

Nonequilibrium system–bath entanglement theorem versus heat transport

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(Dated: May 7, 2021)

In this work, we extend the recently established system–bath entanglement theorem (SBET) [J. Chem. Phys. **152**, 034102 (2020)] to the nonequilibrium scenario, in which an arbitrary system couples to multiple Gaussian baths environments at different temperatures. While the existing SBET connects the entangled system–bath response functions to those of local systems, the extended theory is concerned with the nonequilibrium steady–state quantum transport current through molecular junctions. The new theory is established on the basis of the generalized Langevin equation, with a close relation to nonequilibrium thermodynamics in the quantum regime.

I. INTRODUCTION

Quantum transport of heat and particles has attracted much attention in the past years. On one hand, it is closely related to the fundamental physics such as nonequilibrium thermodynamics in the quantum regime. On the other hand, it also plays important roles in such as energy and quantum information applications. Theoretical studies have been mainly carried out in terms of nonequilibrium Green’s function (NEGF) methods.

In this work, we exploit the well–established system–bath entanglement theorem (SBET),^{1,2} with extension to nonequilibrium transport scenario. Adopted here is the Gauss–Wick’s environment ansatz^{3,4} that is commonly adopted in various quantum dissipation theories. These include the formally exact Feynman–Vernon influence functional theory,⁵ and its derivative–equivalence the hierarchical equations of motion (HEOM) formalism.^{6–13} While the existing SBET deals with for response functions only,^{1,2} the extended theory is concerned with the nonequilibrium steady–state quantum transport current through molecular junctions. In this context, the extended SBET provides an alternative approach to the NEGF formalism. It is worth noting that the new theory is established on the basis of the generalized Langevin equation, which can readily support the evaluation on entangled system–bath correlation functions, which are closely related to nonequilibrium thermodynamics in the quantum regime. The convention fluctuation–dissipation theorem (FDT), which relates correlation functions and response functions, is only applicable to the equilibrium scenario. There are no general relations between the nonequilibrium correlation functions and response functions. It would be anticipated that the present Langevin equation based method be a viable approach toward such as fluctuation theorem far from equilibrium in the quantum regime. For clarity, we focus on the quantum heat transport formalism. The extension to electron current transport would be straightforward on the basis of the fermionic SBET.²

The remainder of this paper is organized as follows. In Sec. II, we present the well–established SBET for the

response functions,¹ with extension to the nonequilibrium transport scenario. In Sec. III, we construct a novel SBET, on the basis of a generalized Langevin equation, which readily leads to NEGF formalism for the quantum heat transport current. We conclude this work to the end of Sec. III.

II. EXTENDED SYSTEM–BATH ENTANGLEMENT THEOREM

A. Langevin equation for hybrid bath dynamics

System–bath entanglement plays a crucial role in dynamic and thermal properties of complex systems. This is concerned with a currently active topic in quantum mechanics of open systems. Recently, we had constructed the SBET.^{1,2} This theorem comprises exact relations between the entangled system–bath response functions and those of local anharmonic systems. Applications had been demonstrated with Fano interference spectroscopy.¹ The SBET had also been exploited in the establishment of the thermodynamic free–energy spectrum theory.²

To extend this theory to the nonequilibrium scenario, we should include multiple bath reservoirs with different temperatures, so that heat transport is anticipated. The total system–and–bath composite Hamiltonian reads

$$H_T = H_S + h_B + H_{SB} = H_S + \sum_{\alpha} h_{\alpha} + \sum_{\alpha u} \hat{Q}_u \hat{F}_{\alpha u}. \quad (1)$$

The system Hamiltonian H_S and dissipative modes $\{\hat{Q}_u\}$ are arbitrary. The α -reservoir bath Hamiltonian and the hybrid bath modes are modelled with

$$h_{\alpha} = \frac{1}{2} \sum_j \omega_{\alpha j} (\hat{p}_{\alpha j}^2 + \hat{x}_{\alpha j}^2) \quad \text{and} \quad \hat{F}_{\alpha u} = \sum_j c_{\alpha u j} \hat{x}_{\alpha j}, \quad (2)$$

respectively, which together constitute the so–called Gauss–Wick’s environment.^{3,4} The simplicity arises from the fact that the interacting bath commutators are all

c-variables; i.e.,

$$\phi_{uv}^\alpha(t) \equiv i[\hat{F}_u^\alpha(t), \hat{F}_v^\alpha(0)] = \sum_j c_{\alpha uj} c_{\alpha vj} \sin(\omega_{\alpha i} t) \quad (3)$$

where $\hat{F}_{\alpha u}^\alpha(t) \equiv e^{ih_B t} \hat{F}_{\alpha u} e^{-ih_B t} = e^{ih_\alpha t} \hat{F}_{\alpha u} e^{-ih_\alpha t}$. Throughout the paper we set $\hbar = 1$ and $\beta_\alpha = 1/(k_B T_\alpha)$, with k_B being the Boltzmann constant and T_α the α -reservoir temperature.

Denote also $\hat{O}(t) \equiv e^{iH_\alpha t} \hat{O} e^{-iH_\alpha t}$, with noticing that $\hat{F}_{\alpha u}(t) \neq \hat{F}_{\alpha u}^\alpha(t)$. The former is defined via the total system-and-bath composite space, whereas the latter is a bare bath subspace property. It is easy to obtain¹

$$\hat{F}_{\alpha u}(t) = \hat{F}_{\alpha u}^\alpha(t) - \sum_v \int_{t_0}^t d\tau \phi_{uv}^\alpha(t-\tau) \hat{Q}_v(\tau). \quad (4)$$

Note that $\phi_{uv}^\alpha(t)$, Eq. (3), can be recast as

$$\phi_{uv}^\alpha(t) = i\langle[\hat{F}_{\alpha u}^\alpha(t), \hat{F}_{\alpha v}^\alpha(0)]\rangle_\alpha, \quad (5)$$

with $\langle(\cdot)\rangle_\alpha \equiv \text{tr}_B[(\cdot)e^{-\beta_\alpha h_\alpha}]/\text{tr}_B e^{-\beta_\alpha h_\alpha}$. The hybridization bath spectral density is given by^{12,14}

$$J_{uv}^\alpha(\omega) \equiv \frac{1}{2} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle[\hat{F}_{\alpha u}^\alpha(t), \hat{F}_{\alpha v}^\alpha(0)]\rangle_\alpha. \quad (6)$$

Its microscopic equivalence reads [cf. Eq. (2)]

$$J_{uv}^\alpha(\omega) = \frac{\pi}{2} \sum_j c_{\alpha uj} c_{\alpha vj} [\delta(\omega - \omega_{\alpha j}) - \delta(\omega + \omega_{\alpha j})]. \quad (7)$$

Evidently, $J_{uv}^\alpha(\omega) = J_{vu}^\alpha(\omega) = -J_{uv}^\alpha(-\omega)$.

It is worth noting that the Langevin equation (4), together with the property of Eq. (3), will give rise to some interesting relations between the entangled system-bath properties and the local system ones, as bridged with the bare-bath $\phi_{uv}^\alpha(t)$ or $J_{uv}^\alpha(\omega)$.

B. The system-bath entanglement theorem for response functions and expectation values

The SBET is a type of input-output formalism, in which the local system properties, such as

$$\chi_{uv}^{\text{SS}}(t) \equiv i\langle[\hat{Q}_u(t), \hat{Q}_v(0)]\rangle \quad (8)$$

are the input functions, whereas the nonlocal correspondences,

$$\begin{aligned} \chi_{uv}^{\text{S}\alpha}(t) &\equiv i\langle[\hat{Q}_u(t), \hat{F}_{\alpha v}^\alpha(0)]\rangle \\ \chi_{uv}^{\alpha\text{S}}(t) &\equiv i\langle[\hat{F}_{\alpha u}^\alpha(t), \hat{Q}_v(0)]\rangle \end{aligned} \quad (9)$$

and

$$\chi_{uv}^{\alpha\alpha'}(t) \equiv i\langle[\hat{F}_{\alpha u}^\alpha(t), \hat{F}_{\alpha'v}^\alpha(0)]\rangle \quad (10)$$

are the output functions. Here,

$$\chi_{AB}(t-\tau) \equiv i\langle[\hat{A}(t), \hat{B}(\tau)]\rangle \quad (11)$$

are defined in the total composite space, at nonequilibrium steady-state scenario. It is easily to verify that the established SBET does include the general nonequilibrium scenario.¹ The final results, in terms of the matrices, are

$$\begin{aligned} \chi^{\alpha\text{S}}(t) &= -\int_0^t d\tau \phi^\alpha(t-\tau) \chi^{\text{SS}}(\tau), \\ \chi^{\text{S}\alpha}(t) &= -\int_0^t d\tau \chi^{\text{SS}}(\tau) \phi^\alpha(t-\tau), \end{aligned} \quad (12)$$

and

$$\begin{aligned} \chi^{\alpha\alpha'}(t) &= \int_0^t d\tau \int_0^\tau d\tau' \phi^\alpha(t-\tau) \chi^{\text{SS}}(\tau') \phi^{\alpha'}(\tau-\tau') \\ &\quad + \delta_{\alpha\alpha'} \phi^\alpha(t). \end{aligned} \quad (13)$$

In the frequency domain, $\tilde{f}(\omega) = \int_0^\infty dt e^{i\omega t} f(t)$, the above expressions read

$$\begin{aligned} \tilde{\chi}^{\alpha\text{S}}(\omega) &= -\tilde{\phi}^\alpha(\omega) \tilde{\chi}^{\text{SS}}(\omega), \\ \tilde{\chi}^{\text{S}\alpha}(\omega) &= -\tilde{\chi}^{\text{SS}}(\omega) \tilde{\phi}^\alpha(\omega), \end{aligned} \quad (14)$$

and

$$\tilde{\chi}^{\alpha\alpha'}(\omega) = \tilde{\phi}^\alpha(\omega) \tilde{\chi}^{\text{SS}}(\omega) \tilde{\phi}^{\alpha'}(\omega) + \delta_{\alpha\alpha'} \tilde{\phi}^\alpha(\omega). \quad (15)$$

Moreover, Eq. (4) will also give rise to the expectation values the following input-output relations,²

$$\langle\hat{F}_{\alpha u}\rangle = -\sum_v \eta_{uv}^\alpha \langle\hat{Q}_v\rangle, \quad (16)$$

where

$$\eta_{uv}^\alpha \equiv \int_0^\infty dt \phi_{uv}^\alpha(t). \quad (17)$$

III. ONSET OF HEAT CURRENT

A. Heat current

Let us start with the heat current transferring from the specified α -reservoir to the central system. The related current operator would read [cf. Eq. (1) with Eq. (2)]

$$\hat{J}_\alpha \equiv -\frac{dh_\alpha}{dt} = -i[H_\alpha, h_\alpha] = \sum_u \hat{Q}_u \hat{F}_{\alpha u}. \quad (18)$$

It is noticed there is another convention of heat current operator definition that engages the hybrid bath modes of $\hat{F}_{\alpha u}$ only.¹⁵⁻¹⁷ Others are just linear combinations of above two definitions. The existing dissipaton equation of motion theory can be exploited to the direct evaluation on the transport current and the noise spectrum.¹⁸⁻²⁰

The quantity of interest in this section is

$$J_\alpha \equiv \langle \hat{J}_\alpha \rangle = \sum_u \langle \hat{Q}_u \hat{F}_{\alpha u} \rangle. \quad (19)$$

The direct evaluation can be carried out by exploiting the established dissipaton equation of motion (DEOM) theory.²⁰ In the following, we will establish the extended SBET for the indirect evaluation of Eq. (19). The new theory can be numerically validated with respect to the aforementioned direct evaluations; See Sec. III C.

B. The extended system–bath entanglement theory

It is noticed that the transport current consists of absorptive ($\omega > 0$) and emissive ($\omega < 0$) components. In this contact, we decompose the hybrid bath operator, $\hat{F}_{\alpha u}$ in Eq. (2) as

$$\hat{F}_{\alpha u} = \sum_{\sigma=+,-} \hat{F}_{\alpha u}^\sigma. \quad (20)$$

Mathematically, $\hat{F}_{\alpha u}^\pm$ comprises the linear combination of the creation/annihilation operators associated with the effective bath modes in the canonical ensembles.²¹ In parallel, Eq. (4) is decomposed into its components,

$$\hat{F}_{\alpha u}^\sigma(t) = \hat{F}_{\alpha u}^{\text{B};\sigma}(t) - \sum_v \int_{t_0}^t d\tau \phi_{uv}^{\alpha;\sigma}(t-\tau) \hat{Q}_v(\tau), \quad (21)$$

The involving $\phi_{uv}^{\alpha;\sigma}(t)$ satisfies not only

$$\phi_{uv}^{\alpha;+}(t) + \phi_{uv}^{\alpha;-}(t) = \phi_{uv}^\alpha(t), \quad (22a)$$

but also

$$\begin{aligned} & \phi_{uv}^{\alpha;+}(t) - \phi_{uv}^{\alpha;-}(t) \\ &= \frac{2}{i\pi} \int_0^\infty d\omega \cos(\omega t) \coth(\beta_\alpha \omega / 2) J_{uv}(\omega), \end{aligned} \quad (22b)$$

for the required canonical ensemble properties.

To compute the heat current, Eq. (19), with Eq. (21), we have

$$\begin{aligned} \hat{F}_{\alpha u}^\sigma(t) &= \hat{F}_{\alpha u}^{\text{B};\sigma}(t) - \sum_v \int_{t_0}^t d\tau \dot{\phi}_{uv}^{\alpha;\sigma}(t-\tau) \hat{Q}_v(\tau) \\ &\quad - \sum_v \phi_{uv}^{\alpha;\sigma}(0) \hat{Q}_v(t). \end{aligned} \quad (23)$$

Moreover, the identities $\hat{F}_{\alpha u}^+ = (\hat{F}_{\alpha u}^-)^\dagger$ and $[\hat{F}_{\alpha u}^\sigma, \hat{Q}_v] = 0$ result in

$$\langle \hat{Q}_u \hat{F}_{\alpha u} \rangle = \sum_{\sigma=+,-} \langle \hat{F}_{\alpha u}^\sigma \hat{Q}_u \rangle = \langle \hat{F}_{\alpha u}^+ \hat{Q}_u \rangle + \text{c.c.} \quad (24)$$

Now, it is readily to obtain

$$\langle \hat{Q}_u \hat{F}_{\alpha u} \rangle = -2\text{Re} \sum_v \int_0^\infty d\tau \dot{\phi}_{uv}^{\alpha;+}(\tau) \langle \hat{Q}_v(0) \hat{Q}_u(\tau) \rangle. \quad (25)$$

The involving $\dot{\phi}_{uv}^{\alpha;+}(\tau)$ is determined via Eq. (22). Simple algebra then gives rise to the transport current the final result,

$$J_\alpha = \frac{2}{\pi} \sum_v \int_{-\infty}^\infty d\omega \frac{\omega}{e^{\beta_\alpha \omega} - 1} J_{uv}^\alpha(\omega) C_{vu}(\omega), \quad (26)$$

where

$$C_{vu}(\omega) \equiv \frac{1}{2} \int_{-\infty}^\infty dt e^{i\omega t} \langle \hat{Q}_v(t) \hat{Q}_u(0) \rangle. \quad (27)$$

It is easy to show that Eq. (26) is identical to the Meir–Wingreen’s NEGF formalism.²²

C. Numerical validations and concluding remarks

For illustrations, consider the total composite Hamiltonian, H_T of Eq. (1), with

$$H_S = V(|1\rangle\langle 2| + |2\rangle\langle 1|), \quad (28)$$

$h_B = h_L + h_R$ and

$$H_{\text{SB}} = \sum_{u=1,2} |u\rangle\langle u| (\hat{F}_{Lu} + \hat{F}_{Ru}). \quad (29)$$

Evidently, $\hat{Q}_u = |u\rangle\langle u|$. Adopt further

$$\tilde{\phi}_{uv}^\alpha(\omega) = \delta_{uv} \frac{\eta_u^\alpha \Omega^2}{\Omega^2 - \omega^2 - i\omega\zeta}. \quad (30)$$

Set $\eta_1^L = \eta_2^R = 0.2V$, $\eta_1^R = \eta_2^L = 0.4V$, $\Omega = 2V$, $\zeta = 10V$ and $k_B T_L = 5V$. Table I reports the results of numerical validation at the specified values of T_R/T_L . As mentioned after Eq. (19), the direct evaluation refers to the DEOM results, whereas the indirect ones arise from Eq. (26), through the local system spectra, Eq. (27). The extended SBET, Eq. (26), does hold for arbitrary systems in the nonequilibrium steady–state scenario.

T_R/T_L	0.5	1	1.5	2
Direct	0.01484	0	-0.008757	-0.01435
Indirect	0.01487	0	-0.008773	-0.01435

TABLE I. Direct versus indirect approach to the heat current J_L , as expressed in Eq. (26).

In summary, we revisit the NEGF formalism via the generalized Langevin equation (4). The present approach can be readily extended to the entangled system–bath correlation functions that would be closely related to nonequilibrium thermodynamics in the quantum regime.

ACKNOWLEDGMENTS

Support from the Ministry of Science and Technology No. 2017YFA0204904 and the Natural Science Foundation of China No. 21633006 is gratefully acknowledged.

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