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非平衡体系-热库纠缠定理与热输运

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摘要 将最近建立的体系-热库纠缠定理(SBET)扩展到非平衡的情形. 其中, 任意体系与处于不同温度的多个高斯型热库环境相耦合. 现有的SBET将体系-热库的纠缠响应函数与体系的局域响应函数联系起来, 而扩展的理论则关注通过分子结的非平衡稳态量子输运流. 新理论是基于广义Langevin方程建立的, 它与量子情形下的非平衡热力学密切相关.

关键词 体系-热库纠缠定理; 广义Langevin方程; 非平衡Green函数; 量子输运
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Nonequilibrium System-Bath Entanglement Theorem *Versus* Heat Transport

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Abstract In this work, we extend the recently established system-bath entanglement theorem (SBET) to the nonequilibrium scenario, in which an arbitrary system couples to multiple Gaussian bath environments at different temperatures. The existing SBET connects the entangled system-bath response functions to those of local systems, while 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.

Keywords System-bath entanglement theorem; Generalized Langevin equation; Nonequilibrium Green's function; Quantum transport

1 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 material and quantum information applications.

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Theoretical studies have been mainly carried out in terms of nonequilibrium Green's function (NEGF) methods[1,2].

In this work, we exploit the well-established system-bath entanglement theorem (SBET)[3,4], with extension to nonequilibrium transport scenario. Adopted here is the Gauss-Wick's environment ansatz[5,6] that is commonly adopted in various quantum dissipation theories. These include the formally exact Feynman-Vernon influence functional theory[7], and its time-derivative equivalence the hierarchical equations of motion (HEOM) formalism[8—14]. While the existing SBET deals with response functions only[3,4], 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 conventional 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 is 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[4].

In the present work, we present the well-established SBET for the response functions[3], with extension to the nonequilibrium transport scenario. 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.

2 Extended System-Bath Entanglement Theorem

2.1 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 have constructed the SBET[3,4]. This theorem comprises exact relations between the entangled system-bath response functions and those of local anharmonic systems. Applications have been demonstrated with Fano interference spectroscopy[3]. The SBET has also been exploited in the establishment of the thermodynamic free-energy spectrum theory[4].

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

$$H_{\mathrm{T}} = H_{\mathrm{S}} + h_{\mathrm{B}} + H_{\mathrm{SB}} = H_{\mathrm{S}} + \sum_{\alpha} h_{\alpha} + \sum_{\alpha u} \hat{Q}_u \hat{F}_{\alpha u} \tag{1}$$

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

$$h_{\alpha} = \frac{1}{2}\sum_{j} \omega_{\alpha j}\left(\hat{p}_{\alpha j}^2 + \hat{x}_{\alpha j}^2\right) \text{ and } \hat{F}_{\alpha u} = \sum_{j} c_{\alpha u j}\hat{x}_{\alpha j} \tag{2}$$

respectively, which together constitute the so-called Gauss-Wick's environment[5,6]. The simplicity arises from the fact that the interacting bath commutators are all c-variables, *i. e.*,

$$\phi_{uv}^{\alpha}(t) \equiv i\left[\hat{F}_{\alpha u}^{\mathrm{B}}(t), \hat{F}_{\alpha v}^{\mathrm{B}}(0)\right] = \sum_{j} c_{\alpha u j} c_{\alpha v j} \sin\left(\omega_{\alpha j} t\right) \tag{3}$$

where $\hat{F}_{\alpha u}^{\mathrm{B}}(t) \equiv \mathrm{e}^{ih_{\mathrm{B}}t}\hat{F}_{\alpha u}\mathrm{e}^{-ih_{\mathrm{B}}t} = \mathrm{e}^{ih_{\alpha}t}\hat{F}_{\alpha u}\mathrm{e}^{-ih_{\alpha}t}$. Throughout the paper we set $\hbar = 1$ and $\beta_{\alpha} = k_{\mathrm{B}}T_{\alpha}$, with k_{B} being the Boltzmann constant and T_{α} the α-reservoir temperature. Denote also $\hat{O}(t) \equiv \mathrm{e}^{iH_{\mathrm{T}}t}\hat{O}\mathrm{e}^{-iH_{\mathrm{T}}t}$, with noticing that

$\hat{F}_{\alpha u}(t) \neq \hat{F}^{\rm B}_{\alpha u}(t)$. 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 obtain[3]

$$\hat{F}_{\alpha u}(t) = \hat{F}^{\rm B}_{\alpha u}(t) - \sum_v \int_{t_0}^{t} {\rm d}\tau\, \phi^{\alpha}_{uv}(t-\tau)\hat{Q}_v(\tau) \tag{4}$$

Note that $\phi^{\alpha}_{uv}(t)$ of Eq. (3) can be recast as

$$\phi^{\alpha}_{uv}(t) = i\left\langle\left[\hat{F}^{\rm B}_{\alpha u}(t),\hat{F}^{\rm B}_{\alpha v}(0)\right]\right\rangle_{\alpha} \tag{5}$$

with $\left\langle(\cdot)\right\rangle_{\alpha} \equiv {\rm tr}_{\rm B}[(\cdot){\rm e}^{-\beta_\alpha h_\alpha}]/{\rm tr}_{\rm B}{\rm e}^{-\beta_\alpha h_\alpha}$. The hybridization bath spectral density is given by[14,15]

$$J^{\alpha}_{uv}(\omega) \equiv \frac{1}{2}\int_{-\infty}^{\infty}{\rm d}t\,{\rm e}^{i\omega t}\left\langle[\hat{F}^{\rm B}_{\alpha u}(t),\hat{F}^{\rm B}_{\alpha v}(0)]\right\rangle_{\alpha} \tag{6}$$

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

$$J^{\alpha}_{uv}(\omega) = \frac{\pi}{2}\sum_j c_{\alpha uj}c_{\alpha vj}\left[\delta\left(\omega-\omega_{\alpha j}\right)-\delta\left(\omega+\omega_{\alpha j}\right)\right] \tag{7}$$

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

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 $\phi^{\alpha}_{uv}(t)$ or $J^{\alpha}_{uv}(\omega)$.

2.2 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

$$\chi^{\rm SS}_{uv}(t) \equiv i\left\langle\left[\hat{Q}_u(t),\hat{Q}_v(0)\right]\right\rangle \tag{8}$$

are the input functions, whereas the nonlocal correspondences,

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

and

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

are the output functions. Here,

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

are defined in the total composite space, at nonequilibrium steady-state scenario, with $\left\langle(\cdot)\right\rangle \equiv {\rm Tr}[(\cdot)\rho^{\rm st}_{\rm T}]$, the ensemble average over the total composite space steady-state density operator. It is easily to verify that the established SBET does include the general nonequilibrium scenario[3]. The final results, in terms of the matrices, are

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

and

$$\boldsymbol{\chi}^{\alpha\alpha'}(t) = \int_0^t{\rm d}\tau\int_0^\tau{\rm d}\tau'\,\boldsymbol{\phi}^{\alpha}(t-\tau)\boldsymbol{\chi}^{\rm SS}(\tau')\boldsymbol{\phi}^{\alpha'}(\tau-\tau') + \delta_{\alpha\alpha'}\boldsymbol{\phi}^{\alpha}(t) \tag{13}$$

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

$$\begin{aligned}\tilde{\boldsymbol{\chi}}^{\alpha{\rm S}}(\omega) &= -\tilde{\boldsymbol{\phi}}^{\alpha}(\omega)\tilde{\boldsymbol{\chi}}^{\rm SS}(\omega)\\ \tilde{\boldsymbol{\chi}}^{{\rm s}\alpha}(\omega) &= -\tilde{\boldsymbol{\chi}}^{\rm SS}(\omega)\tilde{\boldsymbol{\phi}}^{\alpha}(\omega)\end{aligned} \tag{14}$$

and

$$\tilde{\chi}^{\alpha\alpha'}(\omega) = \tilde{\boldsymbol{\phi}}^{\alpha}(\omega)\tilde{\chi}^{\rm SS}(\omega)\tilde{\boldsymbol{\phi}}^{\alpha'}(\omega) + \delta_{\alpha\alpha'}\tilde{\boldsymbol{\phi}}^{\alpha}(\omega) \tag{15}$$

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

$$\left\langle \hat{F}_{\alpha u} \right\rangle = -\sum_v \eta^{\alpha}_{uv} \left\langle \hat{Q}_v \right\rangle \tag{16}$$

where

$$\eta^{\alpha}_{uv} \equiv \int_0^{\infty} {\rm d}t\, \phi^{\alpha}_{uv}(t) \tag{17}$$

3 Onset of Heat Current

3.1 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)]

$$\hat{J}_{\alpha} \equiv -\frac{{\rm d}h_{\alpha}}{{\rm d}t} = -i\left[H_{\rm T}, h_{\alpha}\right] = \sum_u \hat{Q}_u \dot{\hat{F}}_{\alpha u} \tag{18}$$

It is noticed there is another convention of heat current operator definition that engages the hybrid bath modes of $\hat{F}_{\alpha u}$ only[16—18]. The 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[19—21].

The quantity of interest in this section is

$$J_{\alpha} \equiv \left\langle \hat{J}_{\alpha} \right\rangle = \sum_u \left\langle \hat{Q}_u \dot{\hat{F}}_{\alpha u} \right\rangle \tag{19}$$

The direct evaluation can be carried out by exploiting the established dissipaton-equation-of-motion (DEOM) theory[21]. 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.

3.2 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

$$\hat{F}_{\alpha u} = \sum_{\sigma = +,-} \hat{F}^{\sigma}_{\alpha u} \tag{20}$$

Mathematically, $\hat{F}_{\alpha u}$ comprises the linear combinations of the creation/annihilation operators associated with the effective bath modes in the canonical ensembles[22]. In parallel, Eq. (4) is decomposed into its components,

$$\hat{F}^{\sigma}_{\alpha u}(t) = \hat{F}^{{\rm B};\sigma}_{\alpha u}(t) - \sum_v \int_{-\infty}^{t} {\rm d}\tau\, \phi^{\alpha;\sigma}_{uv}(t-\tau)\hat{Q}_v(\tau) \tag{21}$$

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

$$\phi^{\alpha;+}_{uv}(t) + \phi^{\alpha;-}_{uv}(t) = \phi^{\alpha}_{uv}(t) \tag{22}$$

but also

$$\phi^{\alpha;+}_{uv}(t) - \phi^{\alpha;-}_{uv}(t) = \frac{2}{i\pi}\int_0^{\infty} {\rm d}\omega \cos(\omega t)\coth\left(\beta_{\alpha}\omega/2\right) J_{uv}(\omega) \tag{23}$$

for the required canonical ensemble properties.

To compute the heat current, Eq. (19), we use Eq. (21) to obtain

$$\dot{\hat{F}}^{\sigma}_{\alpha u}(t) = \dot{\hat{F}}^{{\rm B};\sigma}_{\alpha u}(t) - \sum_v \int_{-\infty}^{t} {\rm d}\tau\, \dot{\phi}^{\alpha;\sigma}_{uv}(t-\tau)\hat{Q}_v(\tau) - \sum_v \phi^{\alpha;\sigma}_{uv}(0)\hat{Q}_v(t) \tag{24}$$

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

$$\left\langle \hat{Q}_u \dot{\hat{F}}_{\alpha u} \right\rangle = \sum_{\sigma=+,-} \left\langle \dot{\hat{F}}^{\sigma}_{\alpha u} \hat{Q}_u \right\rangle = \left\langle \dot{\hat{F}}^{+}_{\alpha u} \hat{Q}_u \right\rangle + \text{c.c.} \tag{25}$$

Now, it is readily to obtain

$$\left\langle \hat{Q}_u \dot{\hat{F}}_{\alpha u} \right\rangle = -2\mathrm{Re} \sum_v \int_0^\infty \mathrm{d}\tau\, \dot{\phi}^{\alpha;+}_{uv}(\tau) \left\langle \hat{Q}_v(0) \hat{Q}_u(\tau) \right\rangle \tag{26}$$

The involving $\dot{\phi}^{\alpha;+}_{uv}(\tau)$ is determined *via* Eqs. (22) and (23). Simple algebra then gives rise to the transport current the final result,

$$J_\alpha = \frac{2}{\pi} \sum_{uv} \int_{-\infty}^{\infty} \mathrm{d}\omega \frac{\omega}{\mathrm{e}^{\beta_\alpha \omega} - 1} J^\alpha_{uv}(\omega) C_{vu}(\omega) \tag{27}$$

where

$$C_{vu}(\omega) \equiv \frac{1}{2} \int_{-\infty}^{\infty} \mathrm{d}t\, \mathrm{e}^{i\omega t} \left\langle \hat{Q}_v(t) \hat{Q}_u(0) \right\rangle \tag{28}$$

It is easy to show that Eq. (27) is identical to the Meir-Wingreen's NEGF formalism[23]. The latter has been constructed on the basis of Schwinger-Keldysh closed time contour formalism[1,2]. Evidently, the present generalized Langevin equation-based approach is much simpler.

3.3 Numerical Validations

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

$$H_\mathrm{S} = V(|1\rangle\langle 2| + |2\rangle\langle 1|) \tag{29}$$

$h_\mathrm{B} = h_\mathrm{L} + h_\mathrm{R}$ and

$$H_\mathrm{SB} = \sum_{u=1,2} |u\rangle\langle u| \left(\hat{F}_{\mathrm{L}u} + \hat{F}_{\mathrm{R}u} \right) \tag{30}$$

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

$$\tilde{\phi}^\alpha_{uv}(\omega) = \delta_{uv} \frac{\eta^\alpha_u \Omega^2}{\Omega^2 - \omega^2 - i\omega\zeta} \tag{31}$$

Set $\eta^\mathrm{L}_1 = \eta^\mathrm{R}_2 = 0.2V$, $\eta^\mathrm{R}_1 = \eta^\mathrm{L}_2 = 0.4V$, $\Omega = 2V$, $\zeta = 10V$, and $k_\mathrm{B} T_\mathrm{L} = 5V$. Table 1 reports the results of numerical validation at the specified values of $T_\mathrm{R}/T_\mathrm{L}$. As mentioned after Eq. (19), the direct results arise from the DEOM method[21], whereas the indirect ones arise from Eq. (27), through the local system spectra, Eq. (28). The extended SBET, Eq. (27), does hold for arbitrary systems in the nonequilibrium steady-state scenario.

Table 1 Direct *versus* indirect approach to the heat current J_L, as expressed in Eq.(27)

$T_\mathrm{R}/T_\mathrm{L}$	0.5	1	1.5	2.0
Direct approach	0.01484	0	−0.008757	−0.01435
Indirect approach	0.01487	0	−0.008773	−0.01435

4 Conclusions

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.

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