S_2)}^{B >}(t, s) \equiv \sum_{k \in B} V_{(S_1 S_2)}(k) g_k(\tau, \tau') V_{k(S_1 S_2)}(t') \quad \text{(B6)}$$

Graphic representation of the projections in (B5) is given in Fig. 4. We note in passing that suggestion of Ref. [83] to drop same branch projections (e.g., projections (b), (f), (c) and (g) in second order in system-bath coupling) when building thermodynamic description is inconsistent with assumption of von Neumann form of the system entropy. Note also that connection between exact EOM (B5) and approximate quantum master equations for reduced density matrix was discussed in Ref. [73].

Finally, using (A9) and (A10) in (B5) leads to (22).

Appendix C: Derivation of partial Clausius expression for interacting system

We start from von Neumann expression for system entropy, Eq. (21), and take time derivative to get entropy flux

$$\frac{d}{dt} S(t) = -\text{Tr}_S \left[ \frac{d}{dt} \rho_S(t) \ln \rho_S(t) \right] \quad \text{(C1)}$$

Using exact EOM for the system density matrix, Eq. (22), and taking into account that first term in the right of (22) gives zero contribution to the trace in (C1) and second term in the right of (22) is exactly separable into energy-resolved contributions from different baths leads to

$$\frac{d}{dt} S(t) = \sum_B \int dE \frac{d}{dt} S_B(t; E) \quad \text{(C2)}$$

where energy-resolved entropy flux $\frac{d}{dt} S_B(t; E)$ is defined in (27).

Contrary to noninteracting case, second term in the right of (22) is not directly related to particle flux, rather it is probability flux. Indeed, writing Heisenberg EOM for the current at interface $S - B$, Eq. (A14), yields

$$I_B(t) = \frac{d}{dt} \sum_{k \in B} \langle \hat{c}_k(t) \hat{c}_k(t) \rangle$$

$$= -i \sum_{k \in B} \langle [\hat{H}(t), \hat{c}_k^\dagger(t) \hat{c}_k(t)] \rangle$$

$$= -2 \text{Re} \sum_{S_1, S_2 \in S} \sum_{k \in B} V_{(S_1 S_2)}(k) \varrho_{(S_1 S_2)}^{S}(t, s) \quad \text{(h)}$$

$$= 2 \text{Re} \sum_{S_1, S_2 \in S} \sum_{k \in B} \int_0^t ds \left( \Sigma_{(S_1 S_2)}^{B >}(t, s) \varrho_{(S_1 S_2)}^{S}(s, t) \right)$$

which is not equivalent to expression in the right of (22).

Connection between probability and particle fluxes is established considering change in particle number of the
system caused by coupling to baths

\[
\frac{d}{dt} \langle \hat{N}(t) \rangle = \text{Tr}_S \left[ \hat{N} \frac{d}{dt} \hat{\rho}_S(t) \right] = \sum_{S_1 \in S} \sum_B \int \frac{dE}{2\pi} N_{S_1} I_{S_1 S_1}^B(t; E) \tag{C4}
\]

where energy resolved probability flux is defined in \((23)\). Thus, energy-resolved particle flux at interface \(S - B\) is

\[
\sum_{S_1 \in S} N_{S_1} I_{S_1 S_1}^B(t; E) \tag{C5}
\]

Similarly, energy-resolved energy flux at interface \(S - B\) is

\[
\sum_{S_1 \in S} E N_{S_1} I_{S_1 S_1}^B(t; E) \tag{C6}
\]

Expressions \((C5)\) and \((C6)\) are used in definition of heat flux in \((27)\).

Energy resolved partial Clausius expression \((5)\) for interacting system directly follows from \((C1)\) and definitions in \((27)\).

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