

Implications of the detailed fluctuation theorem for the sources of irreversibility in interfacial charge transfer processes

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We investigate from basic principles of nonequilibrium statistical mechanics the general reasons why electron transfer across an interface is associated with irreversible elements (resistances) in equivalent circuit modeling. We apply the detailed fluctuation theorem [C. Jarzynski, *J. Stat. Phys.* **98**, 77 (2000)] to a simple model of an interface between two different materials. The elementary transition rates are interpreted in terms of the evolution of a microstate, and obey a ratio that is related to the heat absorbed from the phonon bath while promoting an electron to a higher energy level. The amount of irreversibility (the entropy production), and also the macroscopic current density, can be both obtained with the additional constraint that the system belongs in a particular mesostate, determined by the distribution of chemical and electrostatic potential.

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I. INTRODUCTION

Interfacial charge transfer occurs in many electrochemical systems and solid state electronic devices. Electrical current is obtained in these systems because either electron or ion transfer is induced at the interfaces between the materials when the device is biased by external potential. In the investigation of these systems by impedance spectroscopy, it is found that most of the devices can be represented by equivalent circuits consisting on certain combinations of resistances and capacitors [1,2]. The capacitors are reversible elements that represent energy storage in the system, either as electrostatic polarization or as chemical energy accumulation [3]. On another hand, the resistance is a dissipative element that consumes the energy supplied by the external power source.

The aim of this paper is to understand the origin of the irreversibility associated to current flow in a biased device, in relation to the elementary charge transfer events. Following a long tradition in physics education, one often tends to view a potentiostat as a device that creates a difference of electrostatic potential between the leads. In addition, a charge transfer process is usually viewed as the event of crossing a potential energy barrier at the interface between two materials. However, the displacement of an electron over electrostatic energy differences is a conservative (reversible) process, and in this view the origin of irreversibility is far from clear. In fact the “voltage” between the leads is the difference of electrochemical potential of electrons [4,5], which creates steps or gradients of quasi-Fermi-level into the device. (Nonequilibrium electrochemical potentials are often denoted quasi-Fermi-levels. The same quantity is denoted the redox potential for species in solution [6].) Explaining the intrinsic irreversibility of charge transfer requires to consider in addition to energy changes the entropy changes of the electrons and of the thermal bath in a far from equilibrium situation.

As a suitable tool for this analysis we will consider the fluctuation theorem for dissipative systems, that refers col-

lectively to a number of results of nonequilibrium statistical mechanics that are valid far from thermal equilibrium [7–9]. The steady state version of the fluctuation theorem can be written as

$$\lim_{\tau \rightarrow \infty} \frac{p_{\tau}(+\bar{\sigma})}{p_{\tau}(-\bar{\sigma})} = \exp\left(\frac{\bar{\sigma}\tau}{k_B}\right) \quad (1)$$

where $p_{\tau}(\bar{\sigma})$ is the probability distribution of observing an average entropy production rate $\bar{\sigma}$ over a time interval τ . The distribution is defined with respect to an ensemble of trajectory segments of duration τ , sampled while the system in question evolves in a nonequilibrium steady state. Relevant to the present work are the applications of the fluctuation theorem for the entropy of mixing [10] and for chemical reaction [11].

We will carry out a discussion using a very simple model that contains the main physical characteristics of a broad family of charge transfer mechanisms. The model is sketched in Fig. 1, and it consists of a contact between two different materials, as indicated by the different energy levels in each phase, E_i , that stand for the electron affinities of the materials when they have achieved equilibrium after having been contacted, Fig. 1(a) [12]. The difference of work functions between the materials creates an energy barrier at the interface, the structure of which is not indicated in detail in Fig. 1, as we only need the energy difference between the phases for the following developments. Electrochemical potential in each of the two phases is controlled by the metal contacts, whose Fermi levels E_{FA} and E_{FB} can be manipulated externally. The current corresponds to the directional increase of electronic transitions across the interface, when the device is biased by a potential V . We restrict our attention mainly to electronic systems, but ionic charge transfer can be treated similarly.

Let us consider some common features of phenomenological models. For example, charge transfer kinetics in electrochemistry generally obeys, at least approximately, an exponential activation law (Tafel’s law) for the relationship

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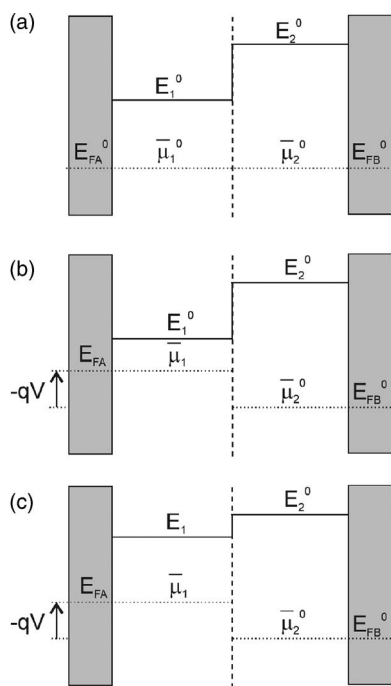


FIG. 1. Scheme of a device formed by two materials in contact, with energies E_1 and E_2 and electrochemical potentials $\bar{\mu}_1$ and $\bar{\mu}_2$. The two phases are separately contacted by reversible metal contacts (shaded areas) with Fermi levels E_{FA} and E_{FB} . The vertical axis represents electron energy, and superscript 0 indicates equilibrium values. (a) Equilibrium. In the lower diagrams the system is biased negatively (potential V) at contact A, causing (b) an increase of the chemical potential in phase 1 or (c) an increase of the energy level E_1 .

between the Faradaic current density and the potential [13]. In terms of the electron flux J , we express this relation as

$$J = J_0(e^{-qV/k_B T} - 1). \quad (2)$$

Here q is the elementary positive charge, k_B is Boltzmann's constant, T is the temperature, and the current increases at negative bias. The term -1 ensures that the current is zero in the absence of applied bias, as required in equilibrium when the same flux J_0 exists in both directions (the so-called exchange current). Equation (2) stands also for the current vs. potential in a metal-semiconductor (Schottky) diode [14].

In a sense, once some reasonable phenomenological model such as Eq. (2) is accepted for the current-potential dependence, the irreversibility is already demonstrated because the flux will follow the direction of the driving force and the production of entropy will be positive [15]. From any expression as Eq. (2), one obtains the charge transfer resistance, which is the reciprocal of the infinitesimal variation of current with respect to voltage, $R_{ct} = [dV/d(qJ)]^{-1}$, and which represents the irreversibility in an equivalent circuit model [2]. A widely used method to justify the phenomenological expressions for charge transfer such as Eq. (2) is the master equation, which can be written

$$\frac{dx_i}{dt} = \sum_j w_{ji}x_j - w_{ij}x_i, \quad (3)$$

where x_i represents a normalized concentration of species in the phase i , and w_{ij} are the transition rates from phase i to j . Transition rates are usually required to satisfy detailed balance, which is the condition that fluxes between different phases must be compensated at equilibrium, implying that the ratio of the probability of a process and the reversed one is the Boltzmann factor of the energy cost. It is required to further assume that the transition rates maintain the form that they have at equilibrium.

The main disadvantage of this approach, for explaining the sources of irreversibility, is that Eq. (3) combines the statistical distribution of carriers in available states and individual transition rates, which obscures the origin of the contributions to positive entropy production. One goal of this paper is to formulate the macroscopic flux equation without postulating a dynamic equation from the equilibrium distribution. The main tool in our derivation is the detailed fluctuation theorem (DFT) derived by Jarzynski [16], which connects the probabilities of an initial and final microstate of the system through a function of the entropy change. We will also need to determine how the probability of a single charge transfer event is governed by the macroscopic variables, i.e., the temperature and the Fermi levels of the contacts, describing, respectively, heat and particle reservoirs that exert an influence over the system. The evolution of microstates must be subjected to the further conditioning that these microstates belong to a particular mesostate. The influence of such prior conditioning in relationships between transition rates is discussed by Gillespie [17] in connection to the fundamental postulate of statistical mechanics and we use here a similar argument.

In the following, we analyze the system of Fig. 1 considering the electron distributions in phase 1 and 2, at both microstate and mesostate levels, in order to find the probabilities of transitions and the different entropy contributions to the electron flux. Thereafter we discuss the significance and interpretation of the results.

II. MICROSCOPIC AND MESOSCOPIC DESCRIPTIONS OF ELECTRON TRANSFER RATES

For concreteness we consider each phase $i=1,2$ in Fig. 1 as composed of a collection of discrete electronic sites, such as in hopping transport through band gap states (traps) in an amorphous semiconductor [18] or in organic conductors [19]. The electrons can move between the different sites in one of the phases and effect as well transitions from one phase to another one, which is interpreted as the interfacial charge transfer event. We assume that the only allowed transitions are those between neighbor sites. The statistical description of this system and the corresponding dynamic transitions can be considered at different levels. The most basic level is a full quantum mechanical description of all the electronic states in the system and the corresponding hamiltonian evolution. This basic description requires to consider the interaction between neighbour sites as well as the coupling to the thermal bath (phonons).

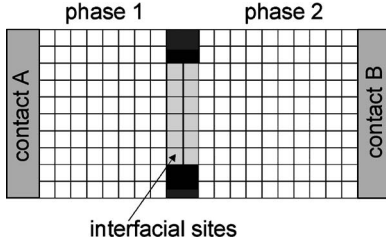


FIG. 2. Scheme of a device formed by two materials in contact. The materials are represented by lattices of discrete sites for electrons. The interface between the materials consists on $N_I=6$ sites (shaded) at each side, across which interfacial charge transfer is possible.

The former detailed description is, however, very often beyond our reach, both for experimental and for numerical model simulation methods, for most macroscopic as well as mesoscopic systems involving charge transfer. At the next level of description, which is quite convenient for numerical modeling of carrier transport [20], we consider the discrete electronic sites with total number N_i in phase i , which can be either singly occupied or empty, i.e., the electrons form a lattice gas, as indicated in the scheme of Fig. 2. The microstate of the system is defined by specifying the occupancy of the sites. If the number of electrons in phase i is n_i , the number of microstates in phase i is

$$\Omega_{N_i}(n_i) = \frac{N_i!}{(N_i - n_i)!n_i!}. \quad (4)$$

We are mainly interested in analyzing the electronic transitions across the interface. Let us assume that the number of sites where interfacial transitions are possible is N_I , as indicated in Fig. 2. Let $Y(j_{s1})$ denote a microstate with an electron in interfacial site j_s at side 1 of the interface, and without an electron in site j_s at side 2 of the interface, with $j_s = 1, \dots, N_I$. We will let $Y(j_{s2})$ represent the same microstate as $Y(j_{s1})$ but with site j_s at side 1 of the interface being empty, and the conjugate interfacial site j_s at side 2 of the interface being occupied by an electron. Note that the microstates $Y(j_{s1})$ and $Y(j_{s2})$ are not subjected to any other restrictions about the distribution of electrons in the rest of lattice sites. The charge transfer event is a change of the microstate $Y(j_{s1}) \rightarrow Y(j_{s2})$ which we may abbreviate as $j_{s1} \rightarrow j_{s2}$. The probability of an interfacial charge transfer event between the neighbor sites j_s , in the unit of time Δt , will be written

$$P_+[Y(j_{s1}); Y(j_{s2})]. \quad (5)$$

The probability of the reverse process $j_{s2} \rightarrow j_{s1}$ in the unit of time will be

$$P_-[Y(j_{s2}); Y(j_{s1})], \quad (6)$$

and it will be assumed that the downward transition occurs with a frequency ν_0 ,

$$P_-[Y(j_{s2}); Y(j_{s1})] = \nu_0. \quad (7)$$

The detailed fluctuation theorem derived by Jarzynski [16] (see also [21]) connects an initial and final microstate of a system of interest, through the expression

$$\frac{P_+(Z_\alpha, +\Delta S_b; Z_\beta)}{P_-(Z_\beta^*, -\Delta S_b; Z_\alpha^*)} = e^{\Delta S_b/k_B} \quad (8)$$

where Z_α and Z_β denote the initial and final microstates of the system of interest, and the asterisk denotes the reversal of the trajectory. The definition of the entropy change ΔS_b in the transition $Z_\alpha \rightarrow Z_\beta$ is an important element in the DFT. The entropy of a macroscopic system in a macrostate M is normally defined as the logarithm of the volume of phase space (number of microstates) when M specifies the locally conserved quantities of the system in thermal equilibrium, but there is no generally accepted definition of entropy far from equilibrium [22]. Equation (4) applies also for systems not in thermal equilibrium and requires a proper choice of the entropy change. Jarzynski [16] introduces in Eq. (4) the entropy generated over the course of the process, which means the quantity

$$\Delta S_b = -\frac{Q}{T} \quad (9)$$

where Q denotes the net heat absorbed by the system from the thermal bath, over the course of the process. Hence we have included the subscript b in Eq. (9), in order to distinguish it from the change of entropy in the system of interest in the transition $Z_\alpha \rightarrow Z_\beta$, ΔS_s .

Applying the DFT, Eq. (8), to the processes of Eqs. (5) and (6) that connect initial and final microstates, we obtain

$$\frac{P_+[Y(j_{s1}); Y(j_{s2})]}{P_-[Y(j_{s2}); Y(j_{s1})]} = e^{\Delta_{12}S_b/k_B T}. \quad (10)$$

For the sake of brevity we have omitted in Eq. (10) the entropy term in the argument of the probabilities as stated explicitly in Eq. (8). The symbol Δ_{12} indicates the change in the process $j_{s1} \rightarrow j_{s2}$.

In a transition $j_{s1} \rightarrow j_{s2}$ the electron gains an energy corresponding to the difference of the electron affinities of the materials, $E_2 - E_1$. This energy is absorbed as heat from the thermal bath (the phonons in the materials [23]), so that Eq. (9) gives

$$\Delta_{12}S_b = -\frac{E_2 - E_1}{T} \quad (11)$$

As a particular example of this kind of process (known since one century ago) the absorption of heat in upward electronic transitions is observed directly in the cooling of the cathode during thermoionic emission of electrons to the vacuum [24]. In this case the energy level E_2 in the diagram of Fig. 1(a) corresponds to the vacuum level, and the energy level E_1 is the work function of the cathode.

Note that the time constant ν_0 in Eq. (7) is actually dependent on the *height* of the energy barrier seen from side 2 of the interface (not shown in Fig. 1). For example, assuming a barrier of height E_0 at the interface, we would obtain an activation energy $E_{act2} = E_0 - E_2$ for the electron hopping from phase 2, and $\nu_0 = \omega_0 e^{-(E_0 - E_1)/k_B T}$, where ω_0 is an attempt-to-

hop frequency. However, deriving the form of ν_0 as in this example requires some specific model for materials and interfacial properties that will not be considered in this paper. Therefore here we are concerned only with the energy *difference* across the interface, Eq. (11), which can be viewed as a difference of activation energies, $E_2 - E_1 = E_{act1} - E_{act2}$, in the models of barrier crossing.

Using Eqs. (9) and (11), Eq. (10) implies the following:

$$P_+[Y(j_{s1}); Y(j_{s2})] = \nu_0 e^{-(E_2 - E_1)/k_B T}. \quad (12)$$

The description at the level of microstates and the DFT has provided an important relationship between the basic transition rates in the forward and backward directions across the interface. However, in the experimental measurements on interfacial charge transfer, the extent to which we can determine the state of the system is not at the microstate level, rather, as discussed in the Introduction, in the normal situations we can control only the electrochemical potential of each phase by means of the external contacts and a power source. In addition, we will assume that the electron transfer process between identical molecules is much faster than that across the interface, so that the latter process is the step determining the electron flux between the electrodes. In other words, we neglect the diffusion in each phase, and assume that electrons in each phase remain in a state of internal equilibrium. Therefore we employ a third level of description, the mesoscopic level, in which each phase is specified only by a number of electrons, which are randomly distributed in the lattice sites (including the interfacial sites).

Let $X(n_1, n_2)$ denote a mesostate in which the number of electrons in the phases are n_1 and n_2 . Such a mesostate is characterized by equilibrium quantities for each electronic subsystem, such as the entropy and the chemical potential. The electronic system as a whole may or may not be at equilibrium, a question that we consider in Sec. III.

If the number of electrons in phase i is n_i , the configurational entropy of the electronic subsystem is given by

$$S_{si} = k_B \ln[\Omega_{N_i}(n_i)]. \quad (13)$$

Let us assume for simplicity that $n_i \ll N_i$, i.e., the electrons form a very dilute solution in a background of vacant sites, so that we can neglect the restrictions due to occupancy of the acceptor site in an electron hop. Assuming also that N_i and n_i are sufficiently large, and applying the Stirling approximation, we obtain

$$S_{si} = -k_B n_i \ln\left(\frac{n_i}{N_i}\right). \quad (14)$$

The free energy of one phase is

$$F_i = n_i E_i - T S_{si} \quad (15)$$

and the electrochemical potential $\bar{\mu}_i = \partial F_i / \partial n_i$ has the expression

$$\bar{\mu}_i = E_i + \mu_i \quad (16)$$

where

$$\mu_i = -T \frac{\partial S_{si}}{\partial n_i} = k_B T \ln\left(\frac{n_i}{N_i}\right) \quad (17)$$

is the chemical potential of the electrons. Note in Fig. 1 that the chemical potential is given in each case by the distance between the electrochemical potential and the energy level. The change of entropy in the electron subsystems when one electron is removed (this process is denoted by subscript r) is

$$\Delta_r S_{si} = -\frac{\partial S_{si}}{\partial n_i} = \frac{\mu_i}{T}. \quad (18)$$

The total change of configurational entropy in the electron distributions when one electron is transferred from phase 1 to phase 2 is

$$\Delta_{12} S_s = \Delta_r S_{s1} - \Delta_r S_{s2} = \frac{\mu_1 - \mu_2}{T}. \quad (19)$$

From the mesoscopic (and experimental) point of view the main quantity that we must consider is the total rate of transitions across the interface, subjected to the condition that the two phases are kept at given mesostates determined by fixed electrochemical potentials. Observe that the number of electrons in the mesostate $X(n_1, n_2)$ can fluctuate around n_1 and n_2 , the fluctuations being given by the chemical capacitance, $\langle (\delta n_i)^2 \rangle = k_B T (dn_i / d\mu_i)$ [3,25]. The elementary transitions between microstates, $Y(j_{s1})$ and $Y(j_{s2})$, discussed before, must be subjected to the further conditioning that these microstates belong to a particular mesostate [17]. We define $Y(j_{s1}, n_1, n_2)$ as a microstate $Y(j_{s1}) \in X(n_1, n_2)$. Similarly we define $Y(j_{s2}, n_1, n_2)$, as a microstate $Y(j_{s2}) \in X(n_1, n_2)$. We consider the probability of a transition

$$P_+(Y(j_{s1}, n_1, n_2); Y(j_{s2}, n_1 - 1, n_2 + 1)) \quad (20)$$

between t and $t + \Delta t$. Equation (20) corresponds to the conditioned probability

$$\text{Prob}\{j_{s1} \rightarrow j_{s2} \text{ in } [t, t + \Delta t] | Y(j_{s1}, t) \in X(n_1, n_2)\} \quad (21)$$

which can be evaluated as the product

$$P_+(Y(j_{s1}, t); Y(j_{s2}, t + \Delta t)) \text{Prob}[Y(j_{s1}, t) | Y(j_{s1}, t) \in X(n_1, n_2)]. \quad (22)$$

The first factor of Eq. (22) is the transition pathway between microstates considered above with the result in Eq. (12). The second factor in Eq. (22) corresponds of the number of configurations in which one electron is in site j_s , with respect to the total number of configurations with n_1 electrons in subsystem 1. Hence

$$\text{Prob}[Y(j_{s1}, t) | Y(j_{s1}, t) \in X(n_1, n_2)] = \frac{\Omega_{N_1-1}(n_1 - 1)}{\Omega_{N_1}(n_1)}. \quad (23)$$

With the definition of entropy, we can write

$$\frac{\Omega_{N_1-1}(n_1 - 1)}{\Omega_{N_1}(n_1)} = e^{[S_1(N_1-1, n_1-1) - S_1(N_1, n_1)]/k_B}. \quad (24)$$

Therefore, in terms of the entropy for the removal of one electron from subsystem 1, given in Eq. (18), we have

$$\text{Prob}[Y(j_{s1}, t) | Y(j_{s1}, t) \in X(n_1, n_2)] = e^{\Delta_r S_{s1}/k_B}. \quad (25)$$

From Eq. (25) and the similar expression for subsystem 2, we obtain using Eq. (19) the result

$$\frac{\text{Prob}[Y(j_{s1}, t) | Y(j_{s1}, t) \in X(n_1, n_2)]}{\text{Prob}[Y(j_{s2}, t) | Y(j_{s1}, t) \in X(n_1 - 1, n_2 + 1)]} = e^{\Delta_{12} S_s/k_B} \quad (26)$$

which relates the probabilities of occurrence of the microstates that are time reverses of each other with respect to the charge transfer event, conditioned to a given macrostate. Similar relationships have been discussed recently [21,26].

Summarizing, we have found for the conditioned transition probabilities that

$$\begin{aligned} P_+(Y(j_{s1}, n_1, n_2); Y(j_{s2}, n_1 - 1, n_2 + 1)) \\ = \nu_0 e^{-(E_2 - E_1)/k_B T} e^{+\Delta_r S_{s1}/k_B} \end{aligned} \quad (27)$$

and

$$P_-(Y(j_{s2}, n_1 - 1, n_2 + 1); Y(j_{s1}, n_1, n_2)) = \nu_0 e^{+\Delta_r S_{s2}/k_B}. \quad (28)$$

The flux in each direction across the interface is given by the addition of all the interfacial transitions. The forward flux is

$$\begin{aligned} J_+ &= \sum_{j_s=1}^{N_I} P_+(Y(j_{s1}, n_1, n_2); Y(j_{s2}, n_1 - 1, n_2 + 1)) \\ &= N_I \nu_0 e^{-(E_2 - E_1)/k_B T} e^{+\Delta_r S_{s1}/k_B} \end{aligned} \quad (29)$$

and the backward flux gives

$$\begin{aligned} J_- &= \sum_{j_s=1}^{N_I} P_-(Y(j_{s2}, n_1 - 1, n_2 + 1); Y(j_{s1}, n_1, n_2 + 1)) \\ &= N_I \nu_0 e^{+\Delta_r S_{s2}/k_B}. \end{aligned} \quad (30)$$

The total flux

$$J = J_+ - J_- \quad (31)$$

is given by the expression

$$J = N_I \nu_0 [e^{-(E_2 - E_1)/k_B T + \Delta_r S_{s1}/k_B} - e^{+\Delta_r S_{s2}/k_B}]. \quad (32)$$

In Eq. (32) it is appreciated that the reduction to the mesoscopic level introduces the terms of activation entropy, related to the number of configurations that contribute to the flux, in addition to the contribution of activation energies ($E_2 - E_1$), which was described in terms of the DFT.

Let us state Eq. (32) in terms of a familiar expression. If we consider the ideal statistics of electrons, applying Eq. (4) we get

$$\frac{\Omega_{N_1-1}(n_1 - 1)}{\Omega_{N_1}(n_1)} = \frac{n_1}{N_1}. \quad (33)$$

Consequently, Eqs. (27) and (28) take the form

$$P_+(Y(j_{s1}, n_1, n_2); Y(j_{s2}, n_1 - 1, n_2 + 1)) = \nu_0 e^{-(E_2 - E_1)/k_B T} \frac{n_1}{N_1}, \quad (34)$$

$$P_-(Y(j_{s2}, n_1 - 1, n_2 + 1); Y(j_{s1}, n_1, n_2 + 1)) = \nu_0 \frac{n_2}{N_2}, \quad (35)$$

so that the flux can be written as the standard expression

$$J = N_I \nu_0 \left(\frac{n_1}{N_1} e^{-(E_2 - E_1)/k_B T} - \frac{n_2}{N_2} \right). \quad (36)$$

III. ELECTRON TRANSFER IN EQUILIBRIUM

We remark that the only hypothesis used so far is the internal equilibrium of each electronic subsystem, so that Eq. (32) is valid for an arbitrary bias potential. The condition of thermal equilibrium between the two phases is determined by the minimization of the total free energy $F = F_1 + F_2$, with respect to the number of electrons, implying equality of the electrochemical potentials of the separate phases,

$$\bar{\mu}_1 = \bar{\mu}_2 \quad (37)$$

as indicated in Fig. 1(a). Equation (37) may be expressed as

$$\Delta_{12} S_{total} = 0 \quad (38)$$

where

$$\Delta_{12} S_{total} = \Delta_{12} S_b + \Delta_{12} S_s, \quad (39)$$

i.e., according to Eq. (38) the total entropy production in the process of transferring one electron is zero, as required in thermal equilibrium. In equilibrium the transition to higher energy requires a negative entropy in the thermal bath, which is compensated by the increase of entropy gained in transferring the electrons from a high to a low density region ($\mu_1 > \mu_2$). Equation (39) can be viewed as the familiar expression of chemical equilibrium with the reaction energy (enthalpy) given in Eq. (11) and the entropy change from reactants to products stated in Eq. (19). In fact our model can be easily adapted to represent the rate of a redox reaction far from equilibrium, for which Eq. (2) is usually a good approximation.

It follows from Eq. (38) that the flux in Eq. (32) is zero when the two electronic subsystems are in a state of equilibrium, as required by thermodynamics. Denoting overall equilibrium quantities by superscript zero, the exchange flux, i.e., the flux in each direction in equilibrium, is given by

$$J_0 = N_I \nu_0 e^{-(E_2^0 - E_1^0)/k_B T + \Delta_r S_{s1}^0/k_B} = N_I \nu_0 e^{+\Delta_r S_{s2}^0/k_B}. \quad (40)$$

IV. ELECTRON TRANSFER IN NONEQUILIBRIUM CONDITIONS

When the system is driven away from the condition of equilibrium described in the previous section, there occur changes of the electrochemical potentials of the electrons.

We will assume that only the phase 1 is modified when the system is biased, so that

$$\bar{\mu}_1 = \bar{\mu}_1^0 - qV \quad (41)$$

while $\bar{\mu}_2 = \bar{\mu}_2^0$. This restriction will simplify the discussion without affecting the general conclusions. In Eq. (41), V is the potential applied to the left electrode with respect to the right one, which determines the relative position of Fermi levels in the contacts as [5]

$$E_{FA} - E_{FB}^0 = -qV. \quad (42)$$

To be precise, the term contact refers to any structure which allows carriers to move from a metastable energy (where they are described by a quasi-Fermi-level, i.e., in a semiconductor) to a stable energy level (where average energy for the carrier is nearly equal to the equilibrium Fermi level, i.e., in a metal) [27]. Furthermore we have assumed ideally reversible contacts [28], in which the quasi-Fermi-level is continuous between the metal and the semiconductor material. These definitions, which in practice are often realized with Ohmic contacts [29], allow us to assume that each phase is separately maintained in quasiequilibrium, because the contacts replenish or remove the defect or excess of carriers due to the interfacial transitions.

Using the exchange flux defined in Eq. (40), Eq. (32) can be written

$$J = J_0(e^{\Delta_{12}S_{total}} - 1). \quad (43)$$

This last result reduces to the well known diode equation in Eq. (2), as discussed in the following, but Eq. (43) displays explicitly the elements of entropy change, both microscopic ($\Delta_{12}S_b$) and mesoscopic ($\Delta_{12}S_s$), in the charge transfer process. The macroscopic current occurs when these entropy contributions remain unbalanced by external influence on the system. The electron flux from phase 1 to phase 2 will be enhanced exponentially when the bias is such that $\Delta_{12}S_{total}$ is positive, otherwise the forward flux will be suppressed and there will remain only the backward equilibrium flux, $J = -J_0$ (the reverse saturation current in the diode).

Let us examine in more detail the conditions in which $\Delta_{12}S_{total}$ is positive. The modification of electrochemical potential in phase 1 may take place in different fashions.

(1) By a change of the chemical potential, $\Delta\bar{\mu}_1 = \Delta\mu_1$. In this case the energy levels E_i remain stationary, and the bias produces a change of the concentration in phase 1, as shown in Fig. 1(b). This case is pertinent when material 1 effectively shields macroscopic electrical fields, by the presence of additional inert species with a high conductivity. This occurs in a wide class of materials generally known as electroactive materials, which precisely have the ability to change markedly the composition as a function of the potential with consequent modification of physical properties that can be used in devices for desired applications. Some examples are intercalation materials applied in Li-ion batteries [30] (in this case the transference across the interface is ionic) and nanostructured semiconductor electrodes used in dye-sensitized solar cells [31].

(2) By a change of the energy level, $\Delta\bar{\mu}_1 = \Delta E_1$, shown in Fig. 1(c). This occurs when the potential V is unshielded in

material 1, so that the applied potential drop takes place at the interface between the two materials and modifies the energy difference across the interfacial barrier. An example is the classical model of Fröhlich for hopping in a two-level system [32].

(3) By a combination of both.

Next we will treat these cases separately

If the negative bias at the left electrode increases the chemical potential in phase 1, as indicated in Fig. 1(b), then the electrochemical potential will be

$$\bar{\mu}_1 = E_1^0 - k_B T \ln\left(\frac{n_1}{N_1}\right) \quad (44)$$

and with Eq. (41), we can express the number of electrons as

$$n_1 = e^{-qV/k_B T} n_1^0. \quad (45)$$

Since the energy levels have not been modified the decrease of entropy in the phonon bath will be the same as in Eq. (11). However the change of entropy in the electronic subsystem 1, Eq. (18), takes the value

$$\Delta_r S_{s1} = k_B \ln\left(\frac{n_1}{N_1}\right) = \Delta_r S_{s1}^0 - \frac{qV}{k_B T}. \quad (46)$$

The total entropy change in the transfer of one electron is

$$\Delta_{12}S_b^0 + \Delta_{12}S_s = -\frac{qV}{k_B T}. \quad (47)$$

The calculation of the entropy production in Eq. (47) shows an excess entropy determined by the free energy per electron, that is given by the difference of Fermi level between the contacts, Eq. (42). This excess entropy is caused by the additional concentration in phase 1, which increases the entropy cost for localizing the electrons in phase 1, as further discussed in Sec. V. In this case Eq. (43) can be written

$$J = J_0(e^{(\mu_1 - \mu_1^0)/k_B T} - 1). \quad (48)$$

A system showing a current of this type, governed by the change of chemical potential, can be termed a chemical diode. It is interesting to observe that Eq. (48) describes the fundamental operation of solar cells in the dark [31].

Next we discuss the case, indicated in Fig. 1(c), in which biasing the system changes the energy difference in the two phases without modifying their concentrations, $\Delta\bar{\mu}_1 = \Delta E_1$. This model can be termed a barrier diode. The electrochemical potential is

$$\bar{\mu}_1 = E_1 - k_B T \ln\left(\frac{n_1}{N_1}\right) \quad (49)$$

where

$$E_1 = E_1^0 - qV. \quad (50)$$

The change of the entropy of the thermal bath in the transference of one electron is

$$\Delta_{12}S_b = -\frac{E_2^0 - E_1}{T} = \Delta_{12}S_b^0 - \frac{qV}{T}, \quad (51)$$

while the entropy change of the electronic subsystems is not modified. The total entropy production in the transfer of one electron

$$\Delta_{12}S_b + \Delta_{12}S_s^0 = -\frac{qV}{k_B T} \quad (52)$$

is the same as in the previous case, Eq. (47).

We remark that in both cases considered, Eq. (47) and (52), $\Delta_{12}S_{total}$ will be positive, and consequently the forward flux of electrons in Eq. (43) will increase, when the bias potential is negative. Considering the general case in which the electrochemical potential of subsystem 1 may be modified either by the chemical potential or energy level of this subsystem, we can write Eq. (43) as

$$J = J_0 (e^{(\bar{\mu}_1 - \bar{\mu}_1^0)/k_B T} - 1) \quad (53)$$

which is equivalent to Eq. (2).

V. DISCUSSION AND PHYSICAL APPLICATIONS

In the previous sections we have explained the origin of the exponential activation of the interfacial current at forward bias usually found in electrochemistry and solid-state electronics. Our approach considers two separate electronic subsystems, each one at internal quasiequilibrium fixed by the Fermi level at the respective contact. The probabilities of fluctuations that realize the nonequilibrium step, involving the electronic transitions from one phase to another one, are described by the DFT [16]. The theorem relates the probability of a particular path of microstates to its time reverse, and reflects a principle of microscopic reversibility. These probabilities, Eqs. (7) and (12), are affected only by the local energy levels (determining the change of entropy in the heat bath), independently of the electronic state of the rest of the materials.

In contrast to this, the usual arguments for deriving far from equilibrium flux equations involving the master equation and detailed balance take the macroscopic flux as the starting point for statements about the microscopic quantities, i.e., the transition rates. This is because detailed balance refers to the probabilities of changing states without reference to a particular path [33]. The rate of elementary transitions are derived from the statistical properties of ensembles of particles that effect such transitions. Reservations about such procedure have been remarked recently [34].

In the application of the DFT to our model we have seen that this theorem accounts for the *activation energy* ($E_2 - E_1$) in the flux of Eq. (32). The further requirement that the electrons distributions in the device belong in a given class of mesostates [17], introduces the terms $\Delta_r S_{si}$ in Eq. (32). These terms are strongly reminiscent of the activation entropy defined in transition state theory (TST) [35]. Note, however, that TST makes the assumption of an ‘‘activated

complex’’ which consists of the carriers at the top of the barrier, which are supposed in equilibrium with the carriers in relaxed states. In the framework of our model the activation entropy obtains a simple interpretation related to the mesoscopic restriction in our system, i.e., the role of the activated complex in TST is taken by one subclass of microstates, those with an electron at the interface, among the relaxed states of each phase. Our form of the activation entropy corresponds to the entropy change for taking an electron from the available sites in material 1 and placing it in the exact site where it may effect a transition. Indeed, the change of configurations from n_1 electrons distributed in N_1 sites, to 1 electron in 1 specific interfacial site, the latter entropy evidently being zero, is $\Delta_{acr} S_{s1} = -\Delta_r S_{s1}$. A similar concept of a change of configurational entropy is used in computations of rate constants for intramolecular chemical reaction [36]: the difference between all accessible ground state conformers and a single ground state conformer *resembling* the transition state.

The understanding of the structure of electron flux may be useful in the modeling of many problems of electron transport and charge transfer that involve a mesoscopic reduction of certain degrees of freedom. Such reduction is quite common in systems with a large extent of structural or energy disorder. In the modeling, carriers can be considered quasifree in spatial domains surrounded by the high barriers that provide the foremost kinetic limitation in the dynamics. Applying our model to these situations, it is appreciated that the mesoscopic flux contains exponential contributions of the entropy of quasifree carriers in the confinement domains. Such entropic contributions have been suggested in recent models of diffusion in glass former materials [37] and for ion conduction in glasses [38]. Further consideration of these topics is reserved for future work. An extended discussion of entropy contributions in mesoscopic modeling of dynamical systems has been presented recently [21].

VI. CONCLUSIONS

The detailed fluctuation theorem allows us to understand the process of interfacial electron transfer starting from the probability of a transition between microstates with electrons localized in the interfacial sites. Further specification of the thermodynamic variables of the mesoscopic phases with quasifree carriers allows to determine the macroscopic flux. The origin of the net entropy production per electron transferred (determined by the voltage across the device) lies either in the heat absorbed from the thermal bath for promoting an upward transition in the energy axis or in the changes of configurational entropy of the electronic system itself, depending on the particular effect of the external bias on the system.

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