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Nonequilibrium Thermodynamics and Steady State Density Matrix for Quantum Open Systems

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Abstract: We consider the generic model of a finite-size quantum electron system connected to two (temperature and particle) reservoirs. The quantum open system is driven out of equilibrium by the presence of both potential temperature and chemical differences between the two reservoirs. The nonequilibrium (NE) thermodynamical properties of such a quantum open system are studied for the steady state regime. In such a regime, the corresponding NE density matrix is built on the so-called generalised Gibbs ensembles. From different expressions of the NE density matrix, we can identify the terms related to the entropy production in the system. We show, for a simple model, that the entropy production rate is always a positive quantity. Alternative expressions for the entropy production are also obtained from the Gibbs–von Neumann conventional formula and discussed in detail. Our results corroborate and expand earlier works found in the literature.

Keywords: quantum open systems; nonequilibrium steady state; generalised Gibbs ensembles; entropy

1. Introduction

The understanding of irreversible phenomena is a long-standing problem in statistical mechanics. Explanations of the fundamental laws of phenomenological nonequilibrium (NE) thermodynamics have been given and applied to quantum open systems for several decades [1,2]. More recent discussions on the origin of thermodynamical laws at the nanoscale can be found in, for example, [3]. Originally the weak coupling limit of a finite-size central region interacting with thermal and/or particle baths was first considered [1,2,4–6]. Methods for dealing with the strong coupling limit have been recently developed [7–14]. One can study the NE thermodynamical properties and the entropy production in such systems when an external driving force is applied to the central region. The time dependence of the external force can be arbitrary or periodic [10,11,13,15]. The long-time limit behaviour of the NE thermodynamics also presents very interesting properties [12–14].

Indeed, after some time much longer than some typical relaxation times of the finite system, a steady state can be obtained. Such a state arises from the balance between irreversible processes (fluxes of particle and/or energy) and the driving forces induced by the reservoirs. The NE steady state presents some analogy to its equilibrium counterpart in the sense that an equilibrium state represents a stationary state of a closed system, while the NE steady state is the time-invariant state of an open system. The fact that the NE steady state can be seen as a pseudo-equilibrium state is central to the construction of the corresponding generalised Gibbs ensembles [16–21] and to the calculation of the entropy, heat or work production under NE conditions.

In the present paper, we construct such a generalised Gibbs expression for the NE density matrix and apply it to the calculation of the entropy production in the system under the presence of both a temperature difference and a chemical potential difference between the two reservoirs. Our approach has no restriction for the nature of the coupling (strong or weak) to the reservoirs, nor for the presence (or absence) of interaction between particle in the central region.

In Section 2, we provide different, but fully compatible, expressions for the NE density matrix and show that the new terms in the NE density matrix (new in the sense that they do not appear in the equilibrium grand-canonical density matrix) are associated with the entropy production under the NE conditions. The entropy production rate is shown to be related to the fluxes of particle and heat across the system (Section 3). We provide in Section 3.2 some numerical calculations of the entropy production rate for a model system of a single electron resonance coupled to two Fermi reservoirs. A comparison to earlier results [11] is also given. In Section 4, we consider the NE entropy production in the entire system obtained from the Gibbs–von Neumann expression based on the NE density matrix. Explicit derivations are provided in some limiting cases and it is shown that NE entropy is produced not only in the central region but also in the reservoirs. For the single resonance model, we also calculate the NE Gibbs–von Neumann entropy in the central region and present the corresponding results in Section 4.2. Our approach corroborates and extends earlier existing results. Furthermore, it opens a new route to the calculations of the full NE response functions of the system, such as the NE charge susceptibility [22] or the NE specific heat of the central region.

2. Non-Equilibrium Steady State

2.1. System and Initial Conditions

We consider a finite-size central region C , with two connected electrodes (left L and right R) acting as thermal and particle reservoirs. These electrodes are described within the thermodynamics limit. Initially, they are at their own equilibrium, characterized by two temperatures T_L and T_R , and by two chemical potentials μ_L and μ_R . Furthermore, we ignore the interaction between particles in the electrodes, although the central region C may contain such kind of interaction. We are interested in steady state regime, and, therefore, we take the initial state of the system to be in the far remote past. The system is then characterised by a Hamiltonian H_0 . After all parts of the system are “connected” together and after some time elapses, the full system is considered to reach an NE steady state. The system is then characterised by the total Hamiltonian $H = H_0 + W$.

The questions related to the possibility of reaching an NE steady-state have been addressed in [23–31]. It has also been argued that a system will always reach a steady-state if it is a (or if it is connected to another) system in the thermodynamic limit, regardless of the presence (or absence) of adiabatic switching of the interactions [32,33].

In the present paper, we consider that the full system is described by the Hamiltonian $H = H_0 + W$, where H_0 is the non-interacting Hamiltonian $H_0 = H_L + H_C + H_R$ built from the three independent regions L, C, R . The interaction W is decomposed into several parts $W = V_{LC} + V_{CL} + V_{RC} + V_{CR} + V_C^{\text{int}}$, where the interaction between particles in region C is given by V_C^{int} and the coupling between the C region and the $\alpha = L, R$ reservoirs is given by $V_{\alpha C} + V_{C\alpha}$. Without specifying explicitly the form of H_0 , there exist different important commutation relations, i.e.,

$$[H_\alpha, H_\beta] = 0, \quad [H_\alpha, N_\beta] = 0, \quad [N_\alpha, N_\beta] = 0, \quad (1)$$

with $\alpha, \beta = L, C, R$ and N_β being the occupation number operator of the different regions $\alpha, \beta = L, C, R$.

Initially, all regions L, C, R are isolated and characterised by their respective density matrix ρ_α with $\alpha = L, C, R$. The macroscopic L and R regions are represented by a density matrix $\rho_{L,R}$ expressed in the grand canonical ensemble, with temperature $T_\alpha = 1/k\beta_\alpha$ and chemical potential μ_α ($\alpha = L, R$):

$$\rho_\alpha = \frac{1}{Z_\alpha} e^{-\beta_\alpha (H_\alpha - \mu_\alpha N_\alpha)}, \quad (2)$$

with $Z_\alpha = \text{Tr}_{(\alpha)} [e^{-\beta_\alpha (H_\alpha - \mu_\alpha N_\alpha)}]$ and $\text{Tr}_{(\alpha)}$ implying a summation only over the states of the region α . The initial density matrix of the central region is assumed to take any arbitrary form ρ_C as this region is not in the thermodynamic limit. Furthermore, considering ρ_C to be given by a canonical or a grand

canonical ensemble would imply the presence of the third reservoir, which is not ideal in the present case. Therefore, we define ρ_C from a microcanonical ensemble where

$$\rho_C = \rho_C(H_C) = Z_C^{-1} \sum_n |C_n\rangle \delta_\Delta(\epsilon_n - E_C) \langle C_n| \quad (3)$$

with the eigenstates $H_C|C_n\rangle = \epsilon_n|C_n\rangle$. The δ_Δ function is the “regularized” delta function defined by $\delta_\Delta(\epsilon_n - E_C) = 1$ for $E_C \leq \epsilon_n \leq E_C + \Delta$ and 0 otherwise, and $Z_C = \text{Tr}_{(C)}[\delta_\Delta(H_C - E_C)]$.

The total density matrix ρ_0 as the non-interacting state defined by H_0 is given by the direct product $\rho_0 = \rho_L \otimes \rho_C \otimes \rho_R$.

2.2. The NE Density Matrix ρ^{NE}

In Reference [34], we used some concepts developed for asymptotic steady-state operators [35–40] and we have shown that the average of any arbitrary operator A in the NE asymptotic steady state is given by

$$\langle A \rangle^{\text{NE}} = \text{Tr}[\rho^{\text{NE}} A], \quad (4)$$

where ρ^{NE} is the NE steady state density matrix. One should also note that the trace in Equation (4) runs over all the states of the three L, C, R regions. The NE density matrix is defined from $\rho^{\text{NE}} = \Omega^{(+)} \rho_0 \Omega^{(+)-1}$, where the Moeller operator [41–44], characterising the asymptotic steady state, is given by: $\Omega^{(+)} = \lim_{\tau \rightarrow -\infty} e^{iH\tau} e^{-iH_0\tau}$. Such an operator presents a central property, the intertwining relation [40–44], $\Omega^{(+)} H_0 = H \Omega^{(+)}$, or equivalently $H_0^{(+)} = \Omega^{(+)} H_0 \Omega^{(+)-1} = H$.

By defining any asymptotic operator as $X_\alpha^{(+)} = \Omega^{(+)} X_\alpha \Omega^{(+)-1}$, it can be shown from Equation (1) that, when $X_\alpha = H_\alpha$ or $X_\alpha = N_\alpha$, we have the following relation:

$$[X_\alpha^{(+)}, H] = \Omega^{(+)} [X_\alpha, H_0] \Omega^{(+)-1} = 0. \quad (5)$$

Hence, any linear combination $Y^a = \sum_\alpha a_\alpha X_\alpha^{(+)}$ also commutes with H : $[Y^a, H] = 0$. The quantity Y^a will be called a conserved quantity in the following. Furthermore, for $Y^b = \sum_\beta b_\beta X_\beta^{(+)}$, it can be shown that $[Y^a, Y^b] = 0$ when $X_{\alpha,\beta} = H_{\alpha,\beta}$ or $N_{\alpha,\beta}$. This follows from Equation (1) and consequently from $[X_\alpha^{(+)}, X_\beta^{(+)}] = 0$.

We have now all the ingredients to study different expressions of the NE density matrix ρ^{NE} in the steady state [35,40]. The latter can be recast as

$$\begin{aligned} \rho^{\text{NE}} &= \Omega^{(+)} \rho_0 \Omega^{(+)-1} = \Omega^{(+)} \rho_L \Omega^{(+)-1} \Omega^{(+)} \rho_C \Omega^{(+)-1} \Omega^{(+)} \rho_R \Omega^{(+)-1} \\ &= Z_L^{-1} Z_R^{-1} e^{-\beta_L(H_L^{(+)} - \mu_L N_L^{(+)})} \rho_C(H_C^{(+)}) e^{-\beta_R(H_R^{(+)} - \mu_R N_R^{(+)})} \\ &= Z^{-1} \exp \left\{ -\beta_L(H_L^{(+)} - \mu_L N_L^{(+)}) - \beta_R(H_R^{(+)} - \mu_R N_R^{(+)}) \right\} \rho_C(H_C^{(+)}) \end{aligned} \quad (6)$$

where, in the last equality, we used $[X_\alpha^{(+)}, X_\beta^{(+)}] = 0$ and $Z = Z_L Z_R$. Finally, one should also note that $H_L^{(+)} + H_R^{(+)} = \Omega^{(+)} (H_L + H_R) \Omega^{(+)-1} = \Omega^{(+)} (H_0 - H_C) \Omega^{(+)-1} = H - H_C^{(+)}$.

2.3. Three Equivalent Expressions for ρ^{NE}

Upon regrouping the different terms in the exponential of Equation (6), one obtains different, but equivalent, expressions for the density matrix. The first expression is a generalisation of the density matrix derived by Hershfield [38,39], the third expression is the so-called McLennan–Zubarev NE statistical operator, while the second expression is an intermediate between the two.

First, we have generalised in [34] the results of Hershfield [38,39] to the presence of both a temperature and a chemical potential differences ($\beta_L \neq \beta_R, \mu_L \neq \mu_R$) between the reservoirs. The NE density matrix is then recast as follows:

$$\rho^{\text{NE}} = Z^{-1} \exp \left\{ -\tilde{\beta}(H - Y^Q + Y^E) \right\} \rho_C(H_C^{(+)} e^{+\tilde{\beta}H_C^{(+)}} , \quad (7)$$

where we have used the definitions and commutators given in Section 2. Note that the generalised Gibbs form of the NE density matrix in Equation (7) is given with an effective temperature T_{eff} defined from $\tilde{\beta} = \frac{1}{2}(\beta_L + \beta_R)$. This temperature is different from the temperature of the reservoirs $T_{L,R}$ since $T_{\text{eff}} = 1/k_B \tilde{\beta} = 2T_L T_R / (T_L + T_R)$.

The conserved quantities Y^Q and Y^E are related to the charge and energy currents respectively via:

$$Y^Q = (\beta_L \mu_L N_L^{(+)} + \beta_R \mu_R N_R^{(+)}) / \tilde{\beta}, \quad \text{and} \quad Y^E = (\beta_L - \beta_R) \frac{1}{2} (H_L^{(+)} - H_R^{(+)}) / \tilde{\beta}. \quad (8)$$

Second, following [40], one can re-express the density matrix in a slightly different form (closer to the grand-canonical ensemble) involving quantities with a more explicit physical meaning. Indeed, by writing $E^{(+)} = \Omega^{(+)} E \Omega^{(+)-1}$ with $E = \frac{1}{2}(H_L - H_R)$ and

$$Y^Q = \bar{\mu} N + \Delta_\mu Q^{(+)} / \tilde{\beta} \quad (9)$$

with $Q = \frac{1}{2}(N_L - N_R)$, the NE density matrix takes the following form (with $X_{L+R} = X_L + X_R$):

$$\begin{aligned} \rho^{\text{NE}} &= Z^{-1} \exp \left\{ -\tilde{\beta}(H_{L+R}^{(+)} - \bar{\mu} N_{L+R}^{(+)} + \Delta_\mu Q^{(+)} - (\beta_L - \beta_R) E^{(+)} \right\} \rho_C(H_C^{(+)}) \\ &= Z^{-1} \exp \left\{ -\tilde{\beta}(H - \bar{\mu} N) + \Delta_\mu Q^{(+)} - (\beta_L - \beta_R) E^{(+)} \right\} \rho_C(H_C^{(+)} e^{+\tilde{\beta}(H_C^{(+)} - \bar{\mu} N_C^{(+)})} , \end{aligned} \quad (10)$$

where $\bar{\mu} = (\beta_L \mu_L + \beta_R \mu_R) / (\beta_L + \beta_R)$, $\Delta_\mu = \beta_L \mu_L - \beta_R \mu_R$ [45]. Note that the passage from the first to the second line requires the use of an intertwining relation for N [46].

Furthermore, the initial density matrix ρ_C could be given by any other form different from Equation (3) as such a choice is completely arbitrary. Indeed, in the steady state, the initial correlation vanishes [47] and the final stationary properties should not dependent on the initial conditions taken for the statistics of the central region. Hence, for convenience and to simplify the notation, we chose ρ_C such that $\rho_C e^{+\tilde{\beta}(\dots)} = \mathbb{1}$ in Equations (6) and (10) [48].

It is also important to note that, in Equation (10), the quantities $Q^{(+)}$ and $E^{(+)}$ are conserved quantities and are directly related to the charge and energy currents. Indeed, in the Heisenberg representation, the energy current operator is given by $j_E(t) = \partial_t E(t) = \frac{i}{\hbar} [H, E(t)]$ and the charge current operator $j_Q(t)$ is given by $j_Q(t) = e \partial_t Q(t) = \frac{ie}{\hbar} [H, Q(t)]$. This results permits us to connect the expressions, Equations (6) and (10), for the NE density matrix to the third formulation, i.e., the McLennan–Zubarev NE statistical operator.

Such a statistical operator is given by [18,26,49]:

$$\rho^{\text{NESO}} = \frac{1}{Z} \exp \left\{ -\sum_\alpha \beta_\alpha (H_\alpha - \mu_\alpha N_\alpha) + \int_{-\infty}^0 du e^{\eta u} J_S(u) \right\}. \quad (11)$$

The quantity $J_S(s)$ is called the non-systematic energy flows [26] and is related to the entropy production rate of the system [25,26,49]. It is given by

$$J_S(u) = \sum_\alpha \beta_\alpha J_{S,\alpha}(u) \quad \text{where} \quad J_{S,\alpha}(u) = \frac{d}{du} (H_\alpha(u) - \mu_\alpha N_\alpha(u)), \quad (12)$$

where all operators are given in the Heisenberg representation, $A(u) = e^{iHu/\hbar} A e^{-iHu/\hbar}$. In the literature, it is also customary to call $J_{S,\alpha}$ the heat current with results from the energy flux $J_\alpha^E(t) = \frac{d}{dt} H_\alpha(t)$ measured with respect to the so-called convective term $\mu_\alpha J_\alpha^Q(t) = \mu_\alpha \frac{d}{dt} N_\alpha(s)$ [50]. Because $J_S(u)$ is the sum of heat flows divided by the subsystem temperature, it is the entropy production rate of the whole system [25,26]. The time integration of $J_S(u)$ in Equation (11) provides the asymptotic steady state value of the energy and charge fluxes J_α^E and J_α^Q , respectively. Hence, the quantity $\int du J_S(u)$ is the entropy production in the NE steady state.

Recently, we have shown [34] the full equivalence between the McLennan–Zubarev NE statistical operator ρ^{NESO} and the other expressions Equations (7) and (10) for ρ^{NE} . The equivalence is based on the so-called Peletminskii lemma [51], which states that the time integral of an operator given in the Heisenberg representation (for example, $\int du J_S(u)$) can be obtained from an infinite series expansion of the time integral of the related quantities expressed in the interaction representation (see Appendix B in [34]).

Hence, such an equivalence implies that the quantities $Y^{Q,E}$ in Equation (7) and the quantities $Q^{(+)}, E^{(+)}$ in Equation (10) can be calculated from the same formal iterative scheme:

$$Y = \sum_{n=0}^{\infty} Y_{n,I} \quad \text{and} \quad \partial_t Y_{n+1,I}(t) = -\frac{i}{\hbar} [W_I(t), Y_{n,I}(t)], \quad (13)$$

where we have used the notation $Y \equiv Y^Q, Y^E, Q^{(+)}$ or $E^{(+)}$ and the interaction representation, $A_I(t) = e^{iH_0 t/\hbar} A e^{-iH_0 t/\hbar}$, for all quantities. The first values ($n = 0$) of the series are $Y_{0,I} = a_L^Q N_L + a_R^Q N_R$ when $Y \equiv Y^Q$ or $Q^{(+)}$ and $Y_{0,I} = a^E (H_L - H_R)$ when $Y \equiv Y^E$ or $E^{(+)}$. The different constants a_α^Q and a^E are given by $a_\alpha^Q = 2\beta_\alpha \mu_\alpha / (\beta_L + \beta_R)$ for $Y = Y^Q$. For $Y = Q^{(+)}$, we have $a_L^Q = \frac{1}{2} = -a_R^Q$. For the energy flux, we have $a^E = \beta_L - \beta_R / (\beta_L + \beta_R)$ for $Y = Y^E$ or $a^E = \frac{1}{2}$ for $Y = E^{(+)}$.

3. Entropy Production

Equations (7) and (10) correspond to the most general expressions of the steady-state NE density matrix in the presence of both heat and charge currents (for a two-reservoir device). We now use them to calculate the entropy production in the system under general NE conditions.

3.1. Entropy Production Rate

As mentioned in the previous section, the different quantities $Y = Y^Q, Y^E, Q^{(+)}$ or $E^{(+)}$ are related to the entropy production (rate) in the system. We can then define the NE entropy production ΔS^{NE} in the steady state from Equations (7) and (10) in the following way:

$$\Delta S^{\text{NE}}/k_B = \Delta_\mu \langle Q^{(+)} \rangle - (\beta_L - \beta_R) \langle E^{(+)} \rangle = \bar{\beta} (\langle Y^Q \rangle + \langle Y^E \rangle - \bar{\mu} \langle N \rangle) = \int d\tau \Delta \dot{S}^{\text{NE}}(\tau)/k_B, \quad (14)$$

where $\Delta \dot{S}^{\text{NE}}$ is the NE entropy production rate. Hence, from the definition of $Q^{(+)}$ and $E^{(+)}$, the NE entropy production rate is directly related to the asymptotic steady state NE current of charge $\langle j_Q \rangle$ and energy $\langle j_E \rangle$:

$$\Delta \dot{S}^{\text{NE}}/k_B = (\beta_L \mu_L - \beta_R \mu_R) \langle j_Q \rangle / e - (\beta_L - \beta_R) \langle j_E \rangle. \quad (15)$$

Such a result has also been used in early work [52].

A few remarks are now in order. At equilibrium when $T_L = T_R$ and $\mu_L = \mu_R$, there are obviously no current flows and no extra entropy is produced (apart from the equilibrium entropy arising from the thermal fluctuations in the L and R reservoirs). When $T_L = T_R$, there is no energy flow and there is a charge current when $\mu_L \neq \mu_R$. By convention, the NE averaged charge current $\langle j_Q \rangle$ is positive (negative) when flowing from $L(R)$ to $R(L)$, i.e., when $\mu_L > \mu_R$ ($\mu_L < \mu_R$). Hence, the contribution $(\mu_L - \mu_R) \langle j_Q \rangle$ to the entropy production is always positive. Similarly, the NE averaged energy current $\langle j_E \rangle$ is positive (negative) when flowing from $L(R)$ to $R(L)$, i.e., when $T_L > T_R$ ($T_L < T_R$). Hence, the

contribution $-(\beta_L - \beta_R)\langle j_E \rangle$ to the entropy production is also always positive. However, the sign of the total contribution from $\langle j_Q \rangle$ and $\langle j_E \rangle$ to the entropy production (under general NE conditions) is not obvious without further investigation. A general argument for the positiveness of the NE entropy production rate was given in [12] and a few numerical examples were given in [11].

Using the same model system, i.e., the non-interacting single level coupled to two reservoirs, we provide in the next section results for the entropy production rate for a wide range of parameters.

3.2. An Example

In the absence of interaction, the Hamiltonian for the central region C is simply given by $H_C^0 = \varepsilon_0 d^\dagger d$, where d^\dagger (d) creates (annihilates) an electron in the level ε_0 . The non-interacting reservoirs are also described by a quadratic Hamiltonian $\alpha = L, R$ with $H_\alpha = \sum_i \varepsilon_\alpha c_{\alpha i}^\dagger c_{\alpha i} + t_\alpha (c_{\alpha i}^\dagger c_{\alpha i+1} + c.c.)$, where αi is an appropriate composite index to label the free electrons on the site i of the α reservoirs. The coupling between the central region and the electrodes is given via some hopping matrix elements v_α , and we have $\sum_\alpha (V_{C\alpha} + V_{\alpha C}) = \sum_\alpha v_\alpha (c_{\alpha 0}^\dagger d + d^\dagger c_{\alpha 0})$. We recall that, by definition, we have $W = H_C^0 + \sum_\alpha (V_{C\alpha} + V_{\alpha C})$. The only non vanishing anti-commutators are $\{d, d^\dagger\} = 1$ and $\{c_{\alpha i}, c_{\beta j}^\dagger\} = \delta_{ij} \delta_{\alpha\beta}$.

The charge and energy currents can be calculated from the NE average expression in Equation (4) [34], from asymptotic steady state scattering techniques [12,53–57] or from an NE Green's function (NEGF) approach [11,13]. The full equivalence between the asymptotic steady state scattering and the NEGF techniques has been shown in [58].

In [49], we have stressed that calculating the NE averages with the NE density matrix and the series expansion of the operators Y in Equation (13) is equivalent to the NEGF approach in the steady-state regime. The Green's functions are correlation functions whose thermodynamical averages are formally identical to those given in Equation (4). Both perturbation series used in the NEGF approach and in the derivations of the equations for the Y operators start from the same nonequilibrium series expansion. They are just two different ways of summing that series. For a non-interacting problem for which the series can be resummed exactly, the NEGF and the NE density matrix with the Y operators approach provide the same result [59,60]. For an interacting system, one must resort to approximations to partially resume the series, and, therefore, the two approaches are similar only when the same approximations are used. For the purpose of the present section, we then use the NEGF approach as the calculations are more straightforward in the non-interacting case. We also note that the NEGF formalism permits us to include local interaction in the central region in a compact and self-consistent scheme, as we have done in [22,61–67].

For the non-interacting system, the charge and energy currents are related to the transmission coefficient $T(\omega)$ of the junction via the moments M_n :

$$M_n = \frac{1}{\hbar} \int \frac{d\omega}{2\pi} \omega^n T(\omega) (f_L(\omega) - f_R(\omega)), \quad (16)$$

where $f_\alpha(\omega)$ is the equilibrium Fermi distribution of the reservoir α . The charge current is $\langle j_Q \rangle = eM_0$ and the energy current is $\langle j_E \rangle = M_1$. The transmission is obtained from $T(\omega) = G^r(\omega) \Gamma_L(\omega) G^a(\omega) \Gamma_R(\omega)$, where the NEGF $G^{r,a}$ are given by $G^r(\omega) = [\omega - \varepsilon - \Sigma_{L+R}^r(\omega)]^{-1} = (G^a(\omega))^*$, with $\Sigma_{L+R}^r = \Sigma_L^r + \Sigma_R^r$ being the reservoirs' self-energy. Furthermore, we have $\Gamma_\alpha(\omega) = \Sigma_\alpha^a(\omega) - \Sigma_\alpha^r(\omega)$ and the reservoir α self-energy is defined by $\Sigma_\alpha^r(\omega) = v_\alpha^2 e^{-ik_\alpha(\omega)} / t_\alpha$ with the dispersion relation $\omega = \varepsilon_\alpha - 2t_\alpha \cos(k_\alpha(\omega))$.

Figure 1 shows the NE entropy production rate $\Delta \dot{S}^{\text{NE}}$ calculated for different transport regimes. The main conclusion is that $\Delta \dot{S}^{\text{NE}}$ is always a positive quantity, as expected. Such a behaviour is obtained for a system with a single chemical potential (see panel (a) in Figure 1). It is also obtained when there are both chemical potential and temperature differences between the reservoirs, regardless of the respective direction of the charge and energy currents (see panel (b) for currents flowing in the same direction and panel (b) for currents flowing in opposite directions).

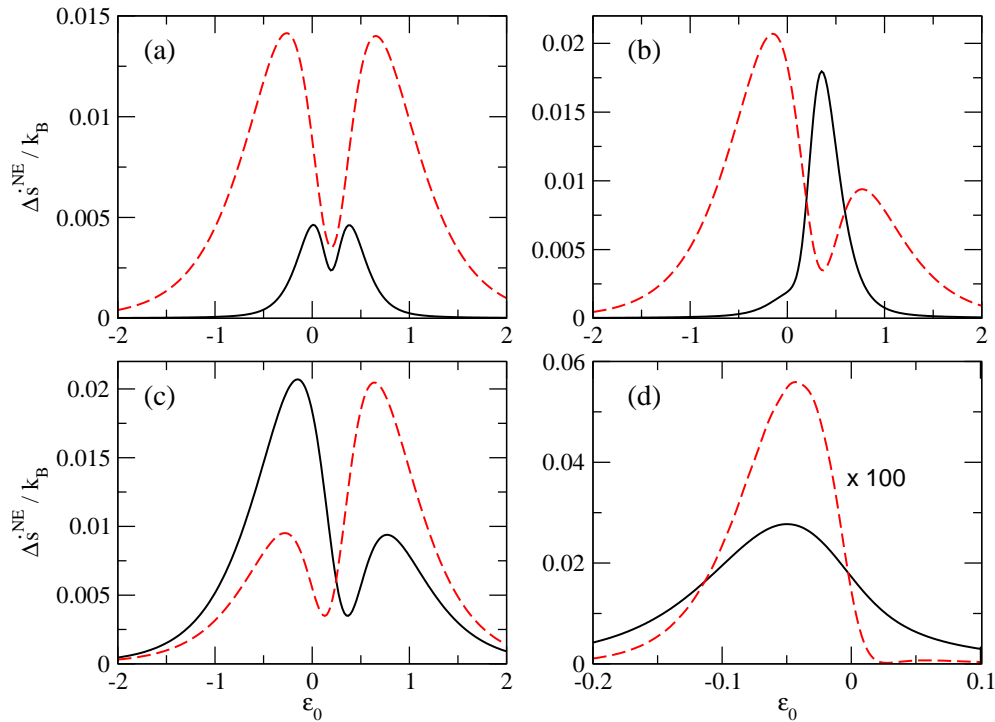


Figure 1. NE entropy production rate $\Delta\dot{S}^{\text{NE}}$ versus the energy level ε_0 for different transport regimes. $\Delta\dot{S}^{\text{NE}}$ is always a positive quantity. (a) only temperature differences ($\mu_L = \mu_R = 0.2$) $k_B T_L = 0.1$, $k_B T_R = 0.05$ (solid line) and $k_B T_L = 0.1$, $k_B T_R = 0.3$ (dashed line); (b) both chemical potential and temperature differences ($\mu_L = 0.3$, $\mu_R = 0.2$) $k_B T_L = 0.1$, $k_B T_R = 0.05$ (solid line) and $k_B T_L = 0.1$, $k_B T_R = 0.3$ (dashed line); (c) both temperature and chemical potential differences ($k_B T_L = 0.1$, $k_B T_R = 0.3$) $\mu_L = 0.3$, $\mu_R = 0.2$ (solid line) and $\mu_L = 0.2$, $\mu_R = 0.3$ (dashed line); (d) comparison with results of Figure 3b in Reference [11]. ($\mu_L = 0.05$, $\mu_R = 0.0$) $k_B T_L = 0.026$, $k_B T_R = 26/30.10^{-3}$, strong coupling $v_L = v_R = 0.2$ (solid line) and weak coupling $v_L = v_R = 0.02$ (dashed line, amplitude rescaled by a factor $\times 100$). The other parameters are $t_L = t_R = 2.0$ and $v_L = v_R = 0.25$ (when not specified otherwise). All parameters are given in dimension of energy in [eV].

In Figure 1d, we have tried to reproduce the results shown in Figure 3b of [11]. The results are qualitatively reproduced apart from the behaviour over the whole amplitude of the entropy production rate. Indeed, in our model, the transmission coefficient $T(\omega)$ has roughly a Lorentzian lineshape, with a maximum amplitude of unity (whatever the values of the parameters are) and a width which scales approximately as $\sum_{\alpha} v_{\alpha}^2 / t_{\alpha}$ versus the coupling parameters between the central region C and the reservoirs. Hence, the width of $T(\omega)$ increases with the strength of the coupling to the reservoirs, and, therefore, the currents will always have a larger values when increasing the strength of this coupling. Consequently, the entropy production rate $\Delta\dot{S}^{\text{NE}}$ defined by Equation (15) is always larger for larger values of the coupling to the reservoirs.

In Figure 2, we show how the NE entropy production rate $\Delta\dot{S}^{\text{NE}}$ depends on the NE conditions, i.e., on the chemical potential difference $\Delta\mu$ (see Figure 2a,c) or on temperature difference ΔT between the reservoirs (see Figure 2b,d). First, it is important to note that, for all the parameters used, the NE entropy production rate $\Delta\dot{S}^{\text{NE}}$ is always a positive quantity (as expected). Furthermore, $\Delta\dot{S}^{\text{NE}}$ increases when the NE conditions are more important, i.e., when $\Delta\mu$ or ΔT increases. In other words, the more the system is out of equilibrium, the larger the entropy production becomes.

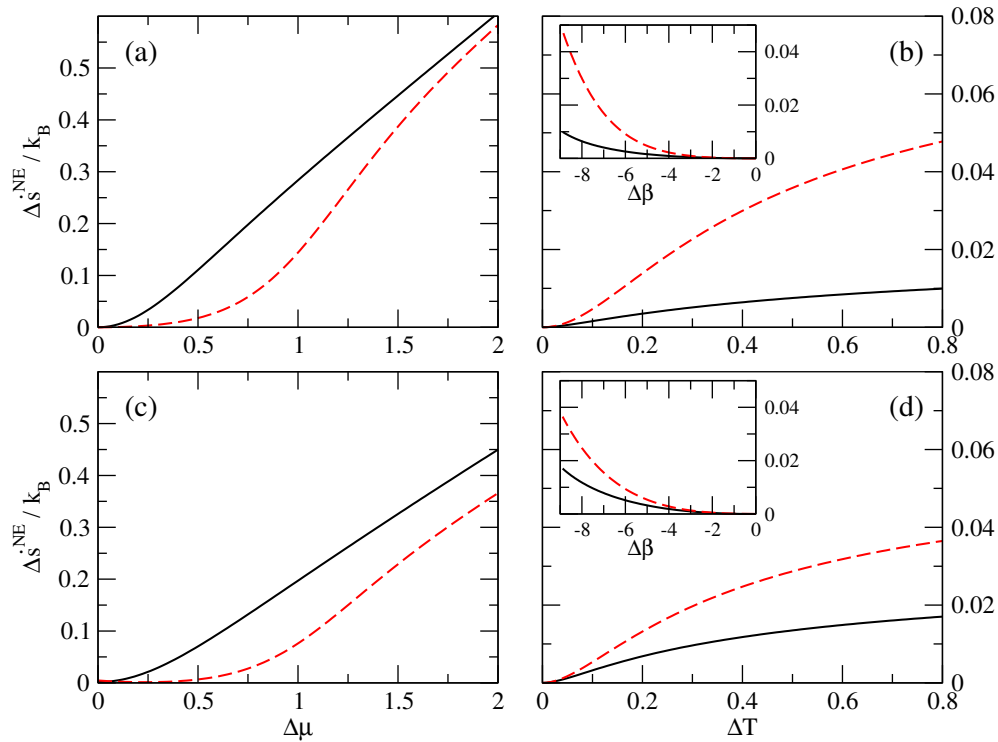


Figure 2. NE entropy production rate $\Delta\dot{S}^{\text{NE}}$ versus the temperature difference ($\Delta T = T_L - T_R$ and $\Delta\beta = \beta_L - \beta_R$) and/or the chemical potential difference ($\Delta\mu = \mu_L - \mu_R$). $\Delta\dot{S}^{\text{NE}}$ is always a positive quantity, and increases when $\Delta\mu$ or ΔT ($|\Delta\beta|$) increases. The solid (dashed) lines are for the resonant (off-resonant) transport regime, i.e., $\varepsilon_0 \sim (>) \mu^{\text{eq}}$ when $\Delta\mu = 0$. (a) system at a unique temperature $k_B T_L = k_B T_R = 0.1$; (b) system with a unique chemical potential $\mu_L = \mu_R = 0.2$. In the inset, we also show the dependence of $\Delta\dot{S}^{\text{NE}}$ vs. $\Delta\beta$; (c) system with a temperature difference $k_B T_L = 0.1, k_B T_R = 0.2$; (d) system with a chemical potential difference $\mu_L = 0.35, \mu_R = 0.05$. The inset shows the $\Delta\dot{S}^{\text{NE}}$ vs. $\Delta\beta$. The other parameters are $t_L = t_R = 2.0$ and $v_L = v_R = 0.25$ (given in [eV]). For the dependence on $\Delta\mu$, we take $\mu_L = \mu^{\text{eq}} + \Delta\mu/2$ and $\mu_R = \mu^{\text{eq}} - \Delta\mu/2$ with $\mu^{\text{eq}} = 0.2$. For the dependence on ΔT , we take and $T_R = T^0 = 0.1, T_L = T^0 + \Delta T$ (hence, $\Delta\beta < 0$ for $\Delta T > 0$).

One should note that the dependence of $\Delta\dot{S}^{\text{NE}}$ on $\Delta\mu$ shows some form of linearity when $\Delta\mu \geq \Delta\mu^*$. This is simply due to the fact that the currents saturate: $\langle j_{Q,E}(\Delta\mu) \rangle = I_{Q,E}^{\text{sat}}$ when $\Delta\mu \geq \Delta\mu^*$. Indeed, in the saturation region, increasing $\Delta\mu$ does not change the value of the moments M_n as the transmission $T(\omega)$ is zero in energy range where $f_L(\omega) - f_R(\omega)$ is modified by an increase of $\Delta\mu$. In this regime, one can easily see that the dependence of $\Delta\dot{S}^{\text{NE}}$ on $\Delta\mu$ is simply linear with a slope given by $(\beta_L + \beta_R)I_{Q,E}^{\text{sat}}/2$. Furthermore, the slope is maximal when $\beta_L = \beta_R$ and smaller for any $\beta_L \neq \beta_R$ as clearly exemplified by the results shown in Figure 2a,c. Such a saturation regime does not exist for increase ΔT differences (at fixed $\Delta\mu$) as shown in Figure 2b,d.

4. Nonequilibrium Gibbs–von Neumann Entropies

In the previous section, we have shown how the NE entropy production rate is related to the charge and energy currents. We have also shown that the NE steady state can be considered as a pseudo equilibrium state with a corresponding (time-independent) density matrix which is given in the form of a generalised Gibbs ensemble. It would therefore be very interesting to be able to define an NE entropy [68,69] from the NE density matrix by using the equivalence between pseudo equilibrium states and equilibrium states. In other words: when we build an NE entropy from the equilibrium expression [68,69] $S = k_B \langle \ln \mathcal{W} \rangle = -k_B \text{Tr}[\rho \ln \rho]$, which density matrix should be used?

4.1. Which Density Matrix?

The first natural choice would be to take the NE density matrix ρ^{NE} derived in the previous section. However, such a choice does not bring any information about entropy production under the NE conditions. Indeed, if we consider the asymptotic operator $A^{(+)}$ being obtained from a unitary transformation ($\Omega^{(+)}\Omega^{(+)-1} = \mathbb{1}$), we can show that for any function $f(A)$:

$$\text{Tr}[A^{(+)}f(A^{(+)})] = \text{Tr}[A^{(+)}\Omega^{(+)}f(A)\Omega^{(+)-1}] = \text{Tr}[\Omega^{(+)}Af(A)\Omega^{(+)-1}] = \text{Tr}[Af(A)]. \quad (17)$$

By taking $A = \rho_0$ and $f(\cdot) = \ln(\cdot)$, one easily see that $\text{Tr}[\rho^{\text{NE}} \ln \rho^{\text{NE}}] = \text{Tr}[\rho_0 \ln \rho_0]$. The quantity $\text{Tr}[\rho_0 \ln \rho_0] = \sum_{\alpha=L,C,R} \text{Tr}_{(\alpha)}[\rho_{\alpha} \ln \rho_{\alpha}]$ defines the entropy of the three separated L, C, R regions. It does not contain any information about the charge and energy currents flowing through the entire system under general NE conditions.

Another possibility would be to take the NE average of the density matrix of the coupled system at equilibrium, i.e., $S^{\text{NE}} = -k_B \text{Tr}[\rho^{\text{NE}} \ln \rho^{\text{eq}}]$, where $\rho^{\text{eq}} = Z^{-1} \exp \{-\beta^{\text{eq}}(H - \mu^{\text{eq}}N)\}$. However, from the intertwining relation, we have $\Omega^{(+)-1}H\Omega^{(+)} = H_0$ and $\Omega^{(+)-1}N\Omega^{(+)} = N$ [46], and we obtain $S^{\text{NE}} = k_B \text{Tr}[\rho^{\text{NE}} \ln \rho^{\text{eq}}] = -k_B \text{Tr}[\rho_0 \ln \rho_0^{\text{eq}}]$ with $\rho^{\text{eq}} \propto \exp \{-\beta^{\text{eq}}(H_0 - \mu^{\text{eq}}N)\}$. Such an entropy contains some information about the NE conditions, considering that $\beta_{L,R}$ and $\mu_{L,R}$ in $\rho_{L,R}$ are different from the equilibrium β^{eq} and μ^{eq} . However, this entropy is defined from the non-interacting Hamiltonian only, and it lacks the presence of the operator W , which is the generator of the different charge and energy currents. Hence, such an entropy does not contain any information about the fluxes, which are the responses to the applied forces $\Delta\mu$ and ΔT .

One has to go back to the definition of the NE steady state averages given in Equation (4). The asymptotic time-dependence, in such average, has been passed on to the NE density matrix which we use to calculate the average of quantum operators. Hence, it follows that one should define the entropy from the NE average of the nominal density matrix ρ_0 , i.e., $S^{\text{NE}} = -k_B \text{Tr}[\rho^{\text{NE}} \ln \rho_0]$.

As the density matrix ρ_0 is the direct product of the individual density matrices of each separate L, C, R regions, it is easy to show that

$$S^{\text{NE}} = -k_B \text{Tr}[\rho^{\text{NE}} \ln \rho_0] = S_L^{\text{NE}} + S_C^{\text{NE}} + S_R^{\text{NE}} \quad \text{where} \quad S_{\alpha}^{\text{NE}} = -k_B \text{Tr}_{(\alpha)}[\rho_{\text{red},\alpha}^{\text{NE}} \ln \rho_{\alpha}]. \quad (18)$$

S_{α}^{NE} is the contribution of the region α and $\rho_{\text{red},\alpha}^{\text{NE}}$ is the corresponding reduced density matrix obtained from $\rho_{\text{red},\alpha}^{\text{NE}} = \text{Tr}_{(\beta,\beta')}[\rho^{\text{NE}}]$ with $\beta, \beta' = L, C, R$ and $\beta \neq \beta' \neq \alpha$. For example, the NE reduced density matrix in the central region $\rho_{\text{red},C}^{\text{NE}}$ is obtained from $\rho_{\text{red},\alpha}^{\text{NE}} = \text{Tr}_{(L,R)}[\rho^{\text{NE}}]$.

The corresponding entropy S_C^{NE} has been the object of recent studies [10–14], but it is clearly only a part of the entire entropy production in the system. For example, the contributions S_L^{NE} and S_R^{NE} are different from their (isolated) equilibrium counterparts $S_{\alpha}^{\text{eq}} = -k_B \text{Tr}_{(\alpha)}[\rho_{\alpha} \ln \rho_{\alpha}]$ ($\alpha = L, R$) since $\rho_{\text{red},\alpha}^{\text{NE}} \neq \rho_{\alpha}$.

We now further comment on this point. For that, we consider small deviations from the equilibrium, where $\mu_{L,R} = \mu \pm \frac{1}{2}\Delta\mu$ and $\beta_{L,R} = \beta \pm \frac{1}{2}\Delta\beta$ with $\Delta\mu \ll 1$ (hence $\Delta\mu \ll 1$) and $\Delta\beta \ll 1$. Hence,

$$\begin{aligned} \rho^{\text{NE}} &\approx Z^{-1} \exp \left\{ -\beta(H_{L+R}^{(+)} - \mu N_{L+R}^{(+)}) \right\} \left(1 + \Delta\mu Q^{(+)} \right) \left(1 - \Delta\beta E^{(+)} \right) \rho_C(H_C^{(+)}) \\ &\approx Z^{-1} \exp \left\{ -\beta(H_{L+R}^{(+)} - \mu N_{L+R}^{(+)}) \right\} \rho_C(H_C^{(+)}) \left(1 + \Delta\mu Q^{(+)} - \Delta\beta E^{(+)} \right), \end{aligned} \quad (19)$$

where we kept only the lowest order terms in $\Delta\mu$ and $\Delta\beta$. Furthermore, if we assume a lowest order expansion of the density matrices $e^{-\beta(H_{\alpha}^{(+)} - \mu N_{\alpha}^{(+)})} \approx e^{-\beta(H_{\alpha} - \mu N_{\alpha})}$ and $\rho_C(H_C^{(+)}) \approx \rho_C(H_C)$, one gets:

$$\rho_{\text{red},L}^{\text{NE}} = \text{Tr}_{(C,R)}[\rho^{\text{NE}}] \approx \rho_L \text{Tr}_{(C,R)} \left[1 + \Delta\mu Q^{(+)} - \Delta\beta E^{(+)} \right], \quad (20)$$

and therefore

$$\begin{aligned} S_L^{\text{NE}} &= -k_B \text{Tr}_{(L)} \left[\rho_{\text{red},L}^{\text{NE}} \ln \rho_L \right] \\ &\approx -k_B \text{Tr}_{(L)} [\rho_L \ln \rho_L] - k_B \text{Tr}_{(L)} \left[\rho_L \text{Tr}_{(C,R)} [\Delta_\mu Q^{(+)} - \Delta\beta E^{(+)}] \ln \rho_L \right]. \end{aligned} \quad (21)$$

The first term in the above equation is simply the entropy S_L^{eq} of the isolated L region with the associated grand canonical density matrix given by Equation (2). The second term can be re-arranged as follows: $-k_B \text{Tr}_{(L)} [\rho_L \text{Tr}_{(C,R)} [\Delta_\mu Q^{(+)} - \Delta\beta E^{(+)}] \ln \rho_L] = -k_B \text{Tr} [\rho_L (\Delta_\mu Q^{(+)} - \Delta\beta E^{(+)}) \ln \rho_L] = \text{Tr} [(\Delta_\mu Q^{(+)} - \Delta\beta E^{(+)}) (-k_B \rho_L \ln \rho_L)]$. Finally, we have

$$S_L^{\text{NE}} \approx S_L^{\text{eq}} + \text{Tr} \left[\frac{\Delta S^{\text{NE}}}{k_b} S_L^{\text{eq}} \right], \quad (22)$$

where ΔS^{NE} is the operator defining the entropy production in Equation (14), and $S_L^{\text{eq}} = -k_B \rho_L \ln \rho_L$ with $S_L^{\text{eq}} = \text{Tr}_{(L)} [S_L^{\text{eq}}]$. Similar expressions can be found for S_C^{NE} and S_R^{NE} .

The results show that, under general NE conditions, NE entropy is produced in the central region and in the reservoirs as well. Such an entropy is always related to the charge and energy currents flowing at the interfaces between the central region and the L and R regions.

The full calculation of the entropy from Equation (18) is a non-trivial task, especially for arbitrary interaction V_C^{int} in the central region. This can, however, be achieved by either determining the asymptotic scattering states $|L_k^{(+)}\rangle = \Omega^{(+)} |L_k\rangle$ for the L region (and for the states $|R_k\rangle$ and $|C_n\rangle$ for the R and C regions, respectively). Following [12,53–57], the scattering states of the L region, for the model described in Section 3.2, are given by: $|L_k^{(+)}\rangle = |L_k\rangle + v_L G^r(\epsilon_{Lk}) |C_n\rangle + \sum_{\alpha=L,R,k'} v_L v_\alpha G^r(\epsilon_{Lk}) / (\epsilon_{Lk} - \epsilon_{\alpha k'} + i0^+) |\alpha_{k'}\rangle$. For the non-interacting case in Section 3.2, the calculations of the entropy can also be easily performed using the NEGF formalism, which we consider in the next section.

4.2. An Example for the Entropy of the Central Region

We now consider numerical calculations for the Gibbs–von Neumann entropy using the single level model described in Section 3.2. We have shown that the NE steady state can be considered as a pseudo equilibrium state with a corresponding generalised Gibbs ensemble given by ρ^{NE} . Following the same principles of equilibrium statistical mechanics, one can define from the generalised Gibbs ensemble a local NE distribution functions [66] in the L, C, R regions. From these NE distribution functions, one can also define the corresponding Gibbs–von Neumann entropies. For example, the NE entropy S_C^{NE} in the central region C can be defined as follows [52]:

$$S_C^{\text{NE}}(\Delta\mu, \Delta T) = -k_B \int \frac{d\omega}{2\pi} A_C(\omega) \left[f_C^{\text{NE}}(\omega) \ln f_C^{\text{NE}} + (1 - f_C^{\text{NE}}(\omega)) \ln(1 - f_C^{\text{NE}}) \right], \quad (23)$$

where $f_C^{\text{NE}}(\omega)$ is the NE distribution function of the central region and $A_C(\omega)$ is the corresponding spectral function defined from the NEGF as $A_C(\omega) = -\text{Im}G^r(\omega)/\pi$. It should be noted that the entropy S_C^{NE} is only a part of the total entropy S^{NE} in Equation (18), which is produced in the entire system under the general NE conditions.

For the non-interacting system considered in Section 3.2, the NE distribution function in the central region is just a weighted averaged of the equilibrium Fermi distributions of the reservoirs $f_C^{\text{NE}}(\omega) = [\Gamma_L(\omega)f_L(\omega) + \Gamma_R(\omega)f_R(\omega)]/\Gamma_{L+R}(\omega)$.

Figure 3 shows the dependence of the entropy S_C^{NE} calculated for different transport regimes. Once more, we can see that S_C^{NE} is always a positive quantity. The positiveness of S_C^{NE} is obtained when the system has a single chemical potential (see Figure 3a) as well as when there are both chemical potential and temperature differences between the reservoirs (see Figure 3b,c). In Figure 3d, we show the behaviour of the entropy for the same parameter used in Figure 1d and we recover the same

qualitative behaviour as shown in Figure 3b of [11]. The amplitude of the entropy is larger in the weak coupling limit in comparison to the strong coupling limit to the reservoirs. One should, however, note that, in Figure 3, S_C^{NE} has the dimension of an entropy, i.e., [energy]/[temperature], while in Figure 3b of [11] and Figure 1, we are dealing with an entropy production rate, i.e., a quantity with dimension [energy]/[temperature \times time].

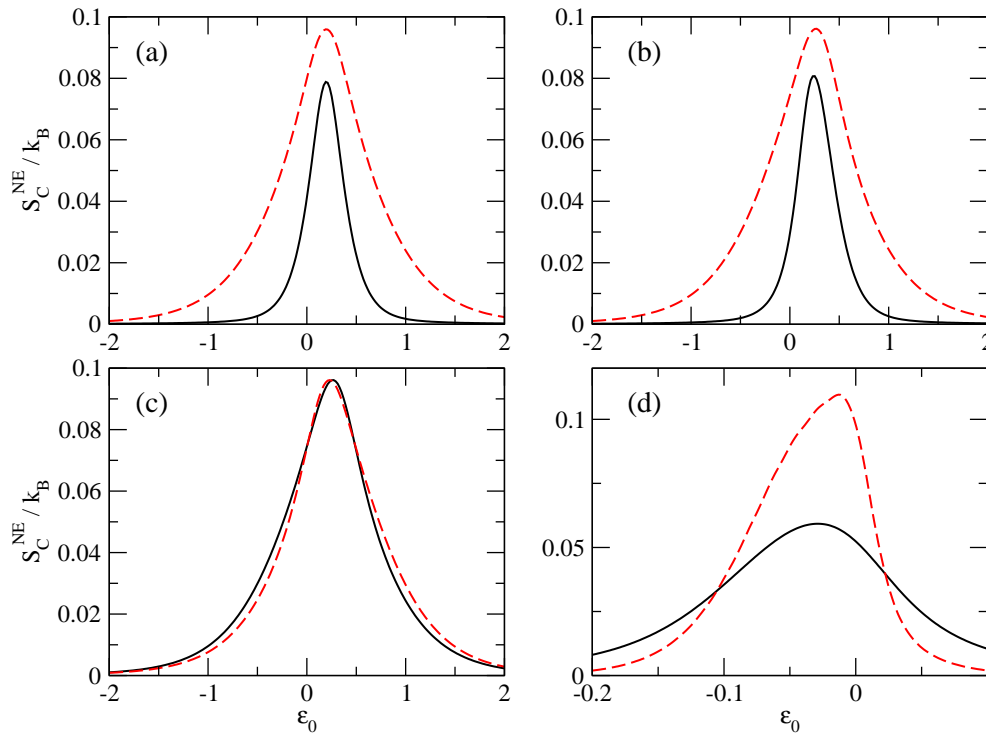


Figure 3. Gibbs–von Neumann NE entropy for the central region S_C^{NE} versus the energy level ϵ_0 for the different transport regimes considered in Figure 1. The Gibbs NE entropy S_C^{NE} is always a positive quantity as expected. (a) ($\mu_L = \mu_R = 0.2$) $k_B T_L = 0.1$, $k_B T_R = 0.05$ (solid line) and $k_B T_L = 0.1$, $k_B T_R = 0.3$ (dashed line); (b) both chemical potential and temperature differences ($\mu_L = 0.3$, $\mu_R = 0.2$) $k_B T_L = 0.1$, $k_B T_R = 0.05$ (solid line) and $k_B T_L = 0.1$, $k_B T_R = 0.3$ (dashed line); (c) both temperature and chemical potential differences ($k_B T_L = 0.1$, $k_B T_R = 0.3$) $\mu_L = 0.3$, $\mu_R = 0.2$ (solid line) and $\mu_L = 0.2$, $\mu_R = 0.3$ (dashed line); (d) comparison with results of Figure 3b in Reference [11]. ($\mu_L = 0.05$, $\mu_R = 0.0$) $k_B T_L = 0.026$, $k_B T_R = 26/30.10^{-3}$, strong coupling $v_L = v_R = 0.2$ (solid line) and weak coupling $v_L = v_R = 0.02$ (dashed line). The other parameters are $t_L = t_R = 2.0$ and $v_L = v_R = 0.25$ (when not specified otherwise) and given in [eV].

In Figure 4, we show the dependence of the entropy S_C^{NE} on the NE conditions, i.e., on the chemical potential difference $\Delta\mu$, as shown in the left panels (a) and (c), and on temperature differences ΔT between the reservoirs, as shown in the right panels (b) and (d). One can see that, for the range of parameters we used, the NE entropy production S_C^{NE} is once more a positive quantity (as expected). Furthermore, the entropy S_C^{NE} increases with the NE conditions, i.e., it increases for increasing values of $\Delta\mu$ and/or ΔT . We also observe a saturation regime in S_C^{NE} with increasing $\Delta\mu$. In the saturation regime, an increase of $\Delta\mu$ changes the features of the NE distribution function $f_C^{\text{NE}}(\omega)$ in an energy range where the spectral function $A_C(\omega)$ has no weight, i.e., where $A_C(\omega) = 0$. Therefore, the energy integral in Equation (23) does not change with increasing $\Delta\mu$ and the entropy S_C^{NE} saturates.

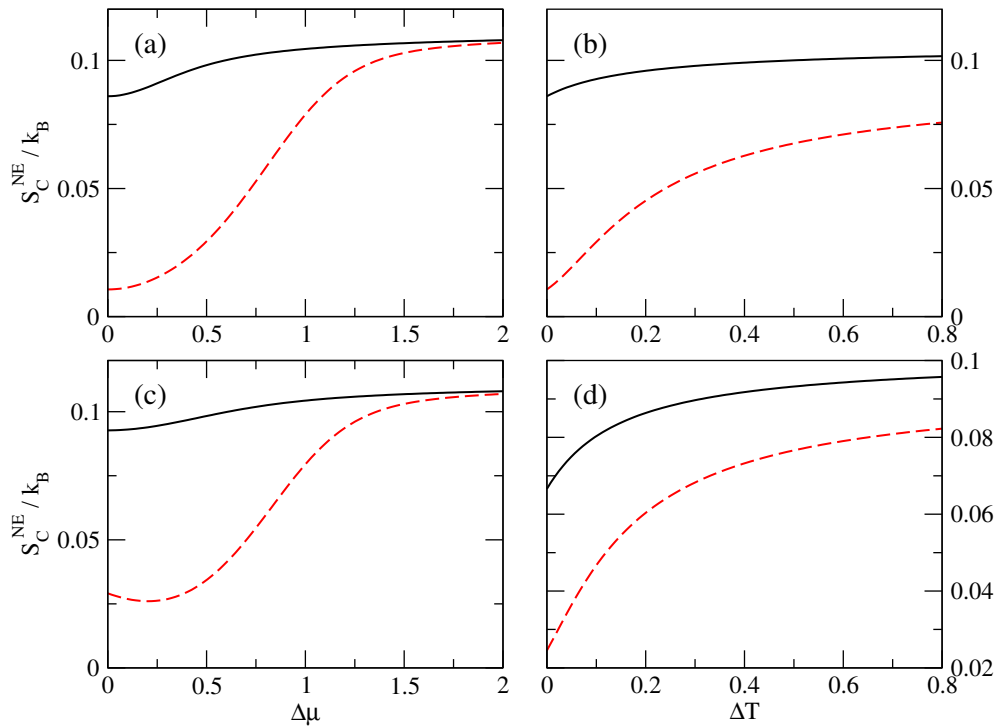


Figure 4. Gibbs–von Neumann NE entropy for the central region S_C^{NE} versus the temperature difference ($\Delta T = T_L - T_R$ and $\Delta\beta = \beta_L - \beta_R$) and/or the chemical potential difference ($\Delta\mu = \mu_L - \mu_R$). $\Delta\dot{S}^{\text{NE}}$ is always a positive quantity, and increases when $\Delta\mu$ or ΔT ($|\Delta\beta|$) increases. The solid (dashed) lines are for the resonant (off-resonant) transport regime, i.e., $\varepsilon_0 \sim (>) \mu^{\text{eq}}$ when $\Delta\mu = 0$. (a) system at a unique temperature $k_B T_L = k_B T_R = 0.1$; (b) system with a unique chemical potential $\mu_L = \mu_R = 0.2$. In the inset, we also show the dependence of $\Delta\dot{S}^{\text{NE}}$ vs. $\Delta\beta$; (c) system with a temperature difference $k_B T_L = 0.1, k_B T_R = 0.2$; (d) system with a chemical potential difference $\mu_L = 0.35, \mu_R = 0.05$. The inset shows the $\Delta\dot{S}^{\text{NE}}$ vs. $\Delta\beta$. The other parameters are $t_L = t_R = 2.0$ and $v_L = v_R = 0.25$ (given in [eV]). For the dependence on $\Delta\mu$, we take $\mu_L = \mu^{\text{eq}} + \Delta\mu/2$ and $\mu_R = \mu^{\text{eq}} - \Delta\mu/2$ with $\mu^{\text{eq}} = 0.2$. For the dependence on ΔT , we take $T_R = T^0 = 0.1, T_L = T^0 + \Delta T$ (hence, $\Delta\beta < 0$ for $\Delta T > 0$).

Finally, one should note that the calculation of the Gibbs–von Neumann NE entropy for the central region as well as the calculation of the entropy production rate Equation (15) can also be performed when interactions are present in the central region. Our expressions for the entropies are generally applicable to the cases with and without interactions in the central region. The latter is directly related to the charge and energy currents that can be calculated for different kinds of interaction in the central region. For example, in [22,61–63,65], we have studied the effect of electron–vibration interaction on the electron current. For Gibbs–von Neumann NE entropy, one can also define an NE distribution function f_C^{NE} which contains all the effects of the interactions as shown in [66]. The interactions will affect the entropy production; however, we expect that, with the so-called conservative approximations for the interaction, the positiveness of the entropy will be conserved. In the presence of interaction with extra degrees of the freedom (vibration or other boson modes), the contribution of their respective entropy production will need to be taken into account. However, such an in-depth study is out of the scope of the present paper.

5. Discussion

We have studied the steady state NE thermodynamical properties of an open quantum system connected to two reservoirs α , and the latter are acting as equilibrium (particle and heat) baths with their respective temperature T_α and chemical potential μ_α . We have shown that the steady state of

the entire system can be seen as a pseudo equilibrium state. The corresponding NE density matrix is expressed in the form of a generalised Gibbs ensemble $\rho^{\text{NE}} = e^{-\tilde{\beta}(H - \tilde{\mu}N + \sum_{a=Q,E} \lambda_a J_a)} / Z$.

The NE density matrix is time independent and built from the so-called conserved quantities: the total Hamiltonian H and the total number of electrons N and the $\mathcal{J}_{Q,E}$ quantities, which are related to the fluxes of charge and energy flowing in between the central region C and the reservoirs. We have given different forms for the NE density matrix and shown their mutual equivalence. The extra terms entering the definition of ρ^{NE} which do not exist in the equilibrium grand canonical representation have been clearly identified and have been shown to be related to the entropy production in the entire system. From their expression, the entropy production rate is given in terms of the charge and energy currents.

We have calculated such an entropy production rate for a model system consisting of a single electron resonance coupled to two Fermi reservoirs. Numerical results performed for different transport regimes have shown that the entropy production rate is always a positive quantity.

Furthermore, based upon the pseudo equilibrium properties of the steady state, we have also calculated a Gibbs–von Neumann entropy for the entire system. Our results show that the NE conditions create extra entropy in the central region as well as in the reservoirs. The former can be derived from the equilibrium expression of the entropy by using the appropriate NE distribution function in the central region.

Our numerical results for the entropy production and production rate corroborate and expand earlier studies [10–14]. These results also open a new route for determining the NE thermodynamical properties of quantum open systems under general conditions. For example, the corresponding NE specific heat or charge susceptibility [22] can be directly obtained from the derivative of the entropy versus the applied temperature or chemical potential biases.

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45. It is known from quantum transport theory [70] that, in the steady state, the currents at the L/C and C/R interfaces are equal to each other (up to the proper sign convention). Hence any linear combination of the type $J = aJ_L - bJ_R$ (with $a + b = 1$) can be used. It is then possible to transform Equation (6) into a form similar to Equation (10), i.e., $\rho^{\text{NE}} \propto \exp \left\{ -\tilde{\beta}(H_{L+R}^{(+)} - \tilde{\mu}N_{L+R}^{(+)} + \Delta_{\mu}Q^{(+)} - \Delta\beta E^{(+)} \right\}$, by using any linear combination of the type $Q = aN_L - (1-a)N_R$ and $E = aH_L - (1-a)H_R$ with $a \in [0, 1]$. Simple mathematical manipulations show that $\Delta_{\mu} = \beta_L\mu_L - \beta_R\mu_R$ and $\Delta\beta = \beta_L - \beta_R$, as in Equation (10), and that $\tilde{\beta} = (1-a)\beta_L + a\beta_R$ and $\tilde{\mu} = (1-a)\beta_L\mu_L + a\beta_R\mu_R$. Obviously, for $a = 1/2$, one recovers the expected Equation (10).
46. In Appendix A of [34], we have demonstrated the intertwining relation $H\Omega^{(+)} = \Omega^{(+)}H_0$. Following the same steps, we can also show that $N\Omega^{(+)} = \Omega^{(+)}N$ when one assumes that the total number of electron operator N commutes with the Hamiltonian H . Hence we have not only $[H_{\alpha}, N_{\beta}] = 0$ but also $[H, \sum_{\beta} N_{\beta}] = 0$. In other words, the total number of electron is conserved and $[W, N_L + N_C + N_R] = 0$, implying to all the electrons coming out (in) the reservoirs are going in (out) the central region C .
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48. Such a fact may not appear as a rigorous mathematical derivation, however it is known that the steady state does not depend of the initial choice of ρ_0 . Furthermore, one could note that another splitting of the total Hamiltonian H can be used to reduce the complexity of the expressions for the NE density matrix. In an earlier work [34], we considered splitting the Hamiltonian H into $H_0 + W$ where H_0 is only $H_0 = H_L + H_R$, hence the initial density matrix is only the direct product $\rho_0 = \rho_L \otimes \rho_R$, and the expected form of the NE density matrix is obtained. A difference however occurs in the construction of the Y operators given in Equation (13). In the present work, the operator W does not include H_C while it does in [34]. In the calculation of the Gibbs-like entropy in the central region, one deals with products of terms including $\rho(H_C^{+}) \ln \rho_C$. The asymptotic operator $\rho(H_C^{+})$ can be expanded in a series of ρ_C^n from the series expansion of Moeller operators. Hence leading to a series of terms in $\rho_C^n \ln \rho_C$. By considering that initially the central region (of finite size) is fully isolate, there cannot be any partial occupation of the electronic levels, and hence the terms $\rho_C^n \ln \rho_C$ expressed in the basis set of the central region will lead to the evaluation of either $1^n \ln 1$ or $0^n \ln 0$. This obviously leads to a zero contribution to the entropy, and therefore the terms in $\rho(H_C^{+})$ in the density matrix can be ignored.
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