

## Generalized thermodynamic potentials for mesoscopic conductors in the presence of transport

Thomas Christen

ABB Corporate Research, CH-5405 Baden-Dättwil, Switzerland

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It is shown that the nonequilibrium steady state of a phase-coherent conductor can be described by a generalized thermodynamic potential based on the concept of partial densities of states. This is possible due to the fact that dissipation takes place only in the contacts for the emitted carriers. Long-range Coulomb interaction is included, and charge conservation and gauge invariance are satisfied. The theory is illustrated for a mesoscopic capacitor with leakage. [S0163-1829(97)05611-7]

The density of states (DOS) is the basic quantity from which equilibrium thermodynamic properties of a system are derived. Once the DOS is known, one can construct an appropriate thermodynamic potential which has to be minimized in order to find the equilibrium state. Due to a production of entropy in driven systems, on the other hand, nonequilibrium states can in general not be obtained by minimizing a thermodynamic potential. In this work I show, however, that generalized thermodynamic potentials still exist in mesoscopic conductors<sup>1</sup> in the presence of transport, provided that dissipation takes place only in the reservoirs.<sup>2</sup> In order to treat the nonequilibrium case, the concept of the DOS is generalized by introducing *partial densities of states*<sup>3</sup> which contain the information from whose reservoir the particles are injected. According to Büttiker,<sup>3</sup> the specific partial DOS used below are called *injectivities*. The injectivities play an important role in the theory of time-dependent and nonlinear electrical transport in mesoscopic conductors.<sup>3-5</sup> One can show that the injectivities are related to the dwell time of the particles in the conductor.<sup>6,7</sup> The injectivities appear naturally within the scattering approach to conduction, and can be expressed in terms of a scattering matrix.<sup>3</sup> Equilibrium thermodynamics in terms of scattering matrices has been formulated in a different context by Dashen, Ma, and Burnstein.<sup>8</sup> Avishai and Band<sup>9</sup> discussed the relation between the scattering matrix and the total DOS of a one-dimensional system.

This paper is organized as follows. First, the definition of the injectivities is recalled for a system of noninteracting particles. Second, the generalized thermodynamic potential, including the Coulomb interaction, is constructed for a phase-coherent multiterminal conductor. The charge distribution is then determined by a minimization of this potential. Finally, the formalism is applied to a symmetric capacitor with tunneling between the capacitor plates, and it is shown that the result is in accordance with Ref. 5.

Consider a phase-coherent conductor connected via contacts to reservoirs  $\alpha = 1, \dots, N$  of noninteracting electrons. Such a conductor is characterized by a unitary single-particle scattering matrix which can be decomposed into submatrices  $s_{\alpha\beta}$ . The indices  $\alpha$  and  $\beta$  label contacts, and the dimensions of the submatrices are equal to the numbers of channels in the associated contacts. The first and second indices of  $s_{\alpha\beta}$  correspond to outgoing and incoming particles, respectively. The scattering matrix is a function of the energy  $E$  of the

scattered particle, and is a functional of the single-particle potential  $eU(x)$ , where  $e$  is the electron charge and  $U(x)$  is the electric potential. Denoting the trace of a matrix by  $\text{Tr}$ , one can write the transmission probability of a carrier from contact  $\beta$  to contact  $\alpha$  as  $T_{\alpha\beta} = \text{Tr}(s_{\alpha\beta}^\dagger s_{\alpha\beta})$ . The reflection probability at contact  $\alpha$  is  $R_\alpha = \text{Tr}(s_{\alpha\alpha}^\dagger s_{\alpha\alpha})$ . At thermodynamic equilibrium, the response of the particle density to a variation of the Fermi energy is characterized by the local DOS, which can be expressed in terms of the scattering matrix elements and its functional derivatives with respect to the potential,<sup>3,7</sup>

$$\frac{dn(x)}{dE} = -\frac{1}{4\pi i} \sum_{\alpha\beta} \text{Tr} \left( s_{\alpha\beta}^\dagger \frac{\delta s_{\alpha\beta}}{\delta U(x)} - \frac{\delta s_{\alpha\beta}^\dagger}{\delta U(x)} s_{\alpha\beta} \right). \quad (1)$$

Equation (1) can be interpreted as the sum of *injectivities*<sup>3</sup>

$$\frac{dn(x, \beta)}{dE} = -\frac{1}{4\pi i} \sum_{\alpha} \text{Tr} \left( s_{\alpha\beta}^\dagger \frac{\delta s_{\alpha\beta}}{\delta U(x)} - \frac{\delta s_{\alpha\beta}^\dagger}{\delta U(x)} s_{\alpha\beta} \right), \quad (2)$$

which are the partial DOS's associated with particles injected at contact  $\beta$ . In a nonequilibrium situation where the electrochemical potential  $\delta\mu_\beta$  in a single reservoir is changed, the response of the particle density is given by  $\delta n(x) = (dn(x, \beta)/dE) \delta\mu_\beta$ . A decomposition of the local DOS into injectivities leads to the following picture. The total sample is decomposed into  $N$  subsystems. Subsystem  $\beta$  consists of all those scattering states which are associated with particles injected at contact  $\beta$ . The local DOS of subsystem  $\beta$  is given by the injectivity  $dn(x, \beta)/dE$ . In a nonequilibrium steady state, these states are filled as if subsystem  $\beta$  were in equilibrium with reservoir  $\beta$ . Dissipation takes place in the reservoirs only for the outgoing particles, which are thermalized to the Fermi distribution of this reservoir. As long as scattering in the conductor is elastic, dissipation does not affect the states inside the sample.

For simplicity, I assume zero temperature, and consider a discretized version of a mesoscopic conductor. Importantly, all nearby conductors and gates are included in this model. The whole system consists of regions  $\Omega_k$  ( $k = 1, \dots, M$ ) with electrostatic potentials  $U_k$ , charges  $q_k$ , and injectivities  $D_{k\alpha}$ . For later convenience, the injectivities are written in the form

$$D_{k\alpha} = e^2 \int_{\Omega_k} d^3x \frac{dn(x, \alpha)}{dE}, \quad (3)$$

which have the dimension of a capacitance. The local DOS of a single region  $\Omega_k$  and the total DOS of the sample are  $D_k = \sum_{\alpha} D_{k\alpha}$  and  $D = \sum_{k\alpha} D_{k\alpha}$ , respectively. If  $eV_{\alpha}^{(\text{eq})}$  denotes the equilibrium electrochemical potential of reservoir  $\alpha$ , the part of the charge on conductor  $k$  which is injected from contact  $\alpha$  for a variation  $\Delta V_{\alpha} = V_{\alpha} - V_{\alpha}^{(\text{eq})}$  of the voltage becomes

$$q_{k\alpha} = \int_{V_{\alpha}^{(\text{eq})}}^{V_{\alpha}} dV D_{k\alpha}(V). \quad (4)$$

The total charge in  $\Omega_k$  is  $q_k = \sum_{\alpha} q_{k\alpha}$ . The energy  $E_D$  of the noninteracting system is given by the sum of the energies over all single-particle states

$$E_D = \sum_{k\alpha} \int_{V_{\alpha}^{(\text{eq})}}^{V_{\alpha}} dV V D_{k\alpha}(V), \quad (5)$$

where the energy scale is defined such that the equilibrium system has zero energy,  $E_D^{(\text{eq})} = 0$ . After an expansion of Eqs. (4) and (5) to second order in  $\Delta V_{\alpha}$ , one can eliminate  $\Delta V_{\alpha}$ , and express the energy as a function of the partial charges  $q_{k\alpha}$ ,

$$E_D(\{q_{k\alpha}\}) = \sum_{k\alpha} (V_{\alpha}^{(\text{eq})} q_{k\alpha} + \frac{1}{2} D_{k\alpha}^{-1} q_{k\alpha}^2). \quad (6)$$

In order to include the long-range Coulomb interaction, it is convenient to introduce a geometric capacitance matrix  $C_{kl}$  for the regions  $\Omega_k$ , which is determined by the Poisson equation. An arbitrary charge distribution  $\{q_l\}$  induces electrostatic potential shifts  $U_k$  given by

$$U_k = \sum_{l=1}^N C_{kl}^{-1} q_l + U_0. \quad (7)$$

Note that a global voltage shift  $U_0$  is always a solution of the Poisson equation. The Coulomb energy of the charge distribution is thus

$$E_C(\{q_{k\alpha}\}) = \frac{1}{2} \sum_{k\alpha l\beta} q_{k\alpha} C_{kl}^{-1} q_{l\beta} + U_0 \sum_{k\alpha} q_{k\alpha}. \quad (8)$$

At zero temperature, the free energy is equal to the total energy of the closed system, and is given by the sum of the kinetic energy  $E_D$  and the Coulomb energy  $E_C$ ,

$$E(\{q_{k\alpha}\}) = \sum_{k\alpha} (U_0 + V_{\alpha}^{(\text{eq})}) q_{k\alpha} + \frac{1}{2} \sum_{k\alpha l\beta} q_{k\alpha} \tilde{C}_{k\alpha l\beta}^{-1} q_{l\beta}, \quad (9)$$

where the following matrix is introduced:

$$\tilde{C}_{k\alpha l\beta}^{-1} = D_{k\alpha}^{-1} \delta_{kl} \delta_{\alpha\beta} + C_{kl}^{-1}. \quad (10)$$

Since the open system is appropriately described by the grand-canonical ensemble, the potential which must be minimized is

$$E(\{q_{k\alpha}\}) - \sum_{k\alpha} V_{\alpha} q_{k\alpha} \equiv \min. \quad (11)$$

Variation with respect to the charges  $q_{k\alpha}$  yields finally a set of  $M \times N$  equations,

$$\sum_{l\beta} \tilde{C}_{k\alpha l\beta}^{-1} q_{l\beta} = \Delta V_{\alpha} - U_0, \quad (12)$$

where  $\Delta V_{\alpha} = V_{\alpha} - V_{\alpha}^{(\text{eq})}$  corresponds to the (electrochemical) voltage shift in contact  $\alpha$ . The still free global shift  $U_0$  of the electric potential is determined by the additional condition of charge conservation,

$$\sum_{k\alpha} q_{k\alpha} = 0. \quad (13)$$

Thus  $U_0$  can be interpreted as a Lagrange parameter associated with condition (13). Charge conservation is a general property of a complete set of conductors connected to electron reservoirs, since electric fields are fully screened in the reservoirs.<sup>3</sup> In order to solve Eq. (12) for  $q_{k\alpha}$ , the matrix  $\tilde{C}_{k\alpha l\beta}$  is introduced as the inverse matrix of  $\tilde{C}_{k\alpha l\beta}^{-1}$ . Note that this quadratic matrix acts on  $M \times N$ -dimensional vectors  $q_{k\alpha}$  (see also the example below). Combination of Eqs. (12) and (13) yields

$$U_0 = \frac{\sum_{k\alpha l\beta} \tilde{C}_{k\alpha l\beta} \Delta V_{\beta}}{\sum_{k\alpha l\beta} \tilde{C}_{k\alpha l\beta}}. \quad (14)$$

Once the partial charges  $q_{k\alpha}$  are known, one can calculate the electrochemical capacitance which relates the static charge distribution  $q_k = \sum_{\alpha} q_{k\alpha}$  to the voltage shifts  $\Delta V_{\alpha}$  in the contacts,

$$C_{\mu, l\alpha} = \frac{\partial q_l}{\partial \Delta V_{\alpha}} = \frac{\sum_{k\beta m\gamma n\delta} (\tilde{C}_{l\beta k\alpha} \tilde{C}_{m\gamma n\delta} - \tilde{C}_{l\beta n\delta} \tilde{C}_{m\gamma k\alpha})}{\sum_{m\gamma n\delta} \tilde{C}_{m\gamma n\delta}}. \quad (15)$$

The nonequilibrium electric potential follows from Eq. (14) and the charge distribution with the help of Eq. (7).

An important consequence of charge conservation is that the electrochemical capacitance matrix satisfies  $\sum_l C_{\mu, l\alpha} = 0$ .<sup>3</sup> Additionally, the result is gauge invariant,  $\sum_{\alpha} C_{\mu, l\alpha} = 0$ ,<sup>3</sup> i.e., it does not depend on a global voltage shift. The global voltage shift is absorbed by the constant  $U_0$ , and does not change the total energy of the system, since the total charge vanishes.

As a simple example, consider a symmetric two-terminal capacitor with tunneling between the capacitor plates (leakage). Assume a single one-dimensional open channel with a transmission probability  $T = 1 - R$ . Equivalently, this system describes a symmetric quantum-point contact with a single open channel, or a one-dimensional conductor containing a symmetric impurity. This system has already been discussed in Ref. 5 in the context of time-dependent transport. I show that the thermodynamic treatment introduced in this work is

in accordance with the results of Ref. 5. Within a semiclassical approximation, the injectivity from reservoir 2 to plate 1 is proportional to one-half of the DOS,  $D_1$  ( $=D_2$ ), of plate 1, and to the transmission probability  $T$ . The factor  $\frac{1}{2}$  occurs since only particles with a velocity in direction to contact 1 contribute to this partial DOS. Due to symmetry,  $D_{12}=D_{21}=D_1T/2$  holds, which implies  $D_{11}=D_{22}=D_1-D_{12}=D_1(1-T/2)$ .<sup>5,7</sup> The diagonal elements  $A \equiv C_{11}^{-1} = C_{22}^{-1}$  and the off-diagonal elements  $B \equiv C_{12}^{-1} = C_{21}^{-1}$  of the inverse geometrical capacitance matrix are given by  $A = C_{11}/(C_{11}^2 - C_{12}^2)$  and  $B = -C_{12}/(C_{11}^2 - C_{12}^2)$ . The effective (charge conserving) geometric capacitance  $C_0$  between the two capacitor plates is given by  $C_0 = (C_{11} - C_{12})/2$ . In order to represent the matrix  $\tilde{C}_{k\alpha l\beta}$  in a simple way, it is convenient to abbreviate  $K_1 = D_{11}^{-1} + A$  and  $K_2 = D_{12}^{-1} + A$ . Equations (12) then read

$$\begin{pmatrix} K_1 & A & B & B \\ B & B & K_2 & A \\ A & K_2 & B & B \\ B & B & A & K_1 \end{pmatrix} \begin{pmatrix} q_{11} \\ q_{12} \\ q_{21} \\ q_{22} \end{pmatrix} = \begin{pmatrix} \Delta V_1 - U_0 \\ \Delta V_1 - U_0 \\ \Delta V_2 - U_0 \\ \Delta V_2 - U_0 \end{pmatrix}. \quad (16)$$

By taking charge conservation [Eq. (13)] into account, these equations can be solved for  $q_{k\alpha}$ . From the charge  $q_1 = -q_2 = q_{11} + q_{12}$  on the capacitor plates, one finds the electrochemical capacitance

$$C_\mu = \frac{\partial q_1}{\partial \Delta V_1} = -\frac{\partial q_1}{\partial \Delta V_2} = \frac{R}{C_0^{-1} + 4D^{-1}}. \quad (17)$$

This result states that, in the case of vanishing transmission, the electrochemical capacitance is the geometrical capacitance in series, with quantum corrections given by the DOS of the plates.<sup>4</sup> In the macroscopic limit where the DOS di-

verges ( $D \rightarrow \infty$ ), one recovers the pure geometric capacitance,  $C_\mu = C_0$ . On the other hand, for increasing transmission the capacitance decreases and vanishes for  $T=1$ . Clearly, without reflection there is no charge dipole at all. A more extensive discussion is provided by Refs. 5 and 11. *Transport* properties such as, e.g., the current cannot be calculated directly from such a generalized thermodynamic potential which contains only information on the charge (or potential) distribution. However, it must be emphasized that a knowledge of the nonequilibrium state is crucial for the determination of the currents beyond linear dc response.<sup>3-5,10,12</sup>

In conclusion, I have shown that it is possible to describe the stationary nonequilibrium charge distribution of a mesoscopic phase-coherent conductor with a generalized thermodynamic potential. The theory is based on the concept of partial densities of states (injectivities). The result includes the long-range Coulomb interaction, and is charge conserving and gauge invariant. To illustrate the theory, I used the simple approximation of a discretized version of the mesoscopic sample. However, in principle the generalization to a field theory, e.g., in the framework of a density-functional theory, is straightforward. The generalization to finite temperatures and to other thermodynamic questions (e.g., mechanical properties of the system), remains an interesting future task but does not require additional concepts. Furthermore, I considered only small deviations from the equilibrium state, but as long as dissipation is restricted to the reservoirs, a nonequilibrium potential also exists in the nonlinear regime.

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<sup>1</sup>For a review see, e.g., S. Datta, *Electronic Transport in Mesoscopic Systems* (Cambridge University Press, Cambridge, 1995); C. W. J. Beenakker and H. van Houten, in *Solid State Physics*, edited by M. Ehrenreich and D. Turnbull (Academic, New York, 1991), Vol. 44, p. 1.

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