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Green's functions perspective on nonequilibrium thermodynamics of open quantum systems strongly coupled to baths

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We give nonequilibrium Green's function (NEGF) perspective on thermodynamics formulations for open quantum systems strongly coupled to baths. Scattering approach implying thermodynamic consideration of a super-system (system plus baths) weakly coupled to external super-baths is compared with consideration of thermodynamics of a system strongly coupled to its baths. We analyze both approaches from the NEGF perspective and argue that the latter yields a possibility of thermodynamic formulation consistent with dynamical (quantum transport) description.

I. INTRODUCTION

Tremendous progress in experimental techniques in the last decade resulted in miniaturization of devices for energy storage and conversion making use of quantum effects possible. One of such experimental developments is study of thermoelectric effects in nanoscale single atom and single molecule junctions¹⁻⁵. Such quantum devices are characterized by efficiency of their performance⁶⁻⁸, and traditional characteristics (such as, e.g., figure of merit) taken from studies on macroscopic equilibrium thermoelectric systems are often utilized. Clearly, macroscopic thermodynamics underlying such characteristics is not applicable at nanoscale. Meaningful description of efficiency in nanoscale junctions requires corresponding development of quantum nonequilibrium thermodynamic theory. Moreover, in junctions with molecules chemisorbed on (at least one of the) macroscopic contacts thermodynamic theory should account for non-negligible (strong) system-baths couplings.

Significant theoretical effort was undertaken to formulate nanoscale thermodynamics at strong system-bath coupling for both classical^{9,10} and quantum¹¹⁻¹³ systems. Arguably, there are two main approaches to the problem. First approach complements physical system strongly coupled to its baths with set of additional super-baths and implements standard methods in consideration of super-system (system plus baths) weakly coupled to its super-baths. System thermodynamics is defined as a difference between thermodynamic characterization of such super-system and that of set of free baths weakly coupled to corresponding super-baths. Second approach builds thermodynamic description for the physical system, i.e. system strongly coupled to its baths. In addition to developments of thermodynamic formulations, an interesting widely debated question is possibility of thermodynamics being consistent with underlying system dynamics^{14,15}.

Here, we consider a generic model of molecular junction with non-negligible (strong) molecule-contacts couplings. We utilize nonequilibrium Green's function (NEGF) to describe dynamics of the system and discuss compatibility of the dynamic consideration with several suggestions for thermodynamic characterization of such

systems available in the literature. We present general NEGF formulations (beyond usually assumed slow driving) for thermodynamic characteristics of the system and argue that difficulties of Green's function based analysis of supersystem-superbath thermodynamic treatments are caused by incompatibility of basic assumptions in the two theories. System-bath thermodynamic formulations are found to be compatible with NEGF dynamics. Structure of the paper is the following. Section II introduces model and presents basics of the dynamical NEGF treatment. Thermodynamic NEGF based formulations are presented in Section III for supersystem-superbath and in Section IV for system-bath considerations. Section V summarizes our findings.

II. DYNAMICAL CONSIDERATION

We consider an open non-interacting nonequilibrium quantum system S (e.g., molecule with its electronic structure calculated using DFT) strongly coupled to its baths $\{B\}$ (e.g., metallic contacts in the junction). The system is subjected to an arbitrary external driving. Hamiltonian of the model is

$$\hat{H}(t) = \hat{H}_S(t) + \sum_B \left(\hat{H}_B + \hat{V}_{SB}(t) \right) \quad (1)$$

where $\hat{H}_S(t)$ and \hat{H}_B are Hamiltonians of the system and bath B , respectively; $\hat{V}_{SB}(t)$ describes coupling (electron transfer) between system S and bath B . Explicit expressions are

$$\hat{H}_S(t) = \sum_{m_1, m_2 \in S} H_{m_1 m_2}^{(S)}(t) \hat{d}_{m_1}^\dagger \hat{d}_{m_2}, \quad (2)$$

$$\hat{H}_B = \sum_{k \in B} \varepsilon_k \hat{c}_k^\dagger \hat{c}_k, \quad (3)$$

$$\hat{V}_{SB}(t) = \sum_{m \in S} \sum_{k \in B} \left(V_{mk}(t) \hat{d}_m^\dagger \hat{c}_k + H.c. \right), \quad (4)$$

where \hat{d}_m^\dagger (\hat{d}_m) and \hat{c}_k^\dagger (\hat{c}_k) create (annihilate) electron in orbital m of the molecule and single-particle state k of a contact, respectively.

For such a non-interacting model one can easily simulate exact projections of the single-electron Green's function

$$G_{n_1 n_2}(\tau_1, \tau_2) \equiv -i \langle T_c \hat{a}_{n_1}(\tau_1) \hat{a}_{n_2}^\dagger(\tau_2) \rangle \quad (5)$$

Here, n_i are indices for single-particle state either on the molecule or in the baths, i.e. \hat{a}_n is either \hat{d}_m or \hat{c}_k .

Dynamical (quantum transport) consideration defines particle, I_B , and energy, J_B , fluxes at $S - B$ interface as (minus) rates of change of, respectively, particles and energy in the bath B . Exact expressions for the fluxes in terms of single particle Green's functions are obtained following Jauho-Wingreen-Meir¹⁶ and similar¹⁷ derivations

$$I_B(t) \equiv - \sum_{k \in B} \frac{d}{dt} \langle \hat{c}_k^\dagger(t) \hat{c}_k(t) \rangle = -\text{Tr} \left[\hat{N}_B \frac{d}{dt} \hat{\rho}(t) \right] = \sum_{k \in B} \text{Tr}_S [\mathbf{I}_k^{(+)}(t) - \mathbf{I}_k^{(-)}(t)] \quad (6)$$

$$J_B(t) \equiv - \sum_{k \in B} \varepsilon_k \frac{d}{dt} \langle \hat{c}_k^\dagger(t) \hat{c}_k(t) \rangle = -\text{Tr} \left[\hat{H}_B \frac{d}{dt} \hat{\rho}(t) \right] = \sum_{k \in B} \varepsilon_k \text{Tr}_S [\mathbf{I}_k^{(+)}(t) - \mathbf{I}_k^{(-)}(t)] \quad (7)$$

Here, $\hat{N}_B \equiv \sum_{k \in B} \hat{c}_k^\dagger \hat{c}_k$ is the operator of particle number in bath B , $\hat{\rho}(t)$ is the total (system plus baths) density operator, $\text{Tr}[\dots]$ and $\text{Tr}_S[\dots]$ are traces over total (system plus baths) and system (molecular) degrees of freedom, $\mathbf{I}_k^{(+)/(-)}$ are matrices in subspace S representing k -resolved in-/out-scattering particle fluxes at the $S - B$ interface

$$[\mathbf{I}_k^{(+)}]_{m_1 m_2} = 2 \text{Re} \int_{-\infty}^t dt' (V_{m_1 k}(t) g_k^<(t-t') V_{k m_2}(t') G_{m_2 m_1}^>(t', t)) \quad (8)$$

$$[\mathbf{I}_k^{(-)}]_{m_1 m_2} = 2 \text{Re} \int_{-\infty}^t dt' (V_{m_1 k}(t) g_k^>(t-t') V_{k m_2}(t') G_{m_2 m_1}^<(t', t)) \quad (9)$$

$G_{m_2 m_1}^{\lessgtr}$ are lesser/greater projections of the molecular space single particle Green's function (5), and $g_k(\tau_1, \tau_2) \equiv -i \langle T_c \hat{c}_k(\tau_1) \hat{c}_k^\dagger(\tau_2) \rangle$ is Green's function of free electron in bath B . Note, definition (7) assumes $\langle \hat{H}_B \rangle$ to be energy of bath B , so that dynamical approach sets

$$E_S(t) = \left\langle \hat{H}_S(t) + \sum_B \hat{V}_{SB}(t) \right\rangle \quad (10)$$

as energy of the system.

III. SUPERSYSTEM WEAKLY COUPLED TO SUPERBATHS

At equilibrium, thermodynamics of the system strongly coupled to its bath (one bath, B , is enough at equilibrium) is modeled as difference in thermodynamic description (difference of grand potentials) of supersystem (system plus bath) weakly coupled to superbath (additional external bath) and bath weakly coupled to the superbath. The approach was pioneered in Refs. 18,19. It allows to utilize standard (weakly coupled) thermodynamic description to derive grand potential, entropy and

energy of the system as²⁰

$$\Omega_S^{eq} = \frac{1}{\beta_B} \int \frac{dE}{2\pi} \mathcal{A}_B(E) \ln[1 - f_B(E)] \quad (11)$$

$$S^{eq} \equiv - \frac{\partial \Omega_S^{eq}}{\partial T_B} = \int \frac{dE}{2\pi} \mathcal{A}_B(E) \sigma_B(E) \quad (12)$$

$$\begin{aligned} E_S^{eq} &\equiv \Omega_S^{eq} + \mu_B N_B^{eq} + \frac{1}{\beta_B} S^{eq} = \Omega_S^{eq} - \mu_B \frac{\partial \Omega_S^{eq}}{\partial \mu_B} + \frac{1}{\beta_B} S^{eq} \\ &= \int \frac{dE}{2\pi} E \mathcal{A}_B(E) f_B(E) \end{aligned} \quad (13)$$

Here, $\beta_B = 1/k_B T_B$, $\sigma_B(E)$ is the energy-resolved Shannon entropy

$$\sigma_B(E) = - \left(f_B(E) \ln f_B(E) + [1 - f_B(E)] \ln[1 - f_B(E)] \right) \quad (14)$$

and $\mathcal{A}_B(E)$ is the renormalized spectral function

$$\mathcal{A}_B(E) = A(E) - 2 \text{Im} \sum_{k \in B} \left[G_{kk}^r(E) - g_k^r(E) \right] \quad (15)$$

with

$$A(E) = -2 \text{Im} \sum_{m \in S} G_{mm}^r(E) \quad (16)$$

being the usual spectral function of the system.

At nonequilibrium, expressions (12) and (13) are used as templates for *ad hoc* formulations of energy and entropy by substituting spectral functions and/or Fermi distributions with their nonequilibrium analogs at slow driving^{20–22}. Expressions for system characteristics at slow driving are obtained employing gradient expansion^{23,24}. More consistent approaches to nonequilibrium reformulate equilibrium consideration of Refs. 18,19 in the basis of scattering states²⁵. In this formulation superbaths provide thermal distributions of the scattering states. Parametric dependence of scattering matrix on time developed for adiabatic quantum pumps in Ref. 26 is utilized to obtain nonequilibrium system behavior at slow driving. It was shown within such thermodynamic considerations^{20,27–29} that consistent (dynamic-to-thermodynamic) description can be obtained within the wide-band approximation (WBA) and for driving confined to the system Hamiltonian $\hat{H}_S(t)$, if energy of the system is taken as

$$E_S(t) = \left\langle \hat{H}_S(t) + \frac{1}{2} \sum_B \hat{V}_{SB}(t) \right\rangle \quad (17)$$

Similar separation of the total Hamiltonian is assumed in recent density matrix based approaches^{30–33}. Extension of the formulation to account for driving in the system-bath coupling was claimed⁴² in Ref. 22. Note that definition (17) deviates from the dynamical definition (10).

Before proceeding to Green's function based analysis we want to stress several points. First, definition (17) modifies energies of the baths adding half of system-bath coupling into the bath's energy. This addition induces mixing between baths making full counting statistics formulation impossible. Thus, it is natural that definition (17) fails to describe energy fluctuations³⁴. Second, simple single particle scattering formulation is only possible for noninteracting systems and adiabatically slow driving, when scattering channels are independent of each other. Indeed, scattering theory yields the famous Landauer-Büttiker formalism applicable in description of steady-states in noninteracting systems. Finite driving and/or presence of interactions requires more elaborated description. Third, consistent thermodynamic description employing definition (17) was only possible in the wide-band approximation (WBA) where renormalization of the spectral function is dropped, i.e. $\mathcal{A}(E) = A(E)$. As we show below, extension of the formulation beyond the WBA is impossible when (17) is taken as energy of the system.

We now turn to NEGF analysis of the two definitions for system energy, Eqs. (10) and (17), with the goal to establish their consistency with the expected limiting (equilibrium) expression, Eq. (13), as obtained from general result for a noninteracting system (1)-(4) under arbitrary driving and beyond wide-band approximation. To do so we are going to express contributions to the total energy, i.e. averages of terms in the total Hamiltonian (1), in terms of Green's functions utilizing Wigner representa-

tion in time variables

$$\begin{aligned} F(t; s) &= F(t_1, t_2) \\ F(t; E) &= \int ds e^{-iEs} F(t; s) \end{aligned} \quad (18)$$

Here, $t = (t_1 + t_2)/2$ and $s = t_1 - t_2$.

First, it is straightforward to see that

$$\begin{aligned} \langle \hat{H}_S(t) \rangle &= -i \sum_{m_1, m_2 \in S} H_{m_1 m_2}^{(S)}(t) G_{m_2 m_1}^<(t, t) \\ &= -i \int \frac{dE}{2\pi} \text{Tr}_S [\mathbf{H}^{(S)} \mathbf{G}^<(t; E)] \end{aligned} \quad (19)$$

Second, for system-baths coupling we get

$$\begin{aligned} \sum_B \langle \hat{V}_{SB}(t) \rangle &= 2 \text{Im} \sum_B \sum_{m \in S} \sum_{k \in B} V_{mk}(t) G_{km}^<(t, t) \\ &= 2 \text{Im} \int_{-\infty}^{+\infty} dt' \text{Tr}_S [\Sigma^<(t, t') \mathbf{G}^a(t', t) + \Sigma^r(t, t') \mathbf{G}^<(t', t)] \\ &= 2 \text{Im} \text{Tr}_S \left[\left(i \frac{\partial \mathbf{G}^<(t, t')}{\partial t} \right)_{t=t'} - \mathbf{H}^{(S)}(t) \mathbf{G}^<(t, t) \right] \\ &\equiv -2i \int \frac{dE}{2\pi} E \text{Tr}_S [\mathbf{G}^<(t; E)] - 2 \langle \hat{H}_S(t) \rangle \end{aligned} \quad (20)$$

where transition from first to second line uses integral form of Dyson equation for $G_{km}^<(t, t)$, third line is obtained employs differential from of left side Dyson equation for $G_{m_1 m_2}^<(t, t)$ together with assumption of noninteracting character of the system, i.e. $\Sigma(\tau, \tau') = \sum_B \Sigma_B(\tau, \tau')$, and last line is obtained by using Wigner representation (18) for the first term and by using Eq. (19) for the second term.

Third, for baths contributions to the total energy one has

$$\begin{aligned} \sum_B \langle \hat{H}_B \rangle &= -i \sum_B \sum_{k \in B} \varepsilon_k G_{kk}^<(t, t) \\ &= \sum_B \sum_{k \in B} \text{Im} \left[\left(i \frac{\partial G_{kk}^<(t, t')}{\partial t} \right)_{t=t'} - \sum_{m \in S} V_{km}(t) G_{mk}^<(t, t) \right] \\ &= \text{Im} \left[\sum_B \sum_{k \in B} \left(i \frac{\partial G_{kk}^<(t, t')}{\partial t} \right)_{t=t'} - \sum_{m \in S} \left(i \frac{\partial G_{mm}^<(t, t')}{\partial t} \right)_{t=t'} \right. \\ &\quad \left. + \sum_{m_1, m_2 \in S} H_{m_1 m_2}^{(S)}(t) G_{m_2 m_1}^<(t, t) \right] \\ &= -i \int \frac{dE}{2\pi} E \left(\text{Tr}_B [\mathbf{G}^<(t; E)] - \text{Tr}_S [\mathbf{G}^<(t; E)] \right) + \langle \hat{H}_S(t) \rangle \end{aligned} \quad (21)$$

Here, transitions from first to second and from second to third and fourth lines utilize differential forms of left side Dyson equations for $G_{kk}^<(t, t)$ and $G_{mm}^<(t, t)$, respectively. As previously, last line is obtained by using Wigner representation (18) for the first and second terms and by

using Eq. (19) for the last term. Similarly, for free baths evolution one has

$$\begin{aligned} \sum_B \langle \hat{H}_B \rangle_0 &= -i \sum_B \sum_{k \in B} \varepsilon_k g_k^<(t, t) \\ &= \sum_B \sum_{k \in B} \text{Im} \left[\left(i \frac{\partial g_k^<(t, t')}{\partial t} \right)_{t=t'} \right] \quad (22) \\ &= -i \int \frac{dE}{2\pi} E \text{Tr}_B \mathbf{g}^<(E) \end{aligned}$$

where $\mathbf{g}^<(E)$ does not contain dependence on t due to absence of driving in baths.

We note that contrary to previous considerations expressions (19)-(22) are not limited to slow driving – for non-interacting model (1)-(4) they are exact. Eqs. (19) and (20) show that dynamical definition (10) does not yield expected within the approach equilibrium behavior (13), while scattering theory based suggestion, Eq. (17), leads to

$$\left\langle \hat{H}_S(t) + \frac{1}{2} \sum_B \hat{V}_{SB}(t) \right\rangle = -i \int \frac{dE}{2\pi} E \text{Tr}_S [G^<(t, E)] \quad (23)$$

At equilibrium, this expression yields result similar to (13) but with $\mathcal{A}(E)$ substituted with $A(E)$, i.e. one gets the form of correct limiting expression in the wide band approximation (WBA). It is clear from the derivation above that generalization beyond WBA is not possible when using (17) as definition for system energy.

To get the expected equilibrium behavior, Eq. (13), one has to assume

$$E_S(t) = \left\langle \hat{H}_S(t) + \sum_B \left(\hat{H}_B + \hat{V}_{SB}(t) \right) \right\rangle - \left\langle \sum_B \hat{H}_B \right\rangle_0 \quad (24)$$

as expression for system energy. Here, $\langle \dots \rangle = \text{Tr}[\dots \hat{\rho}(t)]$ and $\langle \dots \rangle_0 = \text{Tr}[\dots \hat{\rho}_0]$ with $\hat{\rho}_0$ being density operator of free decoupled system and baths evolution. Indeed, substituting (19)-(22) into (24) leads to

$$E_S(t) = -i \int \frac{dE}{2\pi} E \left(\text{Tr}[\mathbf{G}^<(t, E)] - \text{Tr}_B[\mathbf{g}^<(E)] \right) \quad (25)$$

which yields the expected equilibrium behavior.

We note that expression (24) is very logical in a sense that it follows philosophy of defining system characteristics as difference between those of supersystem and free baths. At the same time, it reveals basic incompatibility between supersystem weakly coupled to superbaths thermodynamic approach and standard NEGF dynamical formulation. Lack of superbaths concept in the latter does not allow to meaningfully introduce heat in any attempt of combining the two descriptions.

IV. SYSTEM STRONGLY COUPLED TO BATHS

A variant of thermodynamic formulation for system strongly coupled to its baths was proposed in Refs. 35, 36. As expected, in absence of superbaths definition of system energy

$$E_S(t) = \left\langle \hat{H}_S(t) + \sum_B \hat{V}_{SB}(t) \right\rangle - \left\langle \hat{H}_S(t) + \sum_B \hat{V}_{SB}(t) \right\rangle_0 \quad (26)$$

and expression for energy flux are consistent with dynamical NEGF results - Eq. (10) and (7), respectively. Similar to the supersystem-superbath thermodynamics, system-bath formulation is also based on a set of *ad hoc* assumptions. In particular, Ref. 35 assumes entropy of the system strongly coupled to its baths to be given by the Shannon entropy

$$S(t) \equiv -\text{Tr}_S [\hat{\rho}_S(t) \ln \hat{\rho}_S(t)] \quad (27)$$

where $\hat{\rho}_S(t) = \text{Tr}_B[\hat{\rho}(t)]$ is the many-body density operator of the system. Below we show how entropy, Eq. (27), and the second law of thermodynamics can be expressed in terms of Green's functions.

First, we note that for quadratic Hamiltonian (1)-(4) the Wick's theorem holds for the whole universe (system plus baths) or any of its parts. This means that corresponding many-body density operator should have a Gaussian form. In particular, system density operator has the form

$$\hat{\rho}_S(t) = \frac{1}{Z_S(t)} \exp \left(- \sum_{m_1, m_2 \in S} h_{m_1 m_2}^{(S)}(t) \hat{d}_{m_1}^\dagger \hat{d}_{m_2} \right) \quad (28)$$

where $Z_S(t)$ is a normalization constant. The form (28) is mathematically similar to equilibrium case, so that for fixed t standard tools of equilibrium path integral consideration can be applied. In particular, we can consider the form (28) as an equilibrium density matrix with 'effective Hamiltonian' $\sum_{m_1, m_2 \in S} h_{m_1 m_2}^{(S)}(t) \hat{d}_{m_1}^\dagger \hat{d}_{m_2}$ and inverse temperature $\beta_S = 1$.

Using results of equilibrium consideration for non-interacting Hamiltonians³⁷ one gets

$$Z_S(t) = \det [i\mathbf{G}^>(t, t)]^{-1} \quad (29)$$

$$\begin{aligned} e^{-\mathbf{h}^{(S)}(t)} &= (i\mathbf{G}^>(t, t))^{-1} (-i\mathbf{G}^<(t, t)) \\ &= (-i\mathbf{G}^<(t, t)) (i\mathbf{G}^>(t, t))^{-1} \end{aligned} \quad (30)$$

Thus,

$$\begin{aligned} \rho_S(t) &= \frac{1}{Z_S(t)} e^{-\mathbf{h}^{(S)}(t)} \\ &= \det [i\mathbf{G}^>(t, t)] (-i\mathbf{G}^<(t, t)) (i\mathbf{G}^>(t, t))^{-1} \quad (31) \\ &= \det [i\mathbf{G}^>(t, t)] (i\mathbf{G}^>(t, t))^{-1} (-i\mathbf{G}^<(t, t)) \end{aligned}$$

Here, $\mathbf{G}^{\gtrless}(t, t)h$ are matrices of greater/lesser projection of Green's function (5) in the system subspace of the

problem, $\rho_S(t)$ is the system density matrix (representation of operator $\hat{\rho}_S(t)$ in the single-particle basis of S). Similar expressions were derived in Refs. 38–41.

Using (31) in (27) and employing $\ln \det \mathbf{M} = \text{Tr} \ln \mathbf{M}$ (\mathbf{M} is a matrix) leads to

$$S(t) = -\text{Tr}_S \left[-i\mathbf{G}^<(t, t) \ln (-i\mathbf{G}^<(t, t)) \right] - \text{Tr}_S \left[i\mathbf{G}^>(t, t) \ln (i\mathbf{G}^>(t, t)) \right] \quad (32)$$

Here, $-i\mathbf{G}^<(t, t)$ is the single-particle density matrix $\rho_S(t)$ and $i\mathbf{G}^>(t, t) - i\mathbf{G}^<(t, t) = \mathbf{I}$ (\mathbf{I} is the unity matrix). Note that (32) holds for any driving.

Taking time derivative of the entropy (32) leads to the second law of thermodynamics in the form

$$\begin{aligned} \frac{d}{dt} S(t) &= \text{Tr}_S \left[\left(-i \frac{d}{dt} \mathbf{G}^<(t, t) \right) \ln \frac{i\mathbf{G}^>(t, t)}{-i\mathbf{G}^<(t, t)} \right] \\ &\equiv \sum_B \sum_{k \in B} \text{Tr}_S \left[\beta_B (\varepsilon_k - \mu_B) [\mathbf{I}_k^{(+)}(t) - \mathbf{I}_k^{(-)}(t)] + [\mathbf{I}_k^{(+)}(t) - \mathbf{I}_k^{(-)}(t)] \ln \frac{\mathbf{G}^>(t, t) g_k^<(t, t)}{\mathbf{G}^<(t, t) g_k^>(t, t)} \right] \\ &= \sum_B [\beta_B \dot{Q}_B(t) + \Delta_i \dot{S}_B(t)] \end{aligned} \quad (33)$$

Here, $\dot{Q}_B \equiv J_B(t) - \mu_B I_B(t)$ is the heat flux expressed in terms of particle, I_B , and energy, J_B , fluxes at $S - B$ interface, whose definitions are given by the dynamical NEGF expressions (6) and (7), respectively. $\Delta_i \dot{S}(t) = \sum_B \Delta_i \dot{S}_B$ defined by the second term in the middle line of (33) is the rate of entropy production which (as was discussed in Ref. 35) may be negative.

V. CONCLUSION

We considered two different approaches to thermodynamic formulations for open nonequilibrium quantum systems strongly coupled to their baths: supersystem (system plus baths) weakly coupled to superbaths and system strongly coupled to its baths. In particular, the former encompasses popular scattering theory formulations of quantum thermodynamics. We analyzed compatibility of the formulations with dynamical description of the system within the nonequilibrium Green's function approach. We presented thermodynamics formulation within NEGF beyond slow driving. Results for adiabatic driving and equilibrium can be derived from our consideration as limiting cases. Our analysis shows that supersystem-superbath formulations are based on set of assumptions which are incompatible with basics of the dynamical NEGF formulation. In particular, this

is the cause for difference in definition of energy flux accepted in the two approaches. At the same time, the system-bath formulation is consistent with NEGF, and definitions of energy fluxes are equivalent in this thermodynamic formulation to those of dynamic NEGF description. For the system-bath formulation we present expressions for entropy and entropy production in terms of Green's functions. It is interesting to note that while supersystem-superbath formulations postulate energy resolved Shannon-like expression for entropy of the system, system-bath approach assumes entropy of the system to be given by Shannon expression constructed from system characteristics integrated in energy. We note that both expressions for system entropy, nonequilibrium analog of Eq. (12) and Eq. (32), are *ad hoc* formulations, and possibility of construction of energy-resolved formulation consistent with dynamical NEGF description is still an open question.

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